ISSN NO. 2320-5407

Journal homepage:http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Decreasing Iron Content from Egyptian Wet Process Phosphoric Acid using Organic Solvent Extraction

M. I. Amin, H. M. Kamal and M. M. Gouda
Nuclear Materials Authority, Cairo, Egypt.

Manuscript Info

Manuscript History:

Received: 12 November 2013
Final Accepted: 22 December 2013
Published Online: January 2014

Key words:
Decreasing iron, wet phosphoric acid and organic solvent extraction.

Abstract

The solvent extraction of iron from Egyptian wet process phosphoric acid using di-ethylhexyl phosphoric acid was investigated. The effect of the phosphoric acid concentration, organic solvent concentration, organic to aqueous phase ratio, temperature and stirring time were studied. 69.3% iron removal efficiency from 2.0 M phosphoric acid (12% P_2O_5) was obtained using 2.0 M D_2EHPA and organic to aqueous phase ratio 2:1 for stirring time 5 min. under room temperature while the iron removal efficiency percent increases to be 99.9% by applying the recommended optimum conditions on another type of phosphoric acid partially purified by solvent extraction technique using mixture of butanol and octanol.

Introduction

The presence of iron in phosphoric acid results in increasing the viscosity and consequently decreasing the filtration rate. Iron forms precipitates during concentration, clarification and storage accompanied by P_2O_5 loss. In addition, the P_2O_5 water-solubility of fertilizers decreases in the presence of high iron containing acid (H. El-Shall and E.A. Abdel-Aal **2001)** Fertilizer grade (SPA) phosphoric acid of 50% P_2O_5 concentration should contain <1.5% Fe_2O_3, otherwise the P_2O_5 water solubility of the fertilizers prepared from high iron acids will be low (A.K. Ismail 1998). The authors (A. A. Hanna et al. 1996; 1992; Kh. Y. Naguib, 1996; A. F. Ali, 1995) carried out different trials to reduce the iron content in wet process phosphoric acid produced from dissolution of Abu- Tartor phosphate in sulfuric acid. The trials included solvent extraction or precipitation methods, n-butyl alcohol and tributyl phosphate TBP, were used to reduce the iron content from 3.0 to 1.6% from Fe_2O_3. The chemical analysis of the purified phosphoric acid obtained indicated that such method gives acceptable phosphoric acid for chemical industrial uses. Several materials were used to reduce the iron content by precipitation, the most suitable of which were found to be Na_2CO_3, NaOH and KOH while sodium oxalate was found to be a poor precipitating agent. Although potassium ferrocyanide gave good precipitating results but is not recommended because of its poisonous nature (A. A. Hanna 1999). The present work is aimed to study in details the reducing of iron content from wet process phosphoric acid and apply the obtained optimum conditions on the diluted phosphoric acid which partially purified using solvent extraction technique using a mixture of butanol and octanol.

2- Experimental procedure

2.1- Materials

The starting material of the present work is Egyptian wet process phosphoric acid which have the following components (P_2O_5 = 44.0%, Fe = 2.6%, Cu = 0.0012%, Cd = 0.001%, F = 0.7%) was supplied from Abu-Zaabal Co., Cairo, Egypt. Abu Tarturbentonite was used. All chemicals and reagents were of A.R. grade and used without further purification. Fe was determined by GBC 932- AAS.

2.2- Procedure

Before iron extraction process, pretreatment of the crude phosphoric acid must be occurred by removal of organic matters present in the acid (A. A. El-Asmy et al. 2008). Crude phosphoric acid was mixed with bentonite (11.67 g/l) for 30 min. and the acid was left to settle down. Polycrylamide type (0.5 mg/l) as a flocculating agent was added to enhance the settlement of the suspended materials.

Extraction experiments were carried out in a mechanically agitated and thermostatic beakers containing iron in 50 mL of phosphoric acid and 100 mL of D2EHPA. The mixture was agitated by a mechanical device at constant stirring speed 400 rpm. After 5 min, the organic and aqueous phase was separated and the iron concentration was determined in aqueous phase by atomic absorption spectrometer. Whereas the concentration of the iron in the organic phase was calculated from the difference of the iron concentration in the aqueous phase before and after the extraction process, the results were expressed as percent iron extracted.

Concentrated Phosphoric acid (44% P_2O_5) was purified by solvent extraction process using mixture of butanol and octanol in three steps (M. I. Amin 2010), a) first is extraction process for H_3PO_4 by the mixture of butanol and octanol organic solvent, b) the second step is scrubbing process, in this process organic solvent was loaded with H_3PO_4 and some of undesirable impurities such as iron so that washing of loaded organic solvent using pure phosphoric acid is necessary for removal of these impurities and to produce highly pure phosphoric acid, c) the third step is stripping process of H_3PO_4 from loaded organic solvent using distilled water and producing of diluted phosphoric acid. In this work, the removal of iron from Egyptian wet process phosphoric acid was investigated and finally the obtained recommended optimum conditions are applied on another type of phosphoric acid partially purified by solvent extraction process using mixture of butanol and octanol. Many successful trials were achieved to purify phosphoric acid by organic solvent extraction process (A. A. Hanna et al., 1995, 1999; L. James et al., 1977; H. Ahmed et al., 2007) but these trials are expensive because of applying scrubbing process using pure phosphoric acid (step b) so that the main goal of this work is extraction the iron from both Egyptian wet process phosphoric acid and partially purified phosphoric acid without applying the scrubbing during the purification process. For this purpose, 50 mL of partially purified phosphoric acid was agitated with 100 mL of 2M D2EHPA for 5 min under room temperature.

3- Results and Discussions

3.1- Effect of acid concentration

The effect of phosphoric acid concentration on the extraction process was studied in the range 2.0 – 9.2M. The operating conditions used were [Fe] =10000 ppm, phase ratio O/A=2, stirring time= 5 min., [D2EHPA] = 2.0M and the extraction temperature was room temperature. From (Fig. 1) it is noticed that the iron removal efficiency (Fe $E_{removal}$, %) decreased by increasing the phosphoric acid concentration reached 12% removal efficiency at 9.2M phosphoric acid while the Fe $E_{removal}$, % reached 69.3% by using 2.0M phosphoric acid.

3.2- Effect of D2EHPA concentration

The extraction of iron from phosphoric acid (2.0 M) was studied at room temperature. The results (Fig. 2) show that within the concentration range (0.1-2.86 M) of solvent, Fe $E_{removal}$' % increase with the increase of organic solvent concentration.

3.3- Effect of organic to aqueous phase ratio

The effect of changing org. / aq. phase ratio between 1.0 and 6.0 on $E_{removal}$' % of Fe from phosphoric acid (2.0 M), was investigated using D2EHPA organic solvent. (Fig. 3) depicts that $E_{removal}$' % of Fe increases by increasing the organic to aqueous phase ratio.

3.4- Effect of temperature

The removal of Fe from the phosphoric acid (2.0 M) was investigated at different temperature between 25 and 70°C. (Fig. 4) The Org. /Aq. phase ratio was 1:1 and the shaking time was 5 min. It is shown that $E_{removal}$' % of Fe increased from 69.3 to 80.1%. Fig. 4 shows also that the increase of $E_{removal}$' % is less pronounced upon increasing the temperature from 25 to 70°C. This is interesting when energy consumption either for cooling or heating is considered.

The results are also plotted in (Fig. 5) in the form of ln D versus 1000/T °K. The results fit a straight line equation with a slope value -1.34. The relation between the equilibrium constant *K* and the temperature is given by Vant Hoff equation:

$$d\ln K/dT = \Delta H/R.T^2$$

By integration,

$$\ln K = (-\Delta H/R)(1/T)$$

And since the distribution ratio D is related by definition to the equilibrium constant K, the previous equation could be written:

$$\ln D = (-\Delta H/R)(1/T)$$

It was possible to calculate the enthalpy change (ΔH) this value is 11.14 KJ/mol for. The positive values of ΔH refer to the positive effect of extraction temperature.

3.5- Effect of Stirring time

Stirring time is an important factor in determining the efficiency of liquid-liquid extraction processes which involve mass transfer between two liquids. The effect of stirring time was investigated between 0.5 and 6.0 min. under the following conditions: (H_3PO_4 =2.0M, O/A =2:1 and T 25°C). The results are graphically presented in (Fig. 6) evidently the extraction was found to be rapid and 5 min is the prefer stirring time for iron removal from phosphoric acid.

3.6-Mac-Cab Thiele Diagram for removal of iron from phosphoric acid

Considering the optimum conditions for iron extraction from 2.0 M phosphoric acid using 2.0M D2EHPA, stirring time of 5.0min and at room temperature, iron extraction equilibrium curve (Fig. 8), was used to calculate the number of counter current, it is found that four stages required to achieve about 96.9% removal yield at 25 °C.

3.7- Application

Phosphoric acid was purified by solvent extraction process using a mixture of butanol and octanol by Amin et al. [11], to produce highly grade phosphoric acid can be used in food applications. The advantage of this method of purification is production of very highly pure grade phosphoric acid but the main disadvantage of this technique is highly expensive cost because of applying scrubbing process which is an important step to decrease the iron from loaded organic solvent during the purification process. In this work, the recommended optimum conditions (D2EHPA =2.0M, Org. /aq. =2.0, Temperature = 25 C° and H_3PO_4 = 2.0M) were applied on the produced partially purified diluted phosphoric acid by Amin et al., without scrubbing process (Fe = 2344 ppm). The results revealed that iron $E_{removal}$' % from partially purified phosphoric acid reached 99.91%, from this result the removal of iron using solvent extraction technique using D2EHPA organic solvent from diluted partially purified phosphoric acid give satisfactory results hence, the removal of iron from such partially purified phosphoric acid can be achieved using solvent extraction technique instead of applying scrubbing process of loaded organic solvent from economic point of view. The flow sheet1 show all steps for the purification of phosphoric acid and extraction of the iron using D2EHPA as an organic solvent for production highly pure grade phosphoric acid without applying scrubbing process of loaded organic solvent (loaded butanol and octanol). Table 1 show the iron concentration in crude wet process phosphoric acid, partially purified phosphoric acid obtained without scrubbing process and finally purified acid using D2EHPA organic solvent technique.

Table 1- Chemical composition of different types of phosphoric acid

Type of acid	**Fe, ppm**	**Fe $E_{removal}$'%**	**P_2O_5, %**
Crude H_3PO_4	40560	-	44
Stripped H_3PO_4 without scrubbing	2344	78.81	12
Finally purified H_3PO_4	10	99.91	12

Flow sheet 1- Production of highly pure grade phosphoric acid

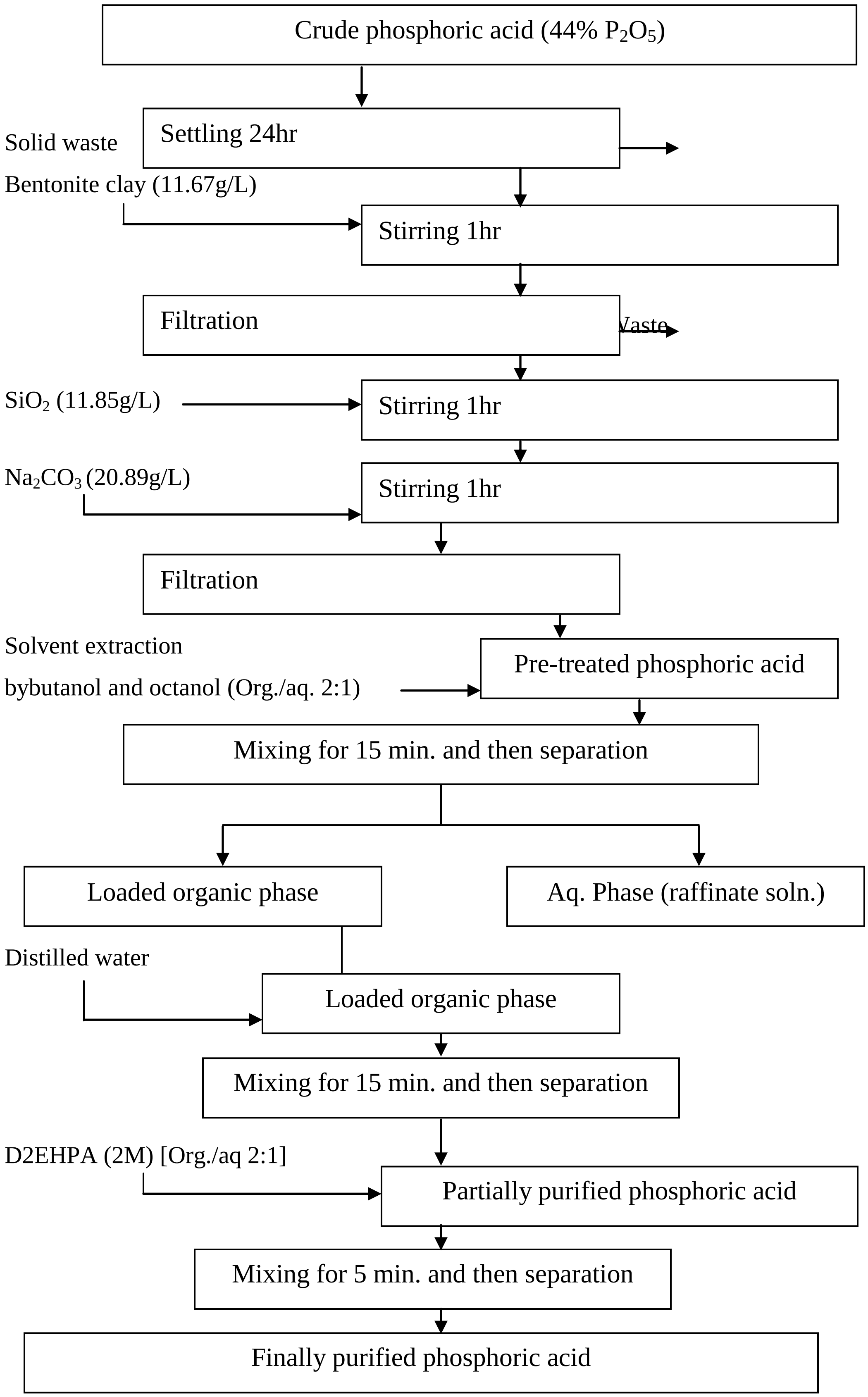


Fig. 1- Effect of phosphoric acid concentration on the iron $E_{removal}$ %

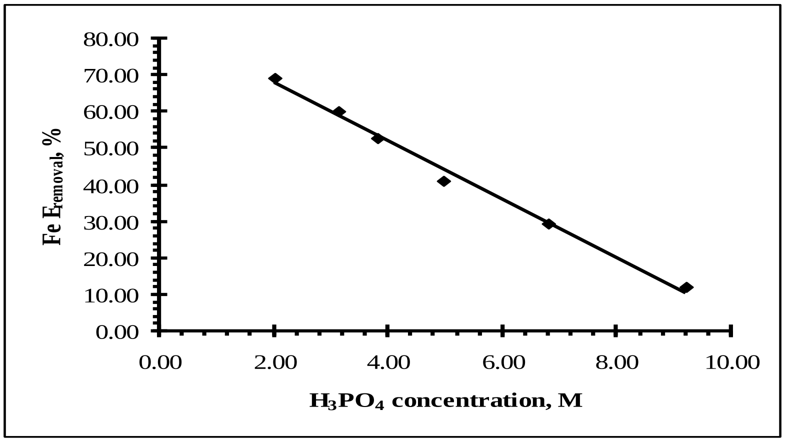


Fig. 2- Effect of D2EHPA concentration on the iron $E_{removal}$ %

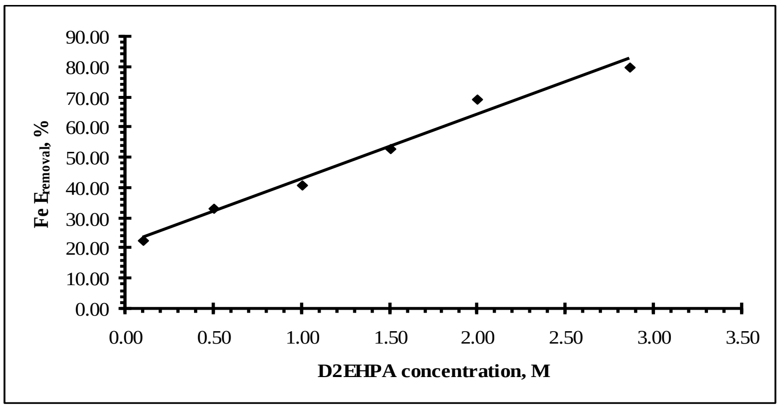


Fig. 3- Effect of organic to aqueous phase ratio on the iron $E_{removal}$ %

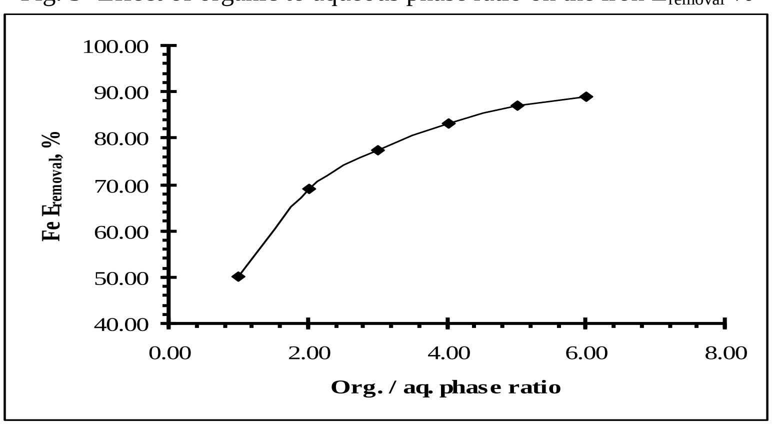


Fig. 4 - Effect of temperature on the iron $E_{removal}$ %

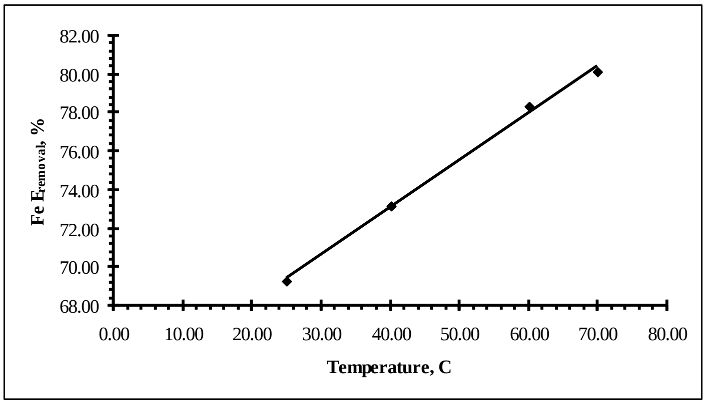


Fig. 5- ln D as a function of 1000/T

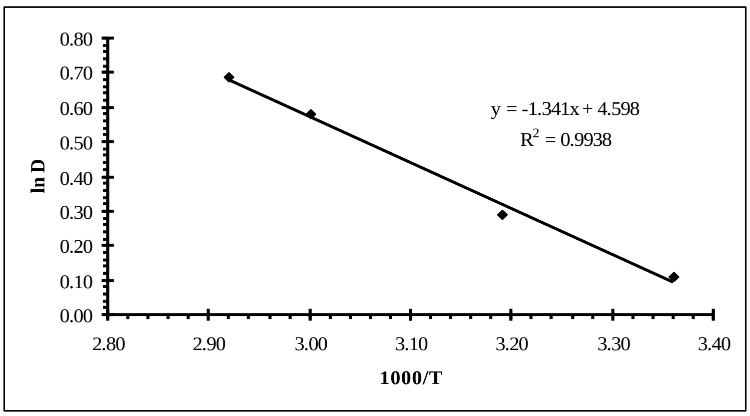


Fig. 6- Effect of stirring time on the iron $E_{removal}$ %

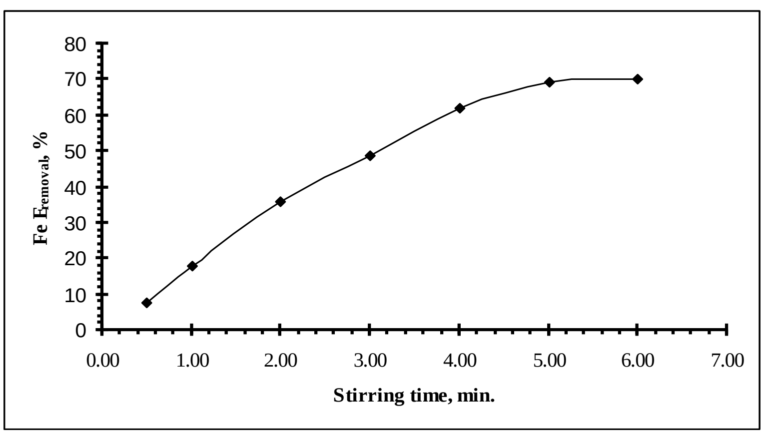
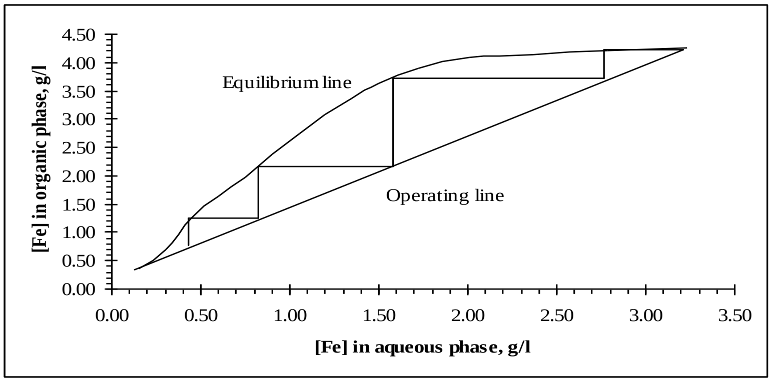


Fig. 7- McCabe-Thiele diagram for the extraction of iron



Conclusion

Removal of iron from wet process phosphoric acid was investigated by solvent extraction using di-ethylhexyl-phosphoric acid. Iron was extracted from 2.0 M H_3PO_4 in four stages at 25 °C with organic/aqueous phase ratio equal 2:1 while the stirring time was 5 min. The percentage of removal was 69.3 and 99.9% for Egyptian phosphoric acid and diluted phosphoric acid obtained by Amin et al., without scrubbing process respectively. ΔH was calculated 11.14 KJ/mol, the positive value of ΔH refer to the positive effect of extraction temperature.

Reference

A. A. Hanna and H. A. Sibak, J Eng. Appl Sci., 43 (1996) 1031.

A. A. Hanna and H. A. Sibak, J Eng. Appl Sci., 44 (1997) 425.

A. A. Hanna and A. F. Ali, J Chem. Technology Biotechnology, 55 (1992) 205.

A. A. Hanna, A. A. Youssef and A. F. Ali Egypt J Chem, 38 (1995) 311.

A. A. Hanna, Reducing iron content in crude phosphoric acid by potassium ferrocyanide, Indian Journal of Chemical Technology, 6 (1999) 276.

A. A. Hanna, N. S. Youssef and A. F. Ali, Purification of Wet Process Phosphoric Acid by Solvent Extraction, Egypt Journal Chemistry, 38(1995)311-317.

A. A. El-Asmy, H. M. Serag, M. A. Mahdy and M. I. Amin, Purification of phosphoric acid by minimizing iron, copper, cadmium and fluoride, Separation and Purification Technology, 61 (2008) 287.

A. E. A. Eid, A. A. Hanna, N. S. Youssef and E. A. M. El-Zahany,Study on Solvent Extraction of Phosphoric Acid From Phosphate Ores-HCl Digestion Liquor Using Pure and Mixed Solvent, Asian Journal of Chemistry, 11(1999)213-224.

A.K. Ismail, "Iron Removal From Phosphoric Acid By Precipitation Process", Central Metallurgicl R&D Institute, Cairo, Egypt, March, 1998.

A. F. Ali, Ph D Thesis, Faculty of Science, CairoUniversity, 1995.

Kh. Y. Naguib, M Sc Thesis, Faculty of EngineeringCairoUniversity 1996.

H. El-Shall and E.A. Abdel-Aal, " Decreasing Iron Content in Wet Process Phosphoric Acid ", Final report, Department of Materials Science and Technology, Florida University, Feb. 2001.

M. I. Amin, M. M. Ali, H. M. Kamal, A. M. Youssef and M. A. Akl, Recovery of high grade phosphoric acid from wet process acid by solvent extraction with aliphatic alcohols, Hydrometallurgy, 105 (2010) 115.

H. Ahmed, H. Diamonta, C. Chaker and R. Abdelhamid, Purification of Wet Process Phosphoric Acid by Solvent Extraction With TBP and MIBK

Mixtures, Separation and Purification Technology, 55(2007) 212-216.
L. James, B. Bradford and Fernando, Extraction Process for Purification of Phosphoric Acid, United States Patent, No. 4,053,564., (1977).