

# Simulation of Multistage Extraction Units for Wet Process Phosphoric Acid Purification

Rania Hamdi, Naima Khleifia, and Ahmed Hannachi

**Abstract**—Liquid-liquid extraction is a widely used unit operation in separation processes. It is omnipresent in all chemical, biochemical and food processing industries. This technique has long been used for purifying the Wet Process Phosphoric Acid (WPA) with fairly good purification performances. The purification is carried out in three step process: extraction, washing and recovery. Each of these steps is a liquid-liquid extraction operation. Because of the complexity of such operations, the choice of the best operating conditions has been a challenging task for engineers. In the present work, the simulation of the WPA has been conducted. The aim was to develop a computer code that helps predicting the overall performance of the purification process for a given set of operating conditions. The adopted approach is based on determining the necessary theoretical stages (NTS) and the contents of acid and impurities in the two phases for each step in the purification process using a numerical technique. The results of the simulation of the WPA purification process by the Tri Butyle Phosphate (TBP) will be shown.

**Index Terms**—Wet Phosphoric Acid, Purification, Solvent extraction, Simulation, NTS.

## I. INTRODUCTION

Two processes are used for the production of phosphoric acid. The thermal process produces a pure acid with huge energy consumption. The so-called Wet Process Phosphoric Acid (WPA) is obtained as a result of a chemical reaction involving the phosphated rock and a mineral acid. This process is economic and practiced in many countries [1-3]. However, most of the fluorapatite impurities are dissolved in the produced acid. The WPA has to be purified before its use in several industrial fields such as food processing, fertilizers and detergent production [4].

Several techniques are available for WPA purification: precipitation, adsorption, ion exchange and solvent extraction [5]. Liquid-liquid extraction is at the heart of many WPA purification processes. While many solvents are available, frequently those that are capable of selectively extracting phosphoric acid ( $H_3PO_4$ ) have been widely used for such task [1, 2, 4, 6].

This technique has long been used for purifying the WPA with fairly good purification performances. The purification is basically carried out in three consecutive operations: extraction, washing and recovery. The acid might be subject to other pretreatment and post-treatment operations. All of these three steps are liquid-liquid extraction operations. Because of the complexity of such operations, it is very difficult to predict the overall performance of the

purification process for a given set of operating conditions making it very hard to find the optimal conditions for conducting the purification process [7-9]. Analysis and optimization of the WPA purification process based only on costly and time consuming experimental investigations have limited outcomes and are short of achieving all goals.

The objective of this work is to develop a numerical tool a method for predicting the overall performance of the purification process by solvent extraction. This technique is based on the simulation of the WPA purification process. The adopted approach is based on the determination of the necessary theoretical stages for each step in the purification process using a numerical technique. Some simulation results of a WPA purification process will be shown.

## II. MODELING OF THE WPA PURIFICATION

Modeling of the phosphoric acid extraction is based on material balances on the extraction column. In Fig 1, a cascade of counter current theoretical stages is shown. The acid feed  $H_3PO_4$  weight percentage and flow rate are designated by  $F$  and  $x_F$  respectively. The extraction is carried with an organic solvent countercurrent feed flow rate of  $S$  with an acid content of  $y_S$ . The WPA is brought into contact with the solvent to lead to a raffinate  $R$  having a residual  $H_3PO_4$  content of  $x_R$ . The extract, designed by  $E$ , leaves with an acid content  $y_E$ .

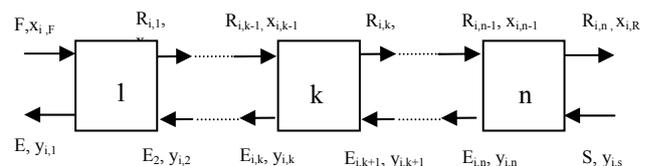


Fig. 1: Cascade of counter current theoretical stages

This yields the following equation for a specific mass balance on the solute for the  $k^{th}$  stage:

$$R_k x_{k-1} + E_{k+1} y_{k+1} = E_k y_k + R_k x_k \quad (1)$$

Since the solvent and water are mutually slightly miscible, and the WPA is 99% made up of water and  $H_3PO_4$ , the assumption of a constant solvent flow rates,  $R_p$  and  $E_p$ , for all extraction stages has been taken [8-9].

$$S (1 - y_S) = S (1 - y_k) = E_p = cte \quad (2)$$

$$F (1 - x_F) = F (1 - x_k) = R_p = cte \quad (3)$$

Combining eq. (1), (2) et (3) leads to:

$$\frac{R_p}{(1 - x_{k-1})} x_{k-1} + \frac{E_p}{(1 - y_{k+1})} y_{k+1} = \frac{E_p}{(1 - y_k)} y_k + \frac{R_p}{(1 - x_k)} x_k \quad (4)$$

When the Bancroft coordinates ( $Y=y/(1-y)$  and  $X=x/(1-x)$ ) are used, equation 4 gives the following expression for the acid content in the  $k^{th}$  stage:

$$Y_k = \frac{(R_p(X_{k-1} - X_k) + E_p Y_{k+1})}{(E_p(1 + Y_{k+1}) + R_p(X_{k-1} - X_k))} \quad (5)$$

For a given feed quality and an acid extraction rate in the extraction phase, the number of theoretical stages is determined by an iterative calculation procedure.

First, the raffinate quality is assumed. The solute composition in the aqueous phase leaving the first stage is determined from the equilibrium curve. An over all balance between the second and the last stage yields the solute composition in the extraction phase leaving the second stage and from the solute distribution isotherm the solute composition in the raffinate phase exiting the same stage is calculated.

This calculation procedure is repeated until the last stage for which inlet extract phase and the outlet raffinate compositions should be consistent with the assumed extraction rate and the solvent composition. If these conditions are not satisfied, the solvent rate has to be modified and the calculation procedure has to be repeated until satisfaction of the convergence criteria.

The same procedure gives also impurities' contents in all fluxes. These iterative computation techniques have been implemented in a computer code that is capable of finding the number of theoretical stages as well as the composition of all fluxes in each step of the purification process.

### III. RESULTS AND DISCUSSION

The computer code has been implemented to simulate the purification process using Tributyle phosphate as  $H_3PO_4$  extractant. In order to simulate the solvent extraction based purification process, the equilibrium data are needed. That is, the phase diagram of the pseudo-ternary system  $H_3PO_4$ -Water-TBP has to be established. The partition ratios for all impurities between organic and aqueous phases have to be determined as well. Then, all equilibrium isotherms have to be approximated using a least square regression.

The  $H_3PO_4$  distribution curve between the organic and the aqueous phases is shown in Fig. 2. For the same solvent, the partition ratios for some impurities as function of the acid concentration in the organic phase are given in Fig. 3.

In this study, each step of the purification process is assumed to be conducted in a cascade of counter current theoretical stages. Performing material balances over these ideal extractors and exploiting the available equilibrium data constitutes the core of this theoretical approach to model the WPA purification process.

The Number of Theoretical Stages' (NTS) is an important parameter which is directly related to the size of the equipments used in the purification process. A large NTS is synonymous of a difficult operation that needs huge equipments to insure adequate mass transfer between phases.

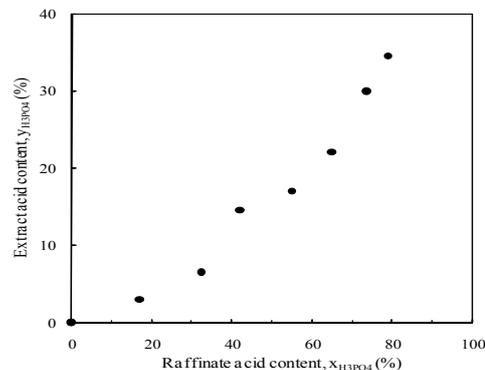


Fig. 2: Equilibrium isotherm ( $H_3PO_4$ - $H_2O$ -TBP) [7]

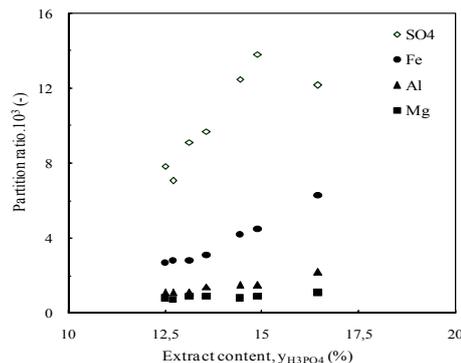


Fig. 3: Major WPA impurities' partition ratios [7]

Simulations were conducted for the purification of WPA titrating 78%  $H_3PO_4$  using fresh TBP as solvent. The feed WPA contents are given in Tables I.

TABLE I. CHEMICAL COMPOSITION OF THE WPA

$H_3PO_4$ (%)	Al (ppm)	Fe (ppm)	Mg (ppm)	$SO_4$ (ppm)
78	3771	2163	6679	1604

For the extraction step, the NTS required for extracting a given amount of  $H_3PO_4$  from the WPA fed is shown in Fig. 4. When the solvent rate decreases the transfer becomes harder to insure as the NTS increases. For any given extraction yield, as the solvent rate decreases below a critical value, there is a sharp rise of the needed NTS. That is, the solvent rate has to be carefully chosen to strike a compromise between the extraction equipment size and the solvent amount.

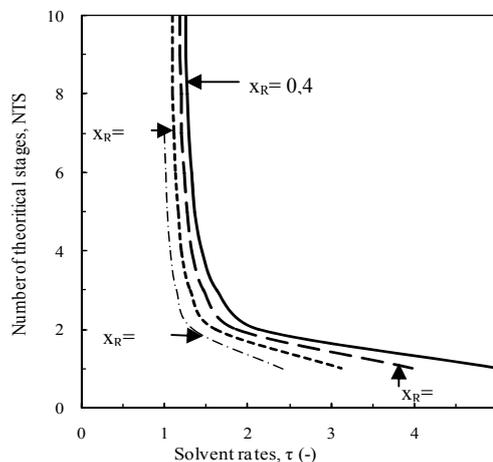


Fig. 4: Number of theoretical stages for extracting  $H_3PO_4$  from the WPA versus the solvent rate

For a given amount of acid extracted by the solvent, the computer code gives the acid as well as impurities' weight fractions in all streams flowing in out of all theoretical stages in the extraction operation. As an illustration, simulations for an operation that requires five stages were conducted. The  $H_3PO_4$  extraction yield was imposed at 82%. Fig. 5 gives  $H_3PO_4$  contents of both extract and raffinate phases for all stages. In this investigation four major WPA impurities were considered. Fig. 6 and 7 give of WPA major impurities' contents in both phases at each of the five stages. These details provide valuable information on the intensity of solute transfer taking place in each stage. It is clear from these figures that much of the transfer is happening in the stages close to the fresh solvent feed.

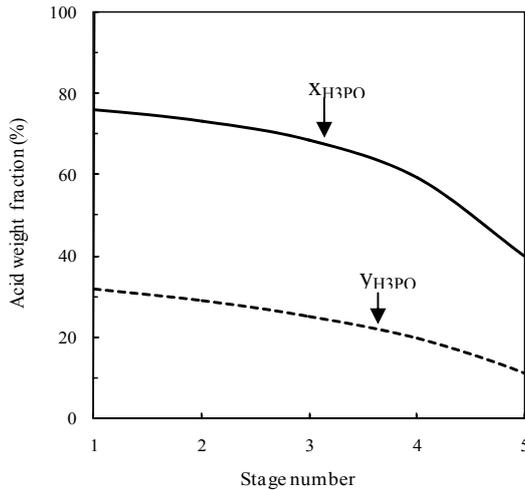


Fig. 5: Raffinate and extract acid contents for extraction stages

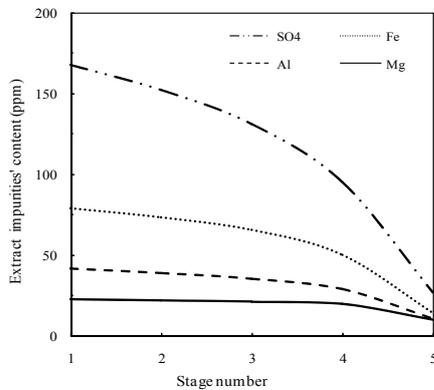


Fig. 6: Extract impurities' contents for extraction stages

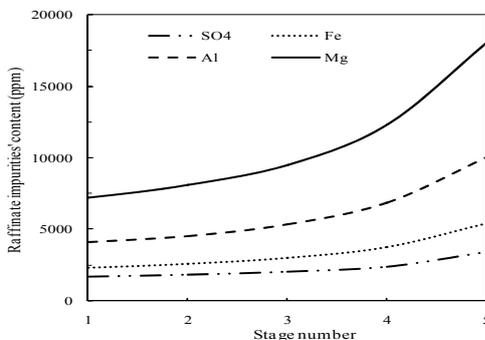


Fig. 7: Raffinate impurities' contents for extraction stages

For the same operating conditions (i.e. feed WPA at 78% and extraction yield 82%), and for various solvent rates, the computed impurities' extraction yields are given in Fig.8. As expected because of the increase of the required NTS,

the extraction yield for the undesired matter intensifies when the solvent rate decreases. Thus, with respect to the extract purity one has to favor higher solvent rates for the extraction phase. In fact, the solvent rate has to be optimized in order to insure a relatively pure acid extract reach with the lowest solvent amount.

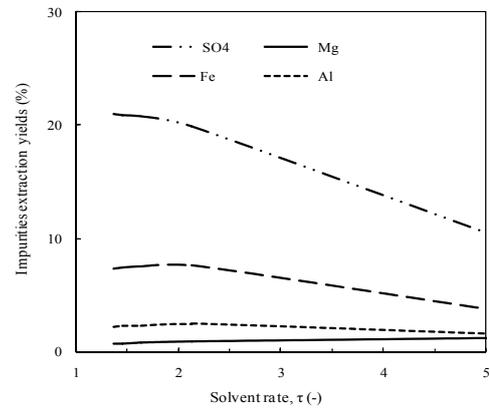


Fig. 8: Impurities' extraction yields versus solvent rates

The simulation results were confronted with those obtained experimentally for single stage extraction operation. A relative good matching has been obtained as demonstrated in fig.9.

After extracting  $H_3PO_4$  from the WPA, the extract phase has to be washed. This treatment is intended to get rid of much of the undesired impurities in the extract. Using the same numerical procedure as for the extraction, the result of the washing operation can also be predicted.

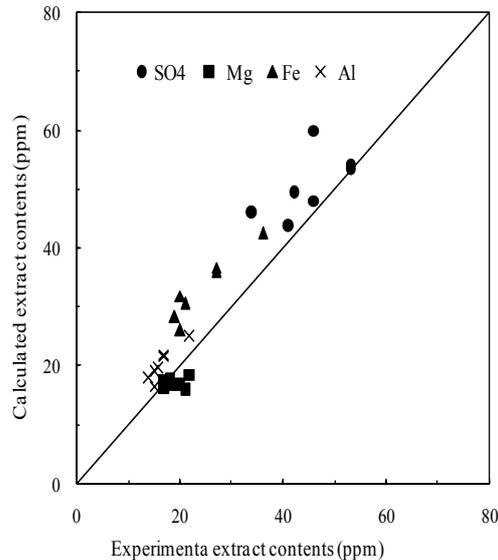


Fig.9: Comparison between experimental and simulation results

For an extract feeding the washing operation at 31%  $H_3PO_4$  and a fixed acid weight fraction of the washed extract at 25%, Tables II gives the amount of major trace impurities discharged with the washing water and their concentration levels in the cleaned extract. As expected from the partitions ratios (Fig.3), the impurities extraction rate in decreasing order is for Mg, Al, Fe and  $SO_4$ .

TABLE II: IMPURITIES' REMOVAL RATES FOR THE WASHING OPERATION

Impurities	Al	Fe	Mg	$SO_4^{2-}$
Removal rates (%)	51	71	38	86
Extract content (ppm)	230	259	161	261

The washed extract is then fed to the stripping operation intended to re-extract the acid to obtain the purified phosphoric acid which eventually will undergo a concentration post treatment process. An identical approach to that applied for the extraction and washing can be implemented for the stripping operation. For a washed extract at 25% H<sub>3</sub>PO<sub>4</sub> supplying the stripping operation and for three acid concentration levels of the purified acid, the concentrations of some trace impurities are given in Table III.

TABLE III: PURIFIED ACID IMPURITIES' CONTENTS

Purified Acid H <sub>3</sub> PO <sub>4</sub> %	Impurities' contents (ppm)			
	SO <sub>4</sub>	Mg	Fe	Al
24	165	3	6	15
37	284	5,5	10,5	28
50	328	10,5	17	50,5

As for membrane separation techniques, a rejection rate for each WPA impurity can be defined as the impurity removal percentage for the WPA. The rejection rates for the WPA major impurities and for three different purified acid concentrations are given in Fig.10. It is clear that one has to find the optimum stripping rate that leads to high acid concentration with minimum impurities' contents in the purified acid. For the three major WPA cationic impurities (Mg, Al and Fe) the rejection rate is very close 100%. For the case of sulfates, the rejection rate is much lower and doesn't fall below 62% for the chosen operating conditions.

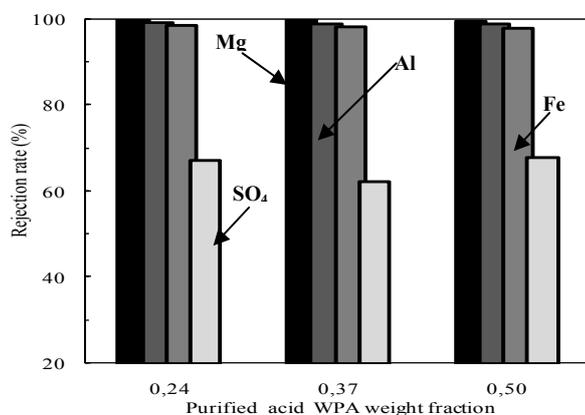


Fig. 10: Rejection rates for major impurities versus the acid content.

#### IV. CONCLUSION

In the present work, simulation of the Wet Process Phosphoric Acid (WPA) purification process was performed. The purification is based on solvent extraction and is carried out in a three step process: extraction, washing and stripping. Each of these liquid-liquid extraction operations were assumed to be conducted in a cascade of counter current theoretical stages.

Steady state material balances over each extractor and equilibrium data was integrated to model the purification process. A computer code was developed and used to simulate the WPA purification.

The conducted simulations provided detailed information such as the NTS required for each step of purifying WPA and the concentrations in all streams flowing in out of all theoretical stages in the purification process. For a given set of operating conditions, the adopted approach allows to predict the rejection rates for all WPA impurities, as well as the quality of the purified acid. This technique can be used to investigate the effect of changing the operating conditions on the overall performances of the purification process. Thus, the developed computer code could be used as a tool for predicting the WPA purification results in order to look for the optimal operating conditions.

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#### REFERENCES

- [1] M.Feki, M.Stambouli, D.Pareau, H.F.Ayedi, "Study of the multicomponent system wet process phosphoric acid-methyl ketone at 40° C phase equilibria and extraction performances," *Chem. Eng. J.*, vol.88, 2002, pp.71–80.
- [2] M.Abdalbake and O.Shino, "Removing the cadmium, arsenic and sulfate ions from wet process phosphoric acid, *Periodica polytechnica Ser.*" *Chem. Eng.* vol. 48, no. 1, 2004, pp. 63–71.
- [3] Alibrahim.M, "Extraction of phosphoric acid from various aqueous solutions using tributylphosphate (TBP), *Periodica Polytechnica, Chemical Engineering*, vol.51, no.1, 2007, pp. 39–42,
- [4] S.Khorfan, O.Shno And A.Wahoud, "Extraction of H<sub>3</sub>PO<sub>4</sub> from wet phosphoric acid by nC<sub>4</sub>-nC<sub>7</sub> alcohols, *Periodica polytechnica ser*".*chem.eng.*vol 45, n°2, 2001, pp. 139-148.
- [5] Gani R., Jiméner- González C., Kate A., Crafts P.A., Powell L., Atherton J.H, Cordiner J.L., "A modern approach to solvent selection," *Chemical Engineering*, vol.113, no.3, 2006, pp. 30-34.
- [6] A.A. El-Asmy, H. Serag, M. A. Mahdy, M. I. Amin, "Purification of phosphoric acid by minimizing iron, copper, cadmium and fluoride," *Separation and Purification Technology*, vol. 61, 2008, pp. 287–292.
- [7] A. Hannachi, R. Labidi, C. Chtara, A. Ouederni, A. Ratel, *Récents Progrès en Génie des Procédés, Lavoisier Tech. & Doc.*, vol. 92, 2005.
- [8] R. Hamdi, N.khleifia, A.Hannachi, N.Abbes, C. Chtara, A. Ratel, "Simulation of the Wet Phosphoric Acid extraction along a continuous column," *International Journal of Chemical Engineering and Applications*, vol.1, no.4, 2010, pp.326-331.
- [9] A. Hannachi, R. Hamdi, N. Abbas, C. Chtara, A. Ratel, "Simulation of the wet process phosphoric acid purification process by solvent extraction," *Proceedings of the COVAPHOS II*, vol. 3 , 2006, pp.251-260.

**Rania Hamdi** holds a master degree and engineer degree in Chemical Engineering from the National Engineering School of Gabes. She is currently pursuing a Ph.D. degree in Chemical Engineering from the same school (e-mail: raniahamdi@live.fr)

**Naima khleifia** holds a master degree and engineer degree in Chemical Engineering from the National Engineering School of. She is currently pursuing a Ph.D. degree in Chemical from the same school (e-mail: naima\_khleifia@yahoo.fr)

**Ahmed hannachi** is a professor in the Chemical Engineering department of the National Engineering School of Gabes. e-mail:ahmed.hannachi@enig.rnu.tn