CI&CEQ
Chemical Industry & Chemical Engineering Quarterly

Available on line at
Association of the Chemical Engineers of Serbia *AChE*
www.ache.org.rs/CICEQ

Chem. Ind. Chem. Eng. Q. 27 (2) 113–119 (2021) CI&CEQ

AHMED MAHROU[1]
R. JOURAIPHY[2]
H. MAZOUZ[3]
A. BOUKHAIR[1,4]
MOHAMMED FAHAD[1]

[1]Laboratory of Physics and Nuclear, Atomic, Molecular, Mechanic and Energy, Department of Physics, Faculty of Sciences; University Chouaïb Doukkali, El Jadida, Morocco
[2]Environmental Sciences and Development Laboratory, Faculty of Science and Techniques, University Hassan I, Settat, Morocco
[3]OCP. SA Jorf Lasfar, El Jadida, Morocco
[4]Regional Center for Education and Training Trades, Casablanca--Settat, El Jadida, Morocco

SCIENTIFIC PAPER

UDC 546.18-3:546.6:66.066.7

MAGNESIUM REMOVAL FROM PHOSPHORIC ACID BY PRECIPITATION: OPTIMIZATION BY EXPERIMENTAL DESIGN

Article Highlights

- High magnesium contents in phosphoric acid increase in the viscosity of the acid
- The removal of magnesium from the acid has important advantages in the phosphoric industry
- The reduction of magnesium by precipitation was achieved by the addition of aluminum and fluorine
- The magnesium is precipitated in one of the following forms: $MgAlF_5$ or $MgAl_2F_8$
- The parameters influencing the removal of magnesium are temperature, fluorine form and F/Mg ratio

Abstract

High content of magnesium in phosphate and phosphoric acid affects negatively the performance and operating conditions in phosphate industry. A content of more than 0.3% in phosphate increases the P_2O_5 losses during phosphate digestion and filtration, and also increases steam consumption and solid settling kinetics during concentration. In this work, the removal of magnesium from phosphoric acid by precipitation in one of the compounds, $MgAlF_5$ or $MgAl_2F_8$, was studied. Magnesium precipitation is achieved by the simultaneous addition of aluminum and fluorine. The experimental design methodology was used to carry out this work. Tests were conducted according to the NEMRODW software using industrial quality phosphoric acid. The screening study of parameters affecting the removal efficiency of magnesium from industrial wet phosphoric acid showed that from the following parameters: temperature, F/Mg and Al/Mg ratios, aluminum form and fluorine form, only temperature and F/Mg ratio have an effective influence on magnesium removal. The optimization of magnesium removal from phosphoric acid was performed according to the response surface methodology using a composite matrix. By applying this methodology, the optimum parameters corresponding to a maximum magnesium removal efficiency in phosphoric acid were determined. The values of the optimum parameters obtained by this method are T = 80 °C, ratios: Al/Mg = 1 and F/Mg = 16.

Keywords: phosphoric acid, impurities, magnesium, optimization, design of experiments.

The manufacture of phosphoric acid by the wet process is carried out by contacting the phosphate rock with sulfuric acid. During this operation, most of the impurities contained in the rock dissolve in the phosphoric acid produced. The presence of magnesium in phosphoric acid affects its quality and the operating conditions in fertilizer and phosphoric production units.

Various works have been published focusing on phosphoric acid treatment and purification in order to remove impurities such as heavy metals, organic matter and uranium [1,2]. Koopman developed a new in-line technique for the removal of impurities from the product acid, and simultaneously avoid their incorporation into the calcium sulfate solids [3]. Other authors

Correspondence: H. Mazouz, OCP. SA Jorf Lasfar, El Jadida, Marocco.
E-mail: h.mazouz@ocpgroup.ma
Paper received: 1 January, 2020
Paper revised: 7 April, 2020
Paper accepted: 6 August, 2020

https://doi.org/10.2298/CICEQ200101030M

were focused on a specific impurity, such as cadmium, iron, aluminum, magnesium, etc. [4-7]. Berglund, for example, described a method for removing cadmium. This method relates to a separation in a solid using sulphur compounds added to the phosphate-containing medium after its neutralization. Abdennebi studied the iron and aluminum removal from phosphoric acid at low pH by the precipitation of an organometallic complex. The latter is formed using an organophosphorus reagent [8]. Nevertheless, no work has tackled the problem of MgO with the method of experimental design.

Phosphate magnesium solubilizes almost entirely in phosphoric acid during the phosphate rock attack by sulfuric acid [9,10]. High magnesium contents in phosphoric acid result in an increase in the viscosity of the acid, making its handling and concentration difficult. It leads also to a decrease in extraction efficiency during phosphoric acid purification and clogging equipment by magnesium-based solid. The removal of magnesium from phosphoric acid, therefore, has important advantages in the phosphoric industry.

Several techniques have been developed for the removal of magnesium from phosphoric acid. Numerous researches on the purification of the acid involved liquid-liquid extraction for the recovery of MgO and other impurities [11,12]. Moreover, Berry and Baroody [13] used a continuous ion exchange approach to recover the magnesium as a minor element. This technique allows the reduction of minor elements with minimal phosphate losses and dilution to produce a phosphoric acid that is suitable for the production of fertilizer products. Mills [14] and Parks [15] argue that the magnesium can be recovered by precipitation. The magnesium is removed by adding calcium or fluoride ion donating compound, such as hydrofluoric acid. The latter was the most widely used [16]. Magnesium can precipitate in phosphoric acid under several compounds such as: $MgSiF_6$; $MgAlF_5$; $MgAl_2F_8$; $NH_4MgAl(F,OH)\cdot H_2O$, $Na_xMg_xAl_{2-x}(F,OH)_6\cdot H_2O$ [17].

The aim of this work is to study the optimization of the removal of magnesium from weak phosphoric acid by its precipitation in one of the forms, $MgAlF_5$ and $MgAl_2F_9$, by applying experimental designs. The experimental design method consists in organizing the experimental approach and decision analysis by applying rigorous rules based on the exploitation of the algebraic and statistical properties of the matrices describing the experiments [18,19]. The parameters were selected to determine their influence in the fixed experimental plan, using Hadamard matrices. Then, the mathematical model explaining the phenomenon was established by using complete factorial designs to determine the interaction effects of the parameters and the experimental conditions corresponding to an optimum (maximum or minimum) of the studied response.

EXPERIMENTAL

The removal of magnesium from weak industrial phosphoric acid 28-30% P_2O_5, by precipitation of the compounds $MgAl_2F_8$, $MgAlF_5$, is achieved by the simultaneous addition of aluminum and fluorine under specific conditions. The tests for the removal of magnesium from industrial weak phosphoric acid by precipitation were carried out in 20 L double-jacketed stirred reactor. The acid is stirred at 350 rpm and heated to 60 and 80 °C. Heating was provided by thermal oil circulation using a thermostat bath. Aluminum and fluorine are added at the same time, according to the Al/Mg and F/Mg ratios given in Table 1. After 2 h, the agitation is stopped; the time agitation was fixed in this work. The precipitate is recovered by vacuum filtration. According to the analysis of the industrial phosphoric acid used in laboratory tests, it is mainly composed of 0.36% of Al_2O_3, 0.52% of CaO, 0.42% of MgO, 1.53% of SO_3, 1.96% of F and 27.10% of P_2O_5; this composition leads to Al/Mg ratio of 0.79 and F/Mg ratio of 7.78. During our tests we used one source quality of industrial wet phosphoric acid, which lead to fixing the P_2O_5 content, with an objective to gives a MgO content less than 1% MgO.

Table 1. Experimental plan used for the removal of magnesium by phosphoric acid precipitation

Name	U1	U2	U3	U4	U5
	Al/Mg	F/Mg	Al Form	F Form	Temperature
Unit	-	-	-	-	°C
Level -1	1	5	Metallic	NaF	60
Level +1	2	16	Salt	HF	80

The tests were carried out according to the experimental design matrix proposed by the NEMRODW software at each stage. The solid formed after each test is separated from the phosphoric acid by settling. The treated phosphoric acid is analyzed by ICP to evaluate magnesium removal efficiency.

Asymmetric screening study

The objective of this part of the study is to select the most influential parameters on the magnesium removal from phosphoric acid by precipitation. In order to evaluate their effects on the response of variations in the factor levels, an asymmetric screening design was used [15]. The asymmetric screening design allows a rapid examination of factors at different numbers of levels. Among different parameters influencing the reaction, the following parameters were selected for the screening study: Al/Mg and F/Mg concentration ratios, forms of added aluminum and fluorine, and temperature. For each parameter the two levels (-1) and (+1) were indicated. Table 1 presents the experimental plan set for screening study. The experiment matrix is constructed from the Hadamard matrix for a number of factor k equal to 5; the experiment matrix in this case consists of 8 experiments. The experimental design is obtained by replacing the -1 and +1 values of the variables in the experimental matrix with the actual values of the corresponding factors (Table 2). These matrices were edited by the NEMRODW.

RESULTS AND DISCUSSION

The tests were performed according to the experimental design in Table 2. The results of the magnesium removal efficiency from phosphoric acid are summarized in Table 3.

The effect of the parameters is estimated by calculating the coefficients of the assumed mathematical model (1):

$$Y = b_0 + b_1U_1 + b_2U_2 + b_3U_3 + b_4U_4 + b_5U_5 \quad (1)$$

Y represents the magnesium removal efficiency from phosphoric acid.

The coefficients of the model (1) are calculated by the least-squares method. The coefficient b_0 represents the average value of the response to the 8 experiments. It is equal to 25.875. The main effect b_1 represents the variation in response Y when the variable U_1 changes from level -1 to level +1. The values of the coefficients b_0 to b_5 obtained are presented in Eq. (2):

$$Y = 25.875 - 4.375U_1 + 24.125U_2 + \\ +3.875U_3 - 9.625U_4 + 7.875U_5 \quad (2)$$

From the results of Eq. (2) and Figure 1, it is noticed that the value b_1 is equal to -4.375, which means that the elimination efficiency of magnesium in phosphoric acid decreases on average by 8.75% when the ratio Al/Mg was increased from value 1 to 2. The value b_2 = 24.12 means that, on average, the efficiency increases by 48.24% when the ratio F/Mg was increased from 5 to 16. The value b_3 = 3.87 means that, on average, the efficiency increases by 3.9% when switching from the metallic aluminum form to the salt form ($Al_2(SO_4)_3$). The value b_4 = -9.62 means that, on average, the yield decreases by 19.24% when switching from the fluorine NaF form to the HF form. The value b_5 = 7.87 means that, on average, the efficiency increases by 15.74% when going from 60 to 80 °C. Analysis of the data in Figure

Table 2. Eight-run asymmetric screening matrix and experimental design used in the screening study

No. Exp.	U_1	U_2	U_3	U_4	U_5	Al/Mg	F/Mg	Aluminum form	Fluorine form	Temperature, °C
1	1	1	1	-1	1	2	16	Salt	NaF	80
2	-1	1	1	1	-1	1	16	Salt	HF	60
3	-1	-1	1	1	1	1	5	Salt	HF	80
4	1	-1	-1	1	1	2	5	Metallic	HF	80
5	-1	1	-1	-1	1	1	16	Metallic	NaF	80
6	1	-1	1	-1	-1	2	5	Salt	NaF	60
7	1	1	-1	1	-1	2	16	Metallic	HF	60
8	-1	-1	-1	-1	-1	1	5	Metallic	NaF	60

Table 3. Experimental design

No. Exp.	Al/Mg	F/Mg	Aluminium form	Fluorine form	Temperature, °C	*Rd* (%)
1	2	16	Salt	NaF	80	65.00
2	1	16	Salt	HF	60	49.00
3	1	5	Salt	HF	80	0.00
4	2	5	Metallic	HF	80	0.00
5	1	16	Metallic	NaF	80	70.00
6	2	5	Salt	NaF	60	5.00
7	2	16	Metallic	HF	60	16.00
8	1	5	Metallic	NaF	60	2.00

2 shows that the parameter F/Mg has a contribution rate in the response of 75.15%, followed by the fluorine form at a rate of 12.02% and then the temperature at a rate of 8.05. The parameters aluminum form and Al/Mg have a low contribution rate in response *Y*. This means that the magnesium removal efficiency of phosphoric acid depends, essentially, on the variation of the F/Mg parameter. These results can be approved by different studies [13-15]. According to the authors, the precipitation and the recovery of magnesium depends on the temperature, Al/Mg ratio, and F/Al ion ratio.

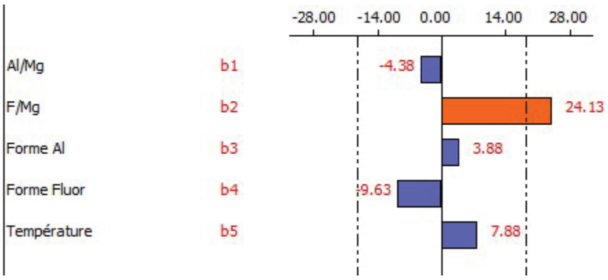

Figure 1. Individual Pareto effects of parameters on Y responses.

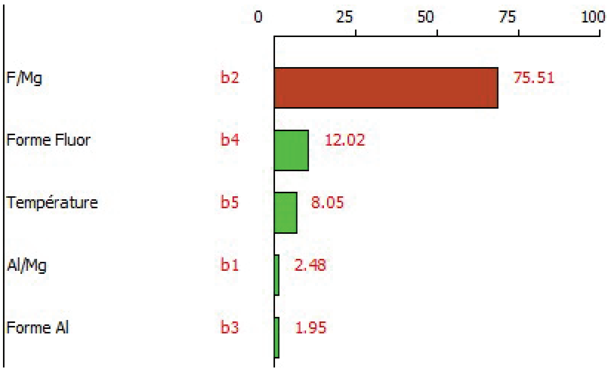

Figure 2. Cumulative Pareto effects of the parameters on the Y response.

The P_2O_5 content does not change during the precipitation of MgO. The choice of doping with alumina and fluorine allows targeting the precipitation of the two compounds $MgAlF_5$ or $MgAl_2F_8$. However, a slight decrease in uranium and calcium has been observed.

Optimization for the MgO removal efficiency from phosphoric acid

The optimization of magnesium removal from phosphoric acid was carried out according to the response surface methodology using the second-degree composite matrix. The objective is to achieve the optimum (maximum or minimum) of the *Y* response (efficiency removal) in the set experimental domain. The parameters selected for the optimization study were as follows: ratios (Al/Mg and F/Mg) and temperature shown in Table 4 with the experimental plan. The postulated model is a complete second-degree plan with the following Eq. (3):

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \tag{3}$$

Table 4. Factors studied and experimental field

Variable	Factor	Center	Pace
U_1	Temperature	65	15
U_2	Al/Mg	1.5	0.5
U_3	F/Mg	10.5	5.5

The tests were carried out according to the experimental plan edited by the software and presented in Table 4. The results of the elimination efficiency obtained for each test performed are presented in the 5th column of Table 5.

From the experimental results of the value of the *Y* response, the software was used, to estimate the model coefficients and statistical analysis. Table 6 presents the values of the model's coefficients and Table 7 presents the result of the statistical analysis. It should be noted that the determination of the coefficients is carried out by the least-squares method.

For the validation of the model, it is required that $0<R^2<1$ and R^2 adjusted $<R^2$. The values of R^2 and R^2 adjusted obtained following the regression analysis are mentioned in Table 7 and show that the model is valid because of $R^2 = 0.981$ ($0<R^2<1$); and R^2 adjusted $= 0.953<R^2$. After the validation of the model, the variation of the response was studied in the plan (F/Mg; temperature) and (F/Mg; Al/Mg).The results are presented in Figures 3 and 4.

The analysis of the results in Figure 3 shows that the value of the response *Y* in the plan (F/Mg; temperature) varies with the variation in the F/Mg ratio and is independent of the variation in temperature in the experimental domain studied. This explains why the magnesium removal efficiency in the plan (F/Mg; Temperature) depends only on the variation in the F/Mg ratio.

The analysis of Figure 4 shows that the value of the response *Y* in the experimental design (F/Mg; Al/Mg) varies with the variation in the F/Mg ratio and is independent of the variation in the Al/Mg ratio in the experimental domain studied. This explains why the magnesium removal efficiency in the plan (F/Mg; Al/Mg) depends only on the variation in the F/Mg ratio. According to these results, only the parameter F/Mg affects the value of the response in the experimental domain. These results were approved by Mills

Table 5. Design of experiments with the response values obtained for each test performed

No. Exp.	Temperature, °C	Al/Mg	F/Mg	*Y* (%)
1	50.00	1.00	5.00	10.90
2	80.00	1.00	5.00	0.00
3	50.00	2.00	5.00	10.90
4	80.00	2.00	5.00	2.20
5	50.00	1.00	16.00	56.50
6	80.00	1.00	16.00	71.70
7	50.00	2.00	16.00	63.00
8	80.00	2.00	16.00	56.50
9	50.00	1.50	10.50	10.90
10	80.00	1.50	10.50	0.00
11	65.00	1.00	10.50	10.90
12	65.00	2.00	10.50	8.70
13	65.00	1.50	5.00	10.90
14	65.00	1.50	16.00	52.20
15	65.00	1.50	10.50	8.70
16	65.00	1.50	10.50	6.50

Table 6. Estimation of the value of the coefficients

No. Exp.	Coefficient	Inflation factor	Standard deviation	t_{exp}	Signif., %
b_0	6.948		2.649	2.62	3.87 *
b_1	-2.180	1.00	1.769	-1.23	26.4
b_2	-0.870	1.00	1.769	-0.49	64.3
b_3	26.500	1.00	1.769	14.98	< 0.01***
b_{11}	-1.172	1.42	3.445	-0.34	74.2
b_{22}	3.178	1.42	3.445	0.92	39.5
b_{33}	24.928	1.42	3.445	7.23	0.0515***
b_{12}	-2.437	1.00	1.978	-1.23	26.4
b_{13}	3.537	1.00	1.978	1.79	12.2
b_{23}	-1.363	1.00	1.978	-0.69	52.2

explaining that the MgO to F ratio is the primordial criterion for the removal of MgO [14].

Using the validated model, the values of the factors were determined at the optimum and then calculated the optimal value of the response in these coordinates. According to the values of the factors edited by the software the optimal temperature is 79.66 °C, the optimal Al/Mg ratio is 1.00 and the optimal F/Mg ratio is 15.99. Tests at the conditions related to the optimum (*Y*) were performed, then com-

Table 7. Statistics of responses

Standard deviation of the response	5.594
R^2	0.981
R^2 Adjusted	0.953
R^2 Predicted	0.732
PRESS	2667.680
Number of degrees	6

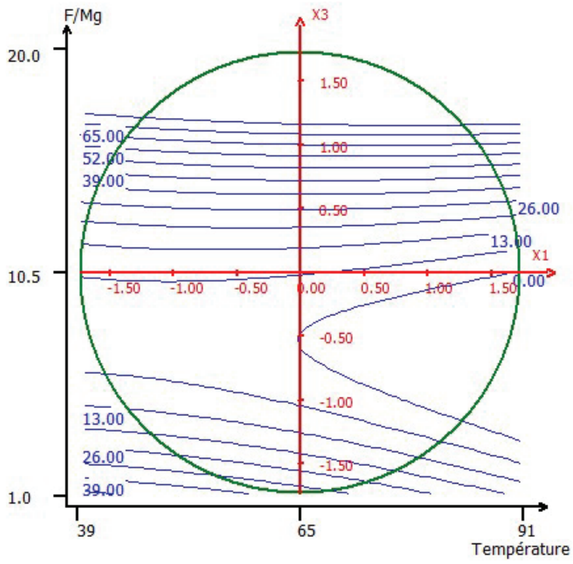

Figure 3. Same response curve variation of in plan (F/Mg; temperature).

pared the calculated *Y* value with the experimental value obtained. The results obtained are presented in Table 8.

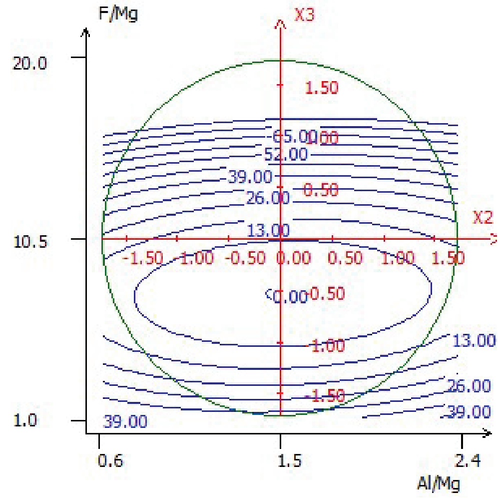

Figure 4. Same response curves variation in plan (F/Mg; Al/Mg).

Table 8. Ycal and Yexp values at optimum

Response	Response name	Value (%)	Residue (*Yexp* - *Ycal*)
Ycal	Calculated yield	66.10	3.2
Yexp	Experimental yield	69.3	

CONCLUSION

The optimization of the reduction of the magnesium concentration in phosphoric acid by experimental designs was the subject of this study. The reduction of magnesium by precipitation was achieved by the simultaneous addition of aluminum and fluorine to precipitate it in one of the following forms: $MgAlF_5$ or $MgAl_2F_8$. With the use of experimental designs, through the postulated models, the most influential parameters on the magnesium elimination phenomenon, and the optimum parameters corresponding to the optimal magnesium elimination efficiency in phosphoric acid were defined. The parameters influencing the removal efficiency of magnesium in phosphoric acid, determined during the screening study, are temperature, fluorine form, and F/Mg ratio. The latter has an influence rate of 75% in relation to all the parameters used. The optimum parameter values determined during the optimization study are temperature *T* = 80 °C, ratio Al/Mg = 1 and F/Mg = 16. The predictive model for the study of magnesium removal from phosphoric acid by precipitation has been validated. The prediction of the value of the response *Y* to the optimum was performed with a low residue compared to the experiment of about 3.2.

REFERENCES

[1] A.B. Gerber, (FED PHOSPHORUS COMPANY), US No. 44224721A, 1921

[2] C.F. Booth, J.E. Malowan, (Monsanto Chemicals), US No. 74282634A, 1937

[3] C. Koopman, G.J. Witkamp, Sep. Sci. Technol. 37 (2007)1273-1290

[4] H. Berglund, (WIPO (PCT)), WO No. 1980002418A, 1980

[5] A.M. Cornelis, A. Johannes, (Stamicarbon B.V. (NL)), No. 07/0912, 1989

[6] S.D. Ukeles, E. Ben-yoseph, N. Philip, (Norsk Hydro ASA), US No. 4986970A, 1991

[7] P.Becker, (Office, Togolais Des Phosphates (Kpeme-Togo, TG), No. 07/793369, 1994

[8] N. Abdennebi, K. Benhabib, C. Goutaudier, M. Bagane, JMES 8 (2017) 557-565

[9] J. Yu, D. Liu, Chem. Eng. Res. Des. 88 (2010) 712-717

[10] I.T. Shamshidinov, K.G. Gafurov, M.M. Ikramov, J. Chem. Technol. Metall 51 (2016) 157-162

[11] H. Ahmed, H. Diamonta, C. Chaker, R. Abdelhamid, Sep. Purif. Technol. 55 (2007) 212-216

[12] R. Hamdi, A. Hannachi, J. Chem. Eng. Process Technol. 3 (2012) 134

[13] W.W. Berry, T.E. Baroody, (K-Technologies Inc), US No. 20150166343A1, 2015

[14] H.E. Mills, (White Springs Agricultural Chemicals Inc), US No. 4243643A, 1978

[15] K.L. Parks, K.D. Clevenger, D.P. Mcdonald, (Agrico Chemical Company), US No. 4299804, 1981

[16] D. Goldstein, (FMC Corp), US 3819810A, 1994

[17] J.R. Lehr, A. W. Frazier, J.P. Smith, J. Agric. Food Chem. 14 (1966) 522-529

[18] G. Jaxques, Introduction aux plans d'expériences, DUNOD Ed, Paris, 2001, p.18

[19] O.W. Gooding, Curr. Opin. Chem. Biol. 28 (2004) 297-304.

AHMED MAHROU[1]
R. JOURAIPHY[2]
H. MAZOUZ[3]
A. BOUKHAIR[1,4]
MOHAMMED FAHAD[1]

[1]Laboratory of Physics and Nuclear, Atomic, Molecular, Mechanic and Energy, Department of Physics, Faculty of Sciences; University Chouaïb Doukkali, El Jadida, Morocco
[2]Environmental Sciences and Development Laboratory, Faculty of Science and Techniques, University Hassan I, Settat, Morocco
[3]OCP. SA Jorf Lasfar, El Jadida, Marocco
[4]Regional Center for Education and Training Trades, Casablanca-Settat, El Jadida, Morocco

NAUČNI RAD

STATISTIČKA OPTIMIZACIJA UKLANJANJA MAGNEZIJUMA IZ FOSFORNE KISELINE PRECIPITACIJOM

Visok sadržaj magnezijuma u fosfatu i fosfornoj kiselini negativno utiče na performanse i radne uslove u industriji fosfata. Dok sadržaj veći od 0,3% u fosfatu povećava gubitke P_2O_5 tokom digestije i filtracije fosfata, a i povećava potrošnju pare i kinetiku taloženja čvrstih čestica tokom koncentrisanja. U ovom radu, proučavano je uklanjanje magnezijuma iz fosforne kiseline taloženjem u obliku jedinjenja $MgAlF_5$ ili $MgAl_2F_8$ primenom metode statističke optimizacije. Taloženje magnezijuma postiže se istovremenim dodavanjem aluminijuma i fluora. Istraživanja su sprovedena prema softveru NEMRODV koristeći fosfornu kiselinu industrijskog kvaliteta. Skrining parametara koji utiču na efikasnost uklanjanja magnezijuma iz industrijske vlažne fosforne kiseline pokazao je da od više parametara (temperatura, odnosi F/Mg i Al/Mg, oblik aluminijuma i oblik fluora), samo temperatura i odnos F/Mg imaju efektivni uticaj na uklanjanje magnezijuma. Optimizacija uklanjanja magnezijuma iz fosforne kiseline izvedena je prema metodologiji površine odziva kombinovanom sa kompozitnim planom. Primenom ove metodologije utvrđeni su optimalni parametri koji odgovaraju maksimalnoj efikasnosti uklanjanja magnezijuma iz fosforne kiseline. Vrednosti optimalnih parametara dobijenih ovom metodom su 80 °C, odnos Al/Mg = 1 i odnos F/Mg = 16.

Ključne reči: fosforna kiselina, nečistoće, magnezijum, optimizacija, planiranje eksperimenata.