



## Cleaning of Extracted Phosphoric Acid

<sup>1</sup>Rashida Mamajanova, <sup>2</sup>Zohidbek Hamrakulov, <sup>3</sup>Mukhayyo Khoshimkhanova, <sup>4</sup>Zulfikahar Dehkanov, <sup>5</sup>Khayrullakhan Aripov, <sup>6</sup>Jamshid Kadirkanov,

<sup>1</sup>Fergana Polytechnic Institute, Republic of Uzbekistan

<sup>2</sup>Fergana Polytechnic Institute, Republic of Uzbekistan

<sup>3</sup>Almalyk branch of Tashkent State technical University after Islam Karimov, Almalyk, Republic of Uzbekistan

<sup>4</sup>Namangan Engineering and Technology Institute, Republic of Uzbekistan

<sup>5</sup>Namangan Engineering and Technology Institute, Republic of Uzbekistan

<sup>6</sup>Namangan Engineering and Technology Institute, Republic of Uzbekistan

(Received: 07 January 2024

Revised: 12 February 2024

Accepted: 06 March 2024)

### KEYWORDS

extraction  
purification,  
phosphoric  
acid,  
extracting,  
phosphorus  
fertilizers

### ABSTRACT:

**Introduction:** World production of extraction phosphoric acid (EPA) amounted to 48.9 million tons of  $P_2O_5$  in 2015 and is projected to increase by 7.7 million tons of  $P_2O_5$  by 2020. The widespread development of the production of purified phosphoric acid (PPA) compared to thermal acid (TPA) is facilitated by lower energy costs (up to 200 kWh per 1 ton of  $P_2O_5$  versus 7500 kWh per 1 ton of  $P_2O_5$ ), high manufacturability and the possibility of producing phosphoric acid of any quality (technical, food, pharmaceutical, reactive). In this regard, they predict an annual growth of OFK production by 3.3% per year, further improvement, and development of its production.

**Objectives:** purification of extractive phosphoric acid from additives and obtaining a suspended complex fertilizer.

**Methods:** Extraction phosphoric acid is in contact with an organic solvent, which is partially or completely immiscible with aqueous. After settling, two phases are separated: the aqueous phase (raffinate) and the organic phase, which contains a significant amount of  $H_3PO_4$  and a small amount of impurities.

**Results:** The results of the study of the FA extraction process with 100% MEA, DEA and TEA are presented in Table 2. A characteristic feature of the FA extraction process with MEA, DEA and TEA is the increase in  $K_d$  with increasing FA concentration, which is associated with a change in the composition of the extracted complex, which is a combination of molecules FA, water and extractant [3]. It should be noted that the  $K_d$  value remains almost constant, about 0.30. During the experiment, at most points the ratio of the volumes of the organic and aqueous phases was equal to 1, while the degree of extraction ( $\varphi$ ) was in the range of 25-30%.

**Conclusions:** Thus, the removal of primary silicon nuclei from the EPA solution is ensured by the movement of sediment particles into organic matter and thereby reducing their concentration in the volume of the solution. The EPA solution sequentially transforms into a single-phase system that does not contain primary sediment particles, which, in turn, are the result of the interaction of complexing ions that prevent the binding of HF into complex compounds, especially into aqua complexes. Along with this, the formation of complex compounds of iron and aluminum is possible in the amorphous phase.

### 1. Introduction

World production of extraction phosphoric acid (EPA) amounted to 48.9 million tons of  $P_2O_5$  in 2015 and is

projected to increase by 7.7 million tons of  $P_2O_5$  by 2020. The widespread development of the production of purified phosphoric acid (PPA) compared to thermal acid



(TPA) is facilitated by lower energy costs (up to 200 kWh per 1 ton of P<sub>2</sub>O<sub>5</sub> versus 7500 kWh per 1 ton of P<sub>2</sub>O<sub>5</sub>), high manufacturability and the possibility of producing phosphoric acid of any quality (technical, food, pharmaceutical, reactive). In this regard, they predict an annual growth of OFK production by 3.3% per year, further improvement, and development of its production. However, the process of obtaining OPA is complicated by the need to remove fluoride compounds, which are characterized by high toxicity and corrosiveness, as well as the possibility of forming stable complexes, the amount of which is largely determined by the concentration of fluoride ion in the solution. This is due to the interaction of hydrofluoric acid with silicic acid and sesquioxides of metals Al and Fe [1].

**Table 1. Compositions and grades of extraction phosphoric acids**

Compound, %	The acid is not evaporated (dihydrate)
Density, g/cm <sup>3</sup>	1,188
F	1,1
P <sub>2</sub> O <sub>5</sub>	20,7
SO <sub>3</sub>	2,53
CaO	0,98
Al <sub>2</sub> O <sub>3</sub>	0,32
Fe <sub>2</sub> O <sub>3</sub>	0,76
SiO <sub>2</sub>	0,2

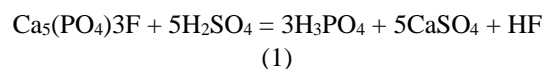
Modern requirements for the production of extraction phosphoric acid, more reliable and flexible dihydrate (DH) schemes, despite various methods for their intensification, do not allow obtaining phosphogypsum suitable for further processing without additional purification [2].

Phosphoric acid is of great importance as one of the most important components of plant nutrition.

For the production of phosphorus and combined fertilizers, orthophosphoric acid is used and the requirements for its quality are constantly increasing.

The most promising raw material for the production of purified phosphoric acid is currently considered to be extraction phosphoric acid (EPA), obtained by acid

opening of phosphorites and having undergone the stage of additional purification from impurities [2]:



The main sources of impurities in EPA are phosphorites and sulfuric acid.

The essence of the method of extraction purification of phosphoric acid (PA) is as follows: EPA is brought into close contact with an organic solvent, which is partially or completely immiscible with aqueous and into which most of the phosphoric acid and a small amount of impurities are extracted. After the two phases are separated, the aqueous phase or raffinate containing some FA and most of the impurities is often used for fertilizer production. Phosphoric acid, being then re-extracted from the extract (organic phase), has a much higher degree of purity than the original [3, 4].

This is due to the interaction of hydrofluoric acid with silicic acid and sesquioxides of metals Al, Fe and F.

The development of a technology for purifying FA begins with studying the main parameters of the extraction system: distribution coefficient (K<sub>d</sub>), degree of extraction of the target component, solution viscosity, etc. Neutral solvents 100% methanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) were used as extractants.

## 2. Objectives

Extractive phosphoric acid is recommended as a raw material for cleaning additives and obtaining quality fertilizers.

## 3. Methods

Extraction phosphoric acid is in contact with an organic solvent, which is partially or completely immiscible with aqueous. After settling, two phases are separated: the aqueous phase (raffinate) and the organic phase, which contains a significant amount of H<sub>3</sub>PO<sub>4</sub> and a small amount of impurities.

When developing purification methods using liquid-liquid extraction, the main attention is paid to the selection of an organic extractant with a high distribution coefficient.

More than 40 solvents were studied, including aliphatic and cyclic alcohols, ethers and esters, amines, ketones,



aldehydes, and hydrocarbons. The studied solvents are arranged in order of decreasing distribution coefficient of phosphoric acid: alcohols, ketones, ethers, aldehydes, hydrocarbons. It has been established that the presence of inorganic acids ( $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ), as well as Fe, Al and Mg compounds in solution promotes the transition of phosphoric acid into the organic phase [5-7].

Water-soluble alcohols have been studied as organic solvents. Of these, the most effective are methyl, ethyl, propyl and isopropyl. However, when alcohol is added to EPA, inorganic impurities are released in the form of slimy sediments, which are very difficult to separate. Monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) are widely used to purify EPA from metal cations and from fluorine.

An effective extractant for EPA solutions is DEA. The amount of metal-containing impurities in phosphoric acid purified using DEA does not exceed 100 wt. hours per million.

Organophosphorus solvents are of particular interest for purifying EPA from impurities. Currently, one of the best extractants is high-boiling, low-soluble in EPA DEA. DEA has high selectivity towards phosphoric acid in a wide range of its concentrations, and high selectivity towards metal cations, sulfates and fluorine.

The experiment was carried out as follows: the aqueous and organic phases were brought into contact and emulsified using a magnetic stirrer MS7-H550-S (speed 0-1500 rpm). The contact time of the phases was 15 min, which corresponds to the achievement of equilibrium during the extraction process. Phase separation was carried out in a separating funnel, the volumes of the phases, the density of the raffinate were measured, and the concentration of FA was determined by titration with a NaOH solution with a metal orange indicator. The concentration of FA in the organic phase was determined by the level of material balance:

$$X_H * V_H^B = X_{kC} V_k^B + Y_k * V_k \quad (2)$$

where  $X_H$  and  $X_k$  are the initial and final concentrations of FA in the photophase;  $Y$  is the concentration of FA in the organic phase (extract);  $V_H^B$  and  $V_k^B$  are the initial and final volumes of the aqueous solution of FA;  $V_k$  is the final volume of the organic phase.

#### 4. Results

The results of the study of the FA extraction process with 100% MEA, DEA and TEA are presented in Table 2. A characteristic feature of the FA extraction process with MEA, DEA and TEA is the increase in  $K_d$  with increasing FA concentration, which is associated with a change in the composition of the extracted complex, which is a combination of molecules FA, water and extractant [3]. It should be noted that the  $K_d$  value remains almost constant, about 0.30. During the experiment, at most points the ratio of the volumes of the organic and aqueous phases was equal to 1, while the degree of extraction ( $\varphi$ ) was in the range of 25-30%.

As a result of the research, MEA was chosen as an extractant for the purification of phosphoric acid.

#### 5. Discussion

The following results were obtained from the IR spectrum shown in Fig.2. From the research results the following were established:

- absorption lines of the  $-\text{OH}$  group have stretching vibrations at  $3410 \text{ cm}^{-1}$ , bending vibrations at  $1450 \text{ cm}^{-1}$ ,  $601 \text{ cm}^{-1}$  and  $599 \text{ cm}^{-1}$ ;
  - absorption lines of the  $-\text{C}=\text{C}$ -group have stretching vibrations at  $1627 \text{ cm}^{-1}$ ; deformation vibrations at  $1821 \text{ cm}^{-1}$ ,  $1734 \text{ cm}^{-1}$ ;
  - absorption lines of the  $-\text{C}-\text{O}-$  group have stretching vibrations at  $1022 \text{ cm}^{-1}$ ;
  - absorption lines  $=\text{CH}-$  have stretching vibrations at  $3040 \text{ cm}^{-1}$ , bending vibrations at  $1327 \text{ cm}^{-1}$ ;
  - $-\text{CH}_2-$  represents stretching vibrations at  $1425 \text{ cm}^{-1}$ .
- The results of the IR spectra confirm that the stretching vibrations of  $1000-1100 \text{ cm}^{-1}$  belong to  $-\text{PO}_4^{3-}$  the organic substance formed as a result of the reaction is monoethanolamine phosphate.

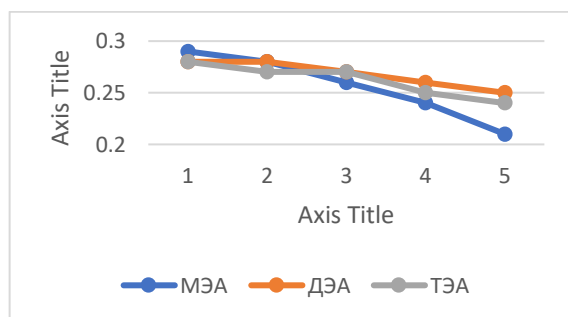
**Table 2. Main parameters of the extraction process of phosphoric acid 100% MEA, DEA and TEA.**

Initial concentration of phosphoric acid	X	Y	Kd	Viscosity (cP),
100% monoethanolamine				
35,3	9,11	2,66	0,29	12,348
30,8	8,56	2,41	0,28	11,762
25,6	7,29	1,89	0,26	11,025
20,7	6,33	1,55	0,24	10,681

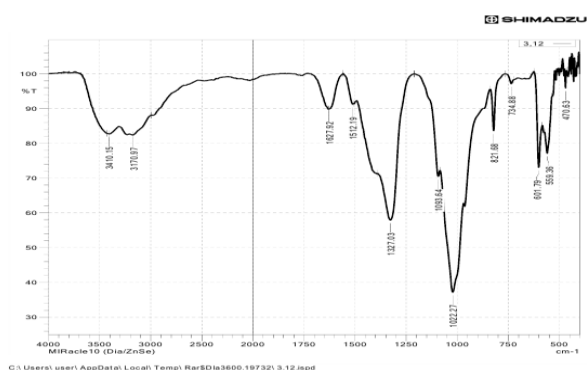


19,1	5,08	1,04	0,21	9,559
100% diethanolamine				
35,3	10,25	2,89	0,28	13,158
30,8	9,09	2,51	0,28	12,225
25,6	8,53	2,31	0,27	11,677
20,7	7,77	2,01	0,26	11,387
19,1	6,45	1,62	0,25	10,701
100% triethanolamine				
35,3	11,28	3,15	0,28	13,879
30,8	10,22	2,75	0,27	13,482
25,6	9,35	2,52	0,27	12,567
20,7	8,12	2,03	0,25	11,861
19,1	7,23	1,73	0,24	10,893

**Fig. 1. Partition coefficients of phosphoric acid during extraction of 100% MEA, DEA and TEA.**



**Fig. 2. IR analysis of the white precipitate formed during the neutralization of extraction phosphoric acid with monoethanolamine.**



## 6. Conclusion

Thus, the removal of primary silicon nuclei from the EPA solution is ensured by the movement of sediment particles into organic matter and thereby reducing their concentration in the volume of the solution. The EPA solution sequentially transforms into a single-phase system that does not contain primary sediment particles,

which, in turn, are the result of the interaction of complexing ions that prevent the binding of HF into complex compounds, especially into aqua complexes. Along with this, the formation of complex compounds of iron and aluminum is possible in the amorphous phase. Complexes of iron and aluminum precipitate together with silica gel as a result of crystallization, form a common precipitate and are in the state of a thick mass.

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