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29% P$_2$O$_5$ Phosphoric Acid Desulphation: Improving the Performance of the Unit of Concentration

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Abstract

Clogging in the heat exchangers of the phosphoric acid concentration unit is a phenomenon which hinders the proper functioning of the installation. It results in the accumulation of undesirable solid deposits on the pipes and consequently a decrease of its performance. This deposit is mainly anhydrous or hemihydrate gypsum in addition to Na$_2$SiF$_6$. Phosphoric acid desulphation before its concentration step allows reducing this undesirable effect. Barium carbonate is used for the retention of sulphate ions using a simple experimental protocol which can easily be inserted into the phosphoric acid manufacturing. Four factors: quality of the phosphoric acid to be concentrated, amount of barium carbonate, temperature and time, were studied using design of experiment (DOE) methodology with two-level full factorial design strategy in order to assess their effects on desulphation. Only the first two factors have significant effects. Therefore, for effective sulphate removal, the validated statistical model (R^2 = 99.96%) allows to predict the amount of barium carbonate to be used, depending on quality of the phosphoric acid to be concentrated and using the available temperature and time in the industrial process.

Keywords

Phosphoric Acid, Barium Carbonate, Desulphation, Protocol Modeling, Full Factorial Design

1. Introduction

Manufacturing of phosphoric acid from natural phosphate by sulfuric acid attack inevitably produces impurities such as sulphates, fluorine, organic matter

and heavy metals. Sulphate ions, in particular, have about 2% weight, and affect undoubtedly the efficiency of 29% P_2O_5 phosphoric acid concentration unit, due to the solid formation which causes premature clogging of the phosphoric acid concentration unit. Consequently, there is a 20% or even 30% if one takes into account the washing downtime and the degradation of the heat exchangers, thus increasing the operating cost. The physical-chemical characterizations allowed its identification. In order to minimize the formation of the solid during the phosphoric acid concentration step, we propose to desulphate 29% P_2O_5 phosphoric acid by barium carbonate using a simple experimental protocol that can be inserted into the industrial process. Design of experiments methodology is used for modeling the process and to determine the optimum conditions depending on the quality of the acid to be pretreated.

2. Instrumentation

Characterization of sediment were carried out by X-ray diffraction (XRD) on the powder (Bruker advance D8 eco diffractometer with CuKα radiation λ = 1.5418 Å). Sulphate was determined by titration with barium chloride and sulfonazo-3 ($C_{22}H_{12}N_4Na_4O_{14}S_4$) as an indicator. The determination of phosphoric acid impurities was carried out by inductively coupled plasma-emission spectroscopy ICP-OES (Jobin Yvon ULTIMA 2).

3. Phosphoric Acid

Phosphoric acid was produced from Moroccan fluoroapatite by wet process according to the following equation [1] [2]:

$$Ca_{10}(PO_4)_6 F_2 + 10H_2SO_4 + 10xH_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot xH_2O \downarrow + 2HF \uparrow$$
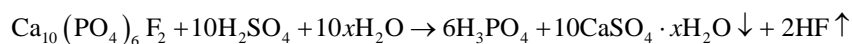
Dependent on the process conditions, such as the temperature, either calcium sulphate hemihydrates (x = 1/2, HH) or dehydrate (x = 2, DH or phospho-gypsum) is formed. In the dihydrate process (DH), the temperature of the reactor is maintained less than 80˚C. The obtained phosphoric acid contains 26% to 29% P_2O_5 with the main impurities shown in Table 1.

The profile of the concentrated acid (exiting the concentration step), obtained by water evaporation under vacuum, is shown in Table 2.

Table 1. Chemical composition of the phosphoric acid before concentration (ρ = 1.267 g/cm^3).

Elements	P_2O_5	Solid	SO_4^{2-}	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2	F^-	Na_2O	K_2O
% weigh	27.12	0.05	1.73	0.73	1.62	0.27	0.16	0.42	0.73	0.06	0.06

Table 2. Chemical composition of the phosphoric acid after concentration (ρ = 1.681 g/cm^3).

Elements	P_2O_5	Solid	SO_4^{2-}	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2	F^-	Na_2O	K_2O
% weigh	54.09	2.24	2.95	0.68	0.97	0.51	0.55	0.17	0.52	0.38	0.1

4. Deposit Identification

The deposited solid during the concentration of 29% P_2O_5 phosphoric acid is identified using ICP-OES, X-ray diffraction and by monitoring the variation of major impurity mass as a function of the %P_2O_5 evolution during the phosphoric acid concentration. Table 3 and Figure 1 show that the solid formed is mainly gypsum [3], sodium fluosilicate [4] and other minor constituents.

Table 4 shows the variation of volume, density, P_2O_5, solid and major impurities during the concentration of phosphoric acid.

Table 3. ICP-OES analysis results for the deposited solid in the heat-exchanger.

Elements	SO_4^{2-}	CaO	Al_2O_3	F	MgO	Na_2O	SiO_2	K_2O	Fe_2O_3	P_2O_5
% weigh	49.5	33.5	2.75	2.5	1.26	0.56	0.52	0.06	0.05	1.75

Table 4. Profile variation of phosphoric acid during the concentration step.

Volume of acid (litre)		1	0.851	0.727	0.651	0.571	0.514	0.487	0.414	0.34
Density (g/litre)		1292	1330	1377	1424	1483	1530	1557	1645	1765
P_2O_5	% w	27.5	31.3	35.4	38.3	41.9	45.1	46.8	52.1	59.2
	weigh (g)	354.78	354.78	354.78	354.78	354.78	354.78	354.78	354.78	354.78
Solid (Ts)	% w	0.08	0.1	0.12	0.24	0.66	1.24	1.83	1.15	1.04
	weigh (g)	1.03	1.13	1.2	2.22	5.591	9.76	13.9	7.83	6.23
Al_2O_3	% w	0.21	0.23	0.28	0.29	0.34	0.36	0.38	0.42	0.45
	weigh (g)	2.71	2.6	2.8	2.69	2.88	2.83	2.88	2.86	2.7
Fe_2O_3	% w	0.27	0.3	0.35	0.38	0.42	0.45	0.47	0.52	0.57
	weigh (g)	3.49	3.4	3.5	3.52	3.558	3.54	3.56	3.54	3.42
MgO	% w	0.47	0.53	0.6	0.65	0.73	0.74	0.77	0.91	1
	weigh (g)	6.07	6	6.01	6.02	6.184	5.83	5.84	6.196	5.99
CaO	% w	0.09	0.07	0.04	0.03	0.02	0.01	0.01	0.01	0.01
	weigh (g)	1.16	0.79	0.4	0.28	0.169	0.08	0.08	0.068	0.06
SO_4^{2-}	% w	1.46	1.61	1.72	1.88	1.97	2.14	2.19	2.42	2.73
	weigh (g)	18.9	18.2	17.2	17.4	16.69	16.8	16.6	16.48	16.4
SiO_2	% w	0.35	0.40	0.44	0.4	0.32	0.22	0.16	0.07	0.02
	weigh (g)	4.52	4.53	4.41	3.71	2.711	1.73	1.21	0.477	0.12
F^-	% w	0.09	0.08	0.08	0.07	0.06	0.05	0.04	0.03	0.03
	weigh (g)	1.16	0.91	0.8	0.65	0.508	0.39	0.3	0.204	0.18
Na_2O	% w	0.05	0.04	0.03	0.02	0.01	0.01	0.01	0.01	0.09
	weigh (g)	0.65	0.45	0.3	0.19	0.085	0.08	0.08	0.068	0.54
K_2O	% w	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.06
	weigh (g)	0.39	0.34	0.3	0.28	0.254	0.24	0.23	0.272	0.36
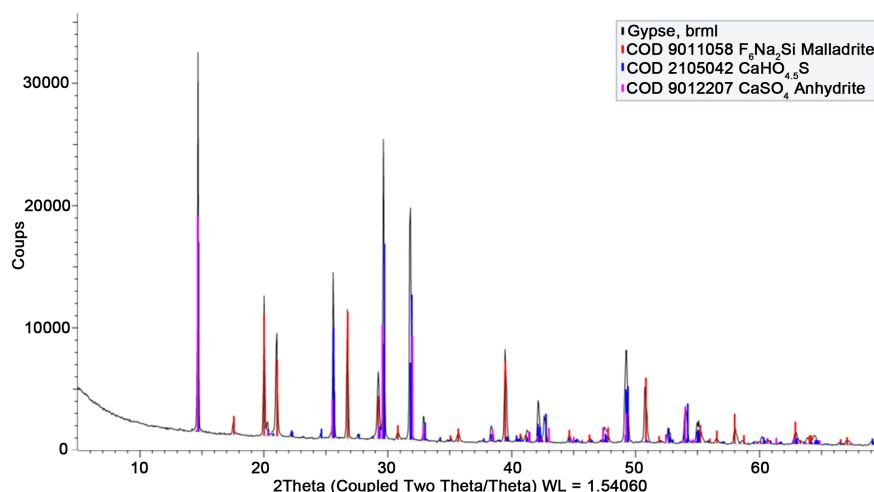
Figure 1. X-ray diffraction for the deposited solid.

Figure 2 shows the profile variation of phosphoric acid during the concentration step. The masses of SO_4^{2-}, CaO, F⁻, SiO_2, K_2O and Na_2O are decreased, while the masses of MgO, Al_2O_3 and Fe_2O_3 remain virtually constant during the concentration. This explains the formation of gypsum and $(Na, K)_2SiF_6$. From 47% of P_2O_5, dissolution of the solid and especially the sodium or potassium fluosilicate due to the evaporation of fluorine and silicon in the form of HF and SiF_4 [5] is observed, which leads to an increase in the solubility of $(Na, K)_2SiF_6$ (**Figure 2(a)**) and consequently the decrease of its content in the formed solid.

Solid deposit accumulation in the heat exchangers reduces the phosphoric acid cross-section and causes additional thermal resistance which subsequently increases the steam specific consumption and the pressure inside the heat-exchangers (**Figure 3**) [6]. As a result, significant decrease in productivity can be estimated to 30% less per production cycle (7 days).

In the light of these results, it is recommended to avoid the formation of this deposit by desulphation of phosphoric acid using barium carbonate before the concentration step.
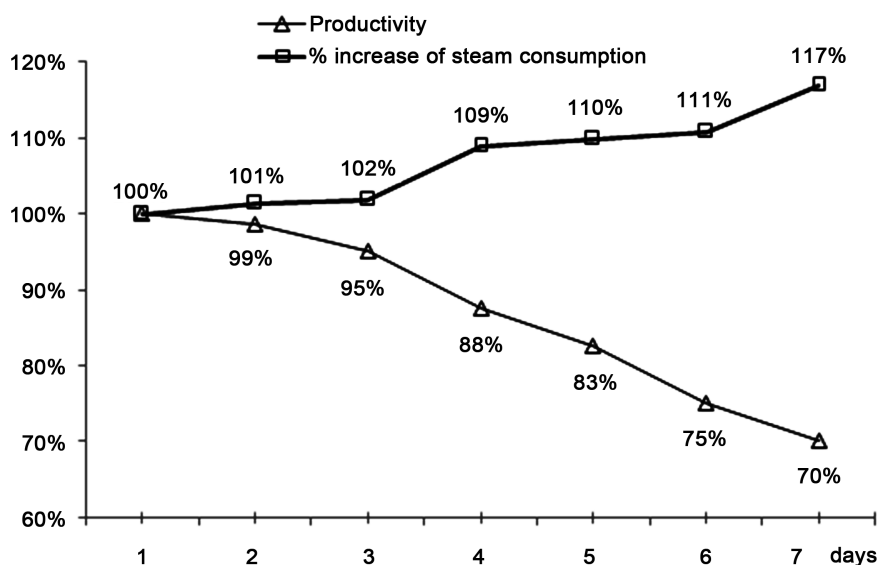
5. Desulphation of 29% P₂O₅ Phosphoric Acid

The protocol of 29% P_2O_5 phosphoric acid desulphation is judiciously chosen to be easily inserted into the phosphoric acid manufacturing process (**Figure 4**). Volume of phosphoric acid containing an initial quantity of H_2SO_4 (X_1 = quantity of initial H_2SO_4 per volume of acid) is heated to the desired temperature (X_3) in a stirred reactor and then a quantity (X_2) of $BaCO_3$ is introduced. After a reaction time (X_4), the mixture is decanted to obtain 29% P_2O_5 acid intended to be concentrated with a low level of sulphate to prevent solid formation at the heat exchangers.

In order to determine the optimum conditions for the desulphation process, we proceed by modeling the amount of residual H_2SO_4 as a function of the inlet phosphoric acid quality and the operating conditions (q, T, t).
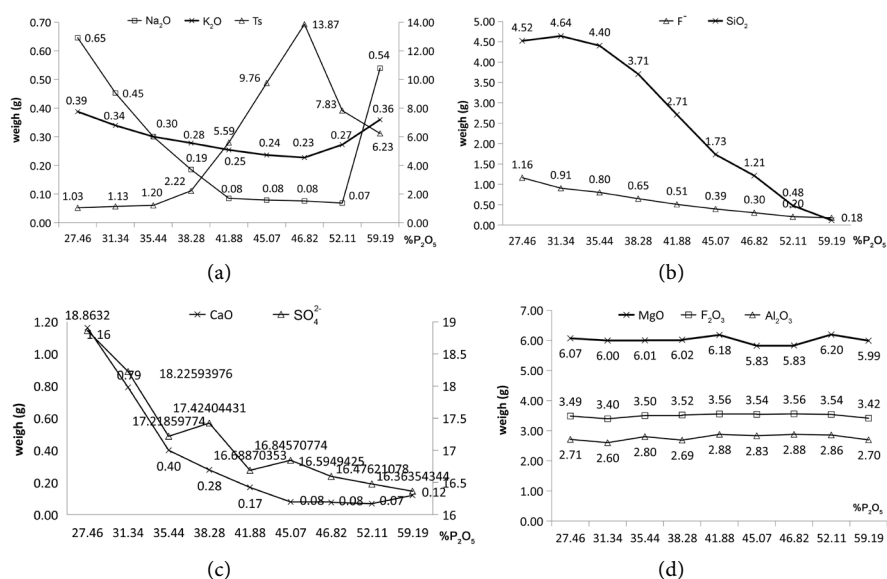
Figure 2. Profile variation of phosphoric acid during the concentration step as a function of the P_2O_5 rate.

Figure 3. % increase of steam consumption and productivity decrease during per production cycle.
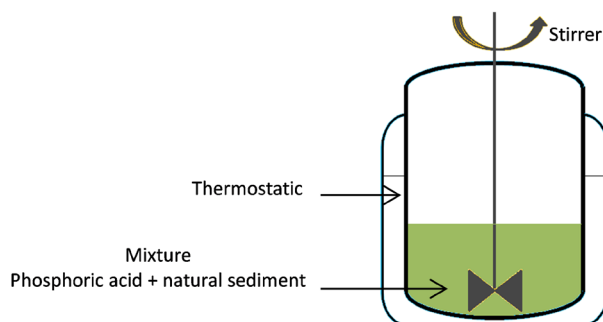
Figure 4. Experimental device for the desulphation of the 29% P_2O_5 phosphoric acid.

6. Results and Discussion

DOE methodology with two-levels full factorial design strategy, which assumes that the mean response can be adjusted correctly using a linear model, reduces the number of trials to determine with great precision the effects of the factors and their interactions on the response and avoids the alias phenomenon [7]. Four factors were studied to determine their effects on the desulphation process, namely: X_1: initial H_2SO_4 rate in g/l (reflecting the quality of phosphoric acid), X_2 the amount of barium carbonate in g/l, X_3 la Temperature in ˚C and X_4 the time in min. The response to be minimized is the residual rate of H_2SO_4 (Y in g/l). The amount of the phosphoric acid to be treated is fixed at 100 ml. The experimental field of variation of these factors (Table 5) takes into account the range of qualities that can be obtained for phosphoric acid and the operating conditions available on the industrial site.

For four factors and two levels, 16 trials (2^4) were performed under the conditions established by the methodology of the two-levels full factorial design. The results obtained are summarized in Table 6.

Table 5. Experimental field.

Factors	Amount of initial H_2SO_4 (in g/l): X_1	Amount of $BaCO_3$ (in g/l): X_2	Temperature (in ˚C): X_3	Time (in mn): X_4
Level (−1)	17.0	15	40	25
Level (+1)	29.4	40	74	60

Table 6. Results of conducted experiments.

N˚	Codified values				True values				Response
	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	Y Obs.
1	−1	−1	−1	−1	17	15	40	25	8.085
2	1	−1	−1	−1	29.4	15	40	25	21.56
3	−1	1	−1	−1	17	40	40	25	0
4	1	1	−1	−1	29.4	40	40	25	6.86
5	−1	−1	1	−1	17	15	74	25	7.84
6	1	−1	1	−1	29.4	15	74	25	21.56
7	−1	1	1	−1	17	40	74	25	0
8	1	1	1	−1	29.4	40	74	25	6.86
9	−1	−1	−1	1	17	15	40	60	7.595
10	1	−1	−1	1	29.4	15	40	60	21.07
11	−1	1	−1	1	17	40	40	60	0
12	1	1	−1	1	29.4	40	40	60	6.615
13	−1	−1	1	1	17	15	74	60	7.84
14	1	−1	1	1	2.94	15	74	60	21.315
15	−1	1	1	1	17	40	74	60	0
16	1	1	1	1	2.94	40	74	60	6.86
17	0	0	0	0	23.2	27.5	57	42.5	9.065

Obs.: Observed.

The codified mathematical model is written in the form (Equation (1))
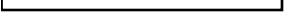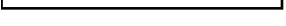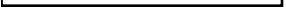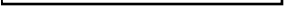
$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4$$
$$+ b_{23} X_2 X_3 + b_{24} X_2 X_4 + b_{34} X_3 X_4 + b_{123} X_1 X_2 X_3 + b_{124} X_1 X_2 X_4 \qquad (1)$$
$$+ b_{134} X_1 X_3 X_4 + b_{234} X_2 X_3 X_4 + b_{1234} X_1 X_2 X_3 X_4 + \varepsilon$$

where Y is the amount of residual sulphate (response to be fitted and to be minimized), X_1, X_2, X_3 and X_4 (factors in codified units), b_0 is the global mean, b_i are the effects of the main and interaction factors and ε is the random error associated with the response. The results of **Table 6** are treated by the JMP-SAS software to evaluate the effects of different factors with and without interaction on the residual rate of H_2SO_4 (Y in g/l) to analyze and validate the mathematical model obtained. Statistical analysis by STUDENT test for 5% risk made it possible to identify the factors having a significant influence on the observed response [8]. **Table 7** present the effects, t ratio and p value of each factor.

Factors that have statistically significant effects on desulphation are: X_1, X_2 and the interaction between them $X_1 \times X_2$ (p value < 0.05).

Taking into account the values of t ratios (**Table 7**) and the factor effects graph (**Figure 5**), it is found that the initial quality of the acid (X_1) and the amount of the barium carbonate (X_2) have a significant and antagonistic effect on the residual content of the sulphates (Y) while the temperature (X_3) and the time (X_4) have no effect on the desulphation process due to the high affinity between barium ions and sulphate ion.

Table 7. Analysis of the effects of variables.

Term	Scaled Estimate	Plot Estimate	Std Error	t Ratio	Prob > |t|
Intercept	9.0074		0.0144	625.00	0.0010
X_1	5.0838		0.0149	342.22	0.0019
X_2	−5.6044		0.0149	−377.26	0.0017
X_3	0.0306		0.0149	2.06	0.2875
X_4	−0.0919		0.0149	−6.18	0.1021
$X_1 \times X_2$	−1.6844		0.0149	−113.39	0.0056
$X_1 \times X_3$	0.0306		0.0149	2.06	0.2875
$X_1 \times X_4$	−0.0306		0.0149	−2.06	0.2875
$X_2 \times X_3$	0.0000		0.0149	0.00	1.0000
$X_2 \times X_4$	0.0613		0.0149	4.12	0.1515
$X_3 \times X_4$	0.0613		0.0149	4.12	0.1515
$X_1 \times X_2 \times X_3$	0.0000		0.0149	0.00	1.0000
$X_1 \times X_2 \times X_4$	0.0000		0.0149	0.00	1.0000
$X_1 \times X_3 \times X_4$	0.0000		0.0149	0.00	1.0000
$X_2 \times X_3 \times X_4$	−0.0306		0.0149	−2.06	0.2875
$X_1 \times X_2 \times X_3 \times X_4$	0.0306		0.0149	2.06	0.2875
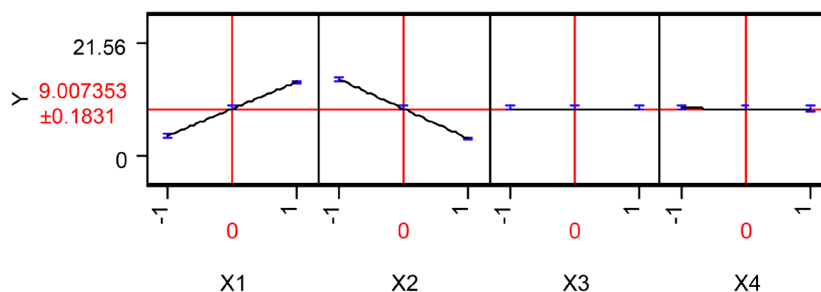
Figure 5. Effects of factors on the desulphation of phosphoric acid 29% P_2O_5.

The mathematical model is therefore written in the form (Equation (2)):

$$Y = 9.0074 + 5.0838 * X_1 - 5.6044 * X_2 - 1.6844 * X_1 * X_2 \qquad (2)$$

ANOVA (Analysis of variance) shown in **Table 8** confirms the statistical validity of the mathematical model with a determination factor R^2 of 99.96%. The graphical fit of the model (**Figure 6**) shows that the estimated responses (Y_{est}) by the experimental data with a correlation factor R^2 = 99.9%.

Additional tests (**Table 9**) were carried out in the experimental field with experimental conditions not used in the experimental matrix (**Table 6**). The residual between the observed (Y_{obs}) and the estimated (Y_{est}) results is not significant. The desulphation protocol can therefore be represented by the mathematical model (Equation (2)) in order to determine the optimum experimental conditions for efficient reduction of sulphates, depending on the quality of the phosphoric acid to be treated (X_1).

For economic reasons, 29% P_2O_5 phosphoric acid can be pre-treated at its temperature upon its arrival in the desulphation reactor (74°C) and for a time which does not affect the phosphoric acid manufacturing process (60 min). Depending on the phosphoric acid quality to be pre-treated, the amount of barium carbonate is determined using Equation (3) where Y Tolerated is the maximum residual amount of H_2SO_4 having no effect on the formation of deposit solid during the phosphoric acid concentration step.

$$X_2 = \frac{9.0074 - Y_{tolerated} + 5.0838 * X_1}{5.6044 + 1.6844 * X_1} \qquad (3)$$

According to **Table 2**, phosphoric acid 54% P_2O_5, obtained from 29% P_2O_5 acid non-desulphated, is saturated with sulphate and calcium (2.95% SO_4^{2-} and 0.68% CaO) which corresponds to a concentration of 49.59 g/l of sulphate and 8.16 g/l of calcium given a solubility product of 404.89 $(g/l)^2$. In the case of desulphation the mass of the calcium initially present in the acid 29% is preserved in the acid 54% with a concentration of 17.25 g/l. Therefore, the sulphate concentration in the 54% acid at saturation should be 23.46 g/l. The maximum residual mass of Tolerated Sulphate $Y_{Tolerated}$ is 8.97 g/l.

For example, for an initial acid with quality of X_1 = 22 g H_2SO_4/l and $Y_{Tolerated}$ = 8.97 g/l, the amount of $BaCO_3$ to be used for desulphation is 25.25 g/l. After concentration of the desulphated acid, the total amount of the formed solid is
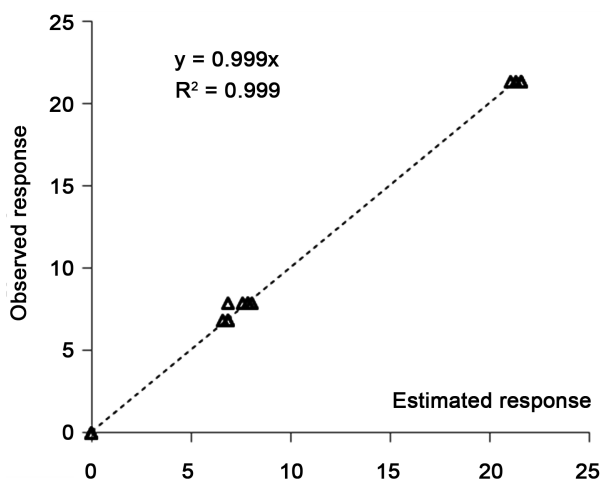
Figure 6. Adjustment graph.

Table 8. Analyze of variance (ANOVA).

	DF	Sum of Squares	Mean Square	F Ratio
Source	3	961.45044	320.4835	11649.09
Error	12	0.33014	0.0275	
Model	15	961.78057	64.1187	

Table 9. Results of additional tests.

| Amount of H_2SO_4 (in g/l): X_1	Amount of $BaCO_3$ (in g/l): X_2	Temperature (in °C): X_3	Time (in mn): X_4	Y Obs. (in g/l)	Y Est. (in g/l)	Residual
21.8	31	57	42.5	6.125	6.397	−0.272
21.8	16	74	25	12.740	12.666	0.074
23.2	27.5	57	42.5	9.065	9.007	0.058
29.4	20	74	25	18.620	18.464	0.156

Obs.: Observed; Est.: Estimated.

0.37% instead of 2.24% (Table 2), without taking into account the solid deposited at the heat exchanger for the second value. This represents a reduction rate of formed solid around 83.5% at least.

For industrial scale, desulphation by barium carbonate can be carried out directly at the level of the aging tank without addition of specific equipment to the phosphoric acid manufacturing unit (Figure 7).

7. Conclusion

Deposition of gypsum during the 29% P_2O_5 phosphoric acid concentration stage is a real technical-economic problem for producing phosphoric acid 54% P_2O_5. Physico-chemical characterization by ICP-OES and X-ray diffraction showed that this deposit is mainly composed by gypsum and low amount of fluosilicates. Desulphation of phosphoric acid 29% P_2O_5 by barium carbonate will reduce the
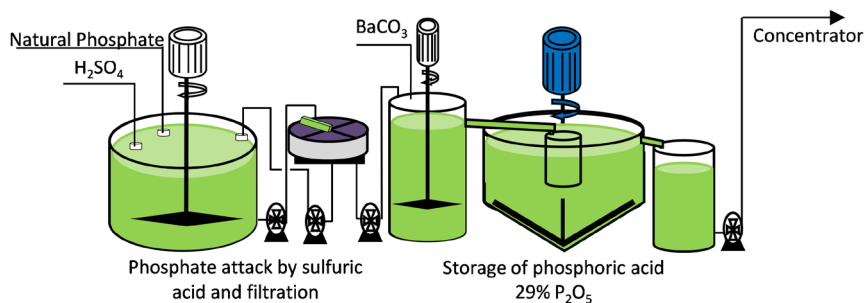
Figure 7. Phosphoric acid manufacturing steps with desulphation by barium carbonate.

formation of gypsum in the concentrator. The proposed desulphation protocol can be easily inserted into the industrial process; it is limited to a simple attack of phosphoric acid 29% P_2O_5 by $BaCO_3$ under stirring. Regarding to DOE methodology based on the strategy of full factorial design, taking into account the initial amount of H_2SO_4 in phosphoric acid 29% P_2O_5, the amount of barium carbonate, temperature and reaction time, it has been shown that only the quality of the acid and the amount of $BaCO_3$ have a significant effect on desulphation. The model obtained is validated with R^2 = 99.96% and can be used to determine the effective amount of $BaCO_3$ as a function of the phosphoric acid quality and the maximum residual mass of H_2SO_4 to avoid the formation of gypsum. The amount of the solid formed can therefore be reduced to 83.5%. This improves the production cycle and reduces maintenance and operating costs.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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