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RESEARCH ARTICLE

Partial Purification of Egyptian Wet Process Phosphoric Acid with concentration of Uranium and Some Hazardous Metals by Precipitation Method

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Abstract

The major disadvantage of the use of Egyptian wet-process phosphoric acid as a fertilizer and in other industries is the presence of undesirable elements such as uranium, iron, cadmium and vanadium. In the present work, an integrated process based on treatment of pretreated phosphoric acid with a miscible solvent, ammonium salt and a reducing agent is described. The precipitate formed consists of a mixture of metals phosphate such as iron, uranium, cadmium. The viscous precipitate is dissolved in mother phosphoric or sulfuric acid for separation. While the phosphoric acid-miscible solvent layer is subjected to condensation and distillation in order to separate the partially purified phosphoric acid from free miscible solvent.

INTRODUCTION

Digestion of Egyptian phosphate rock by sulfuric acid (dihydrate wet process) produce phosphoric acid (28 to 30% P_2O_5) accompanied with the majority of iron, magnesium, uranium, cadmium, fluoride, arsenic and others. An excessive amount of these cations in the produced acid displace ammonia in mono or diammonium phosphate yielding a low grade fertilizer product more over presence of undesirable metals such as uranium, cadmium and others.

The most important fertilizers are mono and diammonium phosphates and ammonium poly phosphate Fertilizers. Such products do not require excessive pure phosphoric acid. it is only necessary that, the fertilizers product meet industry accepted nitrogen and P_2O_5 standards free from radio active materials and not cause handling problems due to hygroscopicity, mainly due to the presence of magnesium or dust. All purification process meet these criteria (**1**).

Many studies have been done in order to purify the Egyptian (wet-process) phosphoric acid by immiscible solvent extraction e.g. tributyl phosphate, methyl iso butyl ketone, butanol and others (**2**). It was found that it is hard to apply this technique on egyptian phosphoric acid because of the high level of impurities. Beside purification of phosphoric acid, different studies are being made all over the world to investigate new resources of uranium to meet the required demands. Among the secondary resources of uranium, natural phosphates are found to be an important resource for uranium and REEs. (**3**). Removal of uranium from phosphoric acid may be done before complete purification of the acid by conventional solvent extraction e.g. D2EHPA and TOPO , TBP or Tri octyl amine or by unconventional process such as emulsion liquid membrane, supported liquid membrane or ion exchange technique (**4**).

Using the technique of addition of miscible organic solvent is the more convenient to the Egyptian phosphoric acid because of the presence of high level of impurities more over the high cost of the other conventional immiscible solvents. The cost of distilling the miscible organic solvent away from the purified phosphoric acid is one of the larger expenses of any purification process. This cost is minimized by using little amount of solvent as possible and using a solvent with low heat of vaporization. Table(1) Show some possible solvents which are being suggested,(**5**).

From Table (1), distillation of acetone is considerably less energy intensive than that of alcohols or water more over its low price than isopropyl alcohol as a solvent precipitation process. Also from the above Table (1), it is clear that heat of vaporization of water is nearly five times of that belongs to the miscible solvent, acetone, this is may be an explanation about the high cost of purification with the immiscible solvents which need higher energy for concentration of the strip solution. For more details, stripping of the purified phosphoric acid from the loaded immiscible solvent such as TBP need a high amount of distilled water forming diluted phosphoric acid product (6-10% P_2O_5). This product need to be concentrated by water condensation and distillation, (**6**). Another cause of the preferential of the miscible solvent technique is that leaving less P_2O_5 with the impurities than do immiscible solvent extraction process.

The wet process phosphoric acid is treated with ammonia and acetone. The precipitate is separated from the phosphoric acid liquor phase, this precipitate is a mixture of metal phosphates, gypsum and fluorosilicates. The organic miscible solvent is combined with the partial purified phosphoric acid.

The high value product, partially purified phosphoric acid, is that associated with the organic miscible solvent. The rest of phosphorous pentoxide with impurities may not consider be lost because of the possibility of blending the impure phase with ammonia or other fertilizers forming low quality fertilizer product (**7**).

A trial to purify the crude phosphoric acid with methanol and ammonia in a continuous method forming a partially purified phosphoric acid and impure phosphoric acid or solid fertilizer. The majority of the impurities are precipitated as ammonium metallic phosphates or fluorine compounds. Firstly, formation of 51% P_2O_5 of ammoniated feed solution with a mole ratio, $NH_3:P_2O_5 = 0.306$ by addition of ammonium bicarbonate and start addition of the reactant, methanol and ammoniated feed solution with a mole ratio equal 2.86 in the reactor which kept at $60C^0$. precipitation of more than 85% of total impurities of Al, Mg, Ca and F by this method (**8**).

Another process for purifying of phosphoric acid containing cationic impurities by using isopropyl alcohol as a dispersant and ammonia as a precipitant leads to removal of more than 99% of iron and other impurities. For more purification, contacting the loaded alcohol with a concentrated solution of inorganic multivalent cationic salt selected from the group consisting of Al, Ca, Mg, Zn, this decrease the iron contamination to reach less than 10 ppm. For ultra purification, the loaded isopropyl alcohol with phosphorous pentoxide is pass through strong acidic cation exchange resin in the H^+ form before condensation and distillation obtaining a high pure phosphoric acid and the recycled miscible organic solvent (**9**).

Weterings and Janssen in 1985 give a study for precipitation of uranium from wet process phosphoric acid by adding ammonium bicarbonate and ammonium fluoride as a precipitant in the presence of iron powder as a reducing agent and also acetone or methyl ethyl ketone as a disperser. A series of different concentration of ammonium bicarbonate ranged from 0.35 to 5 gm per 100gm P_2O_5 showed that, in all proportion of ammonium bicarbonate more than 90% of uranium is precipitated by using acetone or methyl ethyl ketone as a dispersant. Replacing the ammonium fluoride instead of ammonium bicarbonate in the a series ranged from 0.1 to 1.2gm related to wt % of F to P_2O_5 showed precipitation of 95 - 98% of uranium, and after filtrate and vacuum distilled, yielding acetone as a top product and a semi pure phosphoric acid as a bottom product(**10**).

In order to improve the separation and precipitation of uranium and other metals, the sulfate content in the mother acid must be less than o.2% for converting the uranium species $UO_2(SO_4)_3^{-4}$ in the working phosphoric acid to UO_2^{+2} (**11**). Sulfate percent in the commercial phosphoric acid produced by Abo Zaabal Fertilizers Co. ranged from 1.0 to 2.5% in the crude acid.

In the present work, our aim is purification of Egyptian wet process phosphoric acid by precipitation using miscible solvent technique. On the other hand pre-concentration of valuable metal (uranium), in order to decrease the capital cost of its individual separation. The precipitation layer formed after separation process get rich with uranium, vanadium, rare earth elements and other metals. Uranium can be separated by the conventional solvent extraction, Di ethyl hexyl phosphoric acid and Trioctyl phosphine oxide, or separated by ion exchange resin or alkali leaching technique, **(12).**

2-Experimental

In these experiments, organic solvent (acetone), added gradually to the pre-treated and defluorinated phosphoric acid at room temperature till formation of two phases, the first is the loaded organic solvent with P_2O_5 and the other phase is a viscous phase containing the major of elements in addition to Uranium. Viscous phase, dissolved in a convenient amount of crude phosphoric or sulfuric acid for analysis. In all experiments, 100gm of P_2O_5 pretreated phosphoric acid are mixed with a suitable amount of acetone as a miscible solvent with different conditions such as reduction, oxidation or addition of precipitating agent to investigate the optimum conditions for the purification process. In these experiments, the oxidation of the working acid has been performed by addition of drops of hydrogen peroxide with stirring at 250 rpm till reach 550 m.v. while the reduction has been performed by addition of iron by 1% from the weight of working acid.

2. 1. Composition of the Abo Zaabal produced phosphoric acid

In order to improve the purification of the Egyptian concentrated phosphoric acid with solvent precipitation method, humic materials, fluoride and sulfates must be decrease as possible as it is. Table (2) show the composition of abo zaabal produced phosphoric acid.

2. 2. Chemicals and reagents

The applied miscible solvent acetone has been supplied by Fine Chem. Ltd, India. The other chemicals and reagents used for preparing the working phosphoric acid besides those used for chemical analysis have mostly been of analytical grade.

2. 3. Analytical procedures

Several experiment batches have been taken place in order to have a partially purified and a concentrated impure phosphoric acid. Uranium is determined with titration against ammonium metavanadate, while the other cations in the medium are detected with Atomic Absorption Spectroscopy, GBC 932 AA. Phosphoric acid concentration is detected with acid base titration against 0.1 N NaOH while the precipitated P_2O_5 is detected using Spectrophotometer method.

2. 4. Pre-treatment and fluoride elimination

12g clay (calcium bentonite), added to 1L of the crude phosphoric acid 48.2% P_2O_5, and mixing 0.5 hr. The crude acid is settled, filtered and then passed through activated carbon column have a specific length of 80cm and diameter of 3cm, to complete the removal of the humic matters. After that addition of the appropriate amount of calcium carbonate at room temperature in order to precipitate the sulfate remaining through the manufacture process which are found ranged from 0.5 to 2.6% as sulfate. For this purpose and according to table (2) and equation (1), 42.6gm of calcium carbonate added with stirring to the relevant 1L crude phosphoric acid directly after clay addition.

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2O + CO_2. \qquad \text{-----.........} \quad 1$$

Removal of 0.48% fluoride from crude phosphoric acid with 3.8gms fine silica with mixing an hour to form fluoroslilicic acid which precipitated as sodium fluorosilicate with addition of 4.5g sodium carbonate. The amounts of chemicals added stoichiometrically according to the following equations,

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O \qquad \text{--.....................} \quad 2$$

$$H_2SiF_6 + Na_2CO_3 \rightarrow Na_2SiF_6 + H_2O + CO_2 \qquad \text{------...........} \quad 3$$

The acid medium is treated with flocculent solution of 0.2% polyacrylamide salt. The pretreated acid settled and then filtered. So it is ready for solvent addition after measuring the concentration of phosphorus pentoxide. The above pretreated acid was analyzed by atomic absorption spectroscopy, ion selective electrode to measure cations and fluorine respectively and titration method to measure P_2O_5.

2. 5. Factors affecting the precipitation procedures

A series of factors have been studied for precipitate the present impurities in the working acid as sulfate, heavy metals and others to get the optimum conditions for the process. The factors studied as the acid - solvent ratio, precipitating agent - acid ratio and the redox potential of the acid. Acetone was used as a miscible solvent while ammonium bicarbonate was used as a precipitating agent.

3- Results and Discussion

Table (1) Heat of vaporization of some organic solvents compared with water.

Compound	Heat of vap. cal-gm
Acetone	125
Isopropyl alcohol	159
Methyl alcohol	263
Ethyl alcohol	204
Water	539

Table(2): Composition of the Abo Zaabal produced crude acid.

Component	Wt %	Component	ppm
P_2O_5	48.2	**U**	74
SO_4	2.60	**Ca**	54
Fe	2.73	**Cd**	9.7
F	0.48	V	260
Mn	0.155	-	-

3.1. Composition of the working phosphoric acid

In the present work the concentrated commercial phosphoric acid (50% P_2O_5), was used after removal of humic materials, fluoride and sulfate to precipitate the impurities by miscible solvent technique. Table (3) shows the analysis of the pretreated concentrated working acid accompanied by defluorination and desulfurization as previously mentioned in the experimental part.

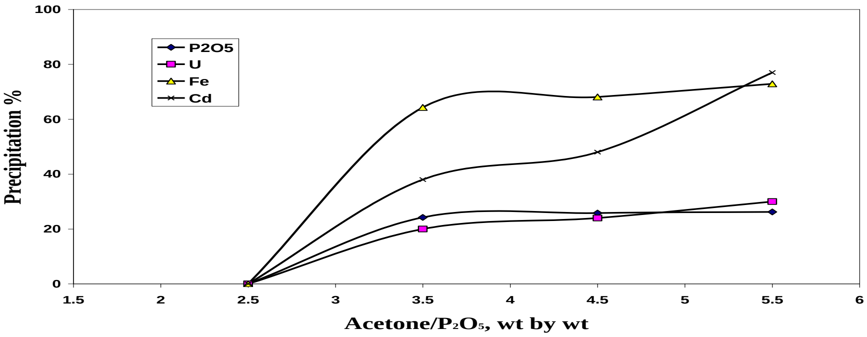
Table (3)The composition of the working acid 50% P_2O_5

Component	Wt. %	Component	Ppm
P_2O_5	50.0	**U**	77.0
SO_4^{-2}	0.34	**Ca**	340.0
Fe	2.88	**Cd**	10.4
F	0.15	V	275
Mn	0.158	-	-

3. 2. Factors affecting precipitation procedure

3. 2. 1. Effect of acetone addition as a dispersing agent

Many types of dispersing agent can be used as alcohols, ketones and ethers. In the present work acetone was used as a dispersing agent with different ratios to P_2O_5 in gms. Table (4) shows the effect of different additions of acetone as disperser on the precipitation of P_2O_5 and the undesirable cations from the concentrated working acid ($50\%P_2O_5$) at 300 rpm mixing speed.



Figuer (1): Effect of acetone addition on the precipitation % from 50% P_2O_5 working acid.

From figure (1) it is noticed that the precipitation of phosphorous pentoxide is increased with increasing the precipitation percent of cationic impurities and this is due to the formation of cationic phosphate precipitate. In the original redox potentioal of the working phosphoric acid, the majority of uranium tend to dissolve with the organic aqueous phase layer except about 35% of its content are co precipitated with other cations. It was considered from figure (1) that the optimum addition of acetone to the working acid is 4.5 :1, respectively.

3. 2. 2. Effect of precipitating agent addition

Nitrogen added to 100 gm P_2O_5 of the working acid (50% P_2O_5)**,** as a precipitating agent stoichiometrically in the form of ammonium bicarbonate with different quantities ranged from 0.1:100 to 0.5:100 N: P_2O_5 ratio respectively, then addition of 450g of acetone. Mixing speed of the addition was kept at 300 rpm at room temperature in all experiments without change in the oxidation potential of the working acid, which was within 300mV.

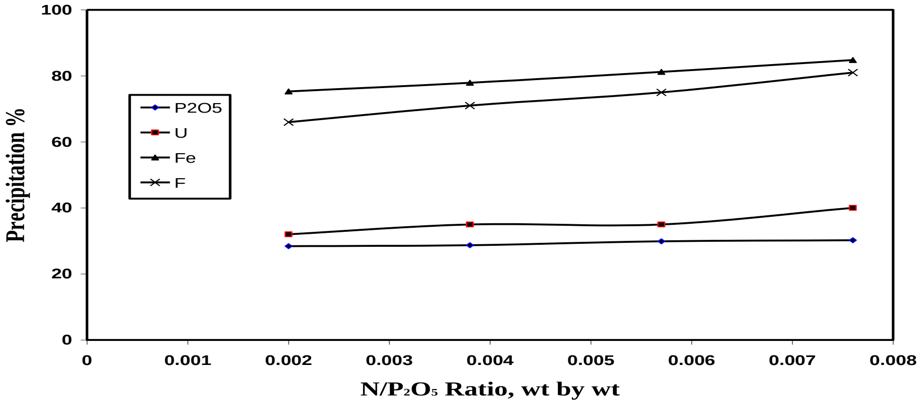


Fig.(2):- Effect of amm. bicarbonate addition on the precipitation % from 50% P_2O_5 working acid

It is clear from figure (2) that the majority of impurities are precipitated with addition of ammonium bicarbonate as a source of nitrogen to P_2O_5 with the ratio 0.35:100 respectively, this is at the addition of 450 g acetone per 100 gm of P_2O_5 at 300 rpm mixing speed. Addition of nitrogen source have a significant effect on the precipitation of all cations in the working acid. Precipitation of uranium have been slightly affected by the addition of nitrogen source which is co precipitated with the other impurities. It was consider that addition of 0.35 N to 100g P_2O_5 is more convenient because more addition will cause lost of excess P_2O_5.

3. 2. 3. Effect of the redox potential of the working acid on the precipitation%

Experiments have been performed at 100 and 550 mv. using iron powder, as reducing agent and hydrogen peroxide as oxidizing agent. The commercially working phosphoric acid, 50% P_2O_5, is subjected to reduction with 0.3% iron powder with respect to P_2O_5 in gs by mixing till 150 mv. After that the rest of iron powder which is un dissolved is eliminated with a magnet. Another batch is subjected to oxidation with drops of hydrogen peroxide till reach 550 mv. After adjusting the redox potential of 200g working acid (50% P_2O_5 at 100 and 550 mV), 2g of ammonium bicarbonate was added to both batches in order to reach the value N: P_2O_5= 0.35:100, respectively with mixing at 300 rpm with magnetic stirrer, then gradually addition of 450g acetone. Two phases are formed due to precipitation of impurities accompanied by part of P_2O_5. The obtained date are shown in Table (6).

Table (6):- Effect of redox potential on precipitation through acetone addition

Component	Precipitation%	
	Reduction to150 mV	Oxidation to 550 mV
P_2O_5	32	29
Fe	91	82
Cd	95	93
U	95	15

From Table (6) it is obvious that 95% uranium precipitation was obtained through reduction of the working acid with addition of 2g ammonium bicarbonate as precipitant and 450g acetone as dispersing agent. So reduction of the working acid to 150 mV is necessary in case of precipitation of uranium. These results can explain the tendency of tetravalent uranium to be precipitated rather than the hexavalent uranium state. It is noticed that an improvement of iron precipitation with reduction which attained 91% of its original content accompanied by the others cations. The precipitation of iron is accompanied by the precipitation of P_2O_5 this may be due to the reaction of ferrous ions, reduction of ferric by iron dust, and phosphates forming $Fe_3(PO_4)_2.8H_2O$. This is in case of reduction while in the precipitation without reduction forming $FePO_4$. The others precipitated cations will be explained through the analysis of the partially purified phosphoric acid. In the same way, it is noticed an increasing of P_2O_5 precipitation through reduction of the working acid and this is result from the formation of ammonium metal phosphate complexes.

3. 2. 4. Composition of the partially purified phosphoric acid

After complete uranium precipitation process from 100g P_2O_5, (200g of 50% P_2O_5, crude phosphoric acid) with 450 g acetone at 150 mv. reduction potential and in the presence of 2g ammonium bicarbonate as precipitant, the loaded acetone with P_2O_5 is filtered and subjected to distillation and condensation by using heat condenser device giving a recycled acetone and 155.2gm partially purified phosphoric acid, 46.2% P_2O_5. The produced phosphoric acid is analyzed to its components which is illustrated in Table(7).

Table (7): Analysis of the components of the partially purified phosphoric acid after acetone treatment.

Component, %		Component, ppm						
P_2O_5	Fe	F	U	Cd	Mn	Ca	V	REES
46.2	0.09	105	4	0.3	92	38	37	52

From table (7), it is clear that an improvement of the degree of phosphoric acid purification especially the uranium decreasing which result from precipitation of more than 90% of its content. Cadmium was precipitated also in the viscous phase in addition to the flour content which was 10.4 and 1500 ppm respectively in the working acid and down to 0.3 and 105 respectively. The partially purified phosphoric acid is still contained 900 ppm Fe more over 92 ppm Mn which need more processes in case of needing higher purification phosphoric acid degree. The path of rare earth metals and vanadium precipitation was not determined through the factors studied but from tables 7 and 8 it is noticed that the majority of rare earth metals and vanadium content in the working acid was precipitated in th e viscous phase.

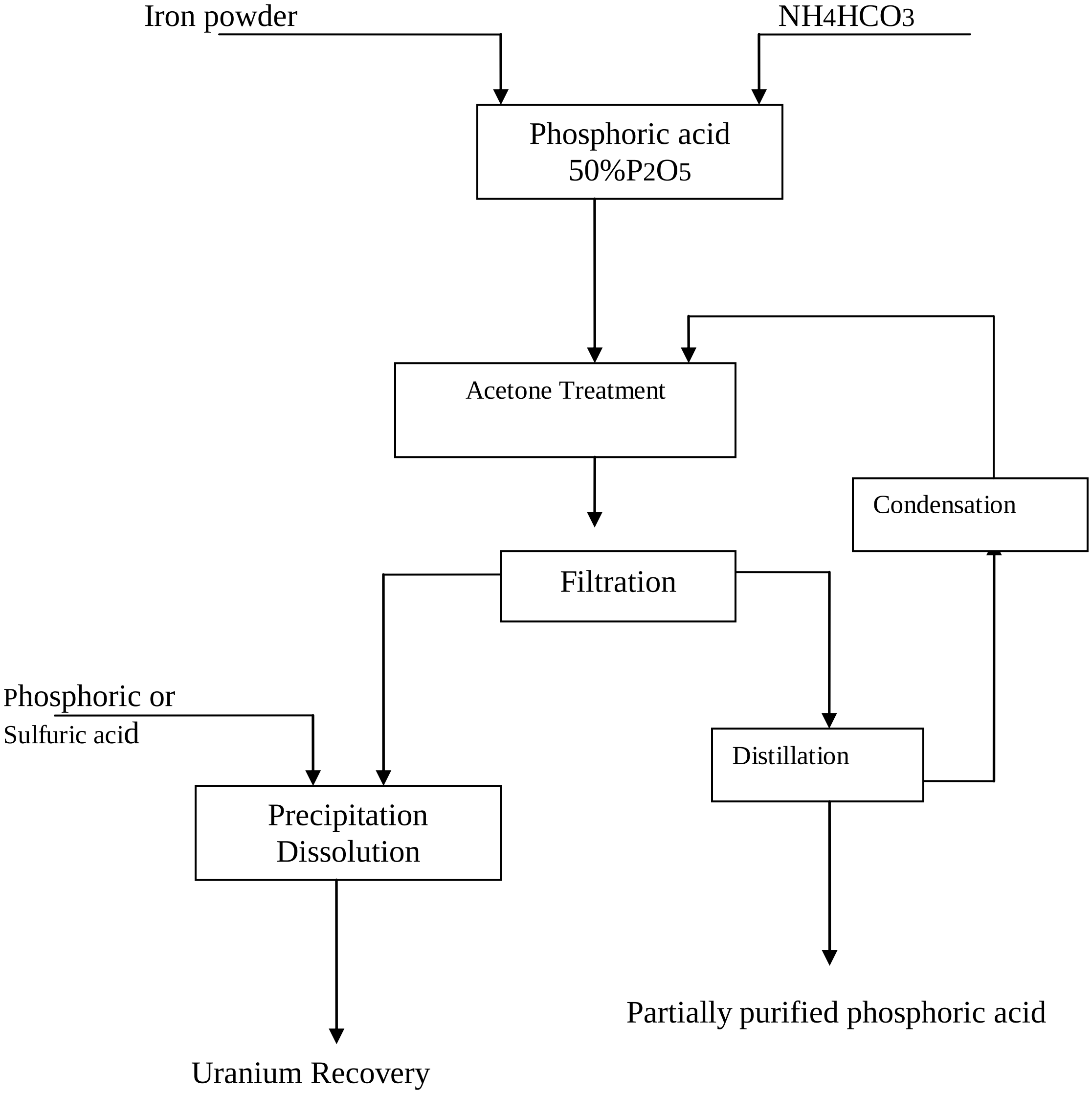
3. 2. 5. Composition of the obtained precipitate.

The obtained precipitate formed after treatment of commercial reduced phosphoric acid (200 g acid equivalent to100g P_2O_5) with acetone in presence of 2g ammonium bicarbonate has been analyzed. The humidity was measured by drying at 120°C for 2hours. The weight of the relevant precipitate is 53.4 g analyzed for iron, cadmium, Table(8).

Table (8): Composition of the obtained viscous precipitate after phosphoric acid partially purification

Component, %					Component, ppm				
P_2O_5	Fe	F	Mn	Moisture	U	Ca	Cd	V	R.E.
52.2	8.8	0.24	0.565	32	310	139	27	610	1410

The precipitate obtained is considered of a high value due to containing a high concentration of uranium, vanadium and rare earthe metals. It is necessary to extract uranium from the obtained metal phosphate precipitate by ion exchange or solvent extraction techniques after dissolution of the precipitate in sulfuric acid or in mother phosphoric acid. So after uranium separation from the viscous phase with appropriate process give a uranium free phosphoric acid fertilizer



Conclusion

It is concluded that the Egyptian phosphoric acid can be partially purified through the dispersion process by using acetone and ammonium bicarbonate. The majority of cationic elements are co precipitated with the uranium as iron, cadmium and vanadium. Many factors including the amount of acetone added and ammonium bicarbonate besides the redox potential of the working acid were studied. The optimum conditions that obtained were 4.5 gm of acetone is sufficient to 1gm of P_2O_5 in case of concentrated acid with reduction to 150mV. Addition of ammonium bicarbonate as a precipitating agent with the ratio N: P_2O_5 = 0.35: 100, respectively, improve the precipitation process. After precipitation process, two phases are formed and separated by filtration. The organic phase contains P_2O_5 and miscible acetone subjected to condensation, distillation produces a partially purified phosphoric acid, and the initial quantity of the acetone added without lost. The second phase is the aqueous product (pre-concentrated viscous phase) which subjected to dissolving with appropriate amount of sulfuric or mother phosphoric acid for passing through ion exchange resin or solvent extraction for uranium separation. A proposed flow sheet for partially purification of the examined phosphoric acid and precipitation of uranium is drown as in Fig.(3).

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