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A NATURAL MATERIAL FOR DESULPHATION OF THE 29% P_2O_5 PHOSPHORIC ACID: MODELING AND OPTIMIZATION

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ABSTRACT
The natural material made from dolomite, quartz and illite is used for 29% P_2O_5 phosphoric acid desulphation in order to reduce the unwanted effects due to a solid genesis during the phosphoric acid concentration process. For eventual valorization and uses of this material on an industrial scale, a simple protocol which can be inserted into the manufacturing process, is proposed for phosphoric acid pre-treatment. This protocol modeling is performed according to the phosphoric acid quality obtained by sulfuric acid attack, and considering three main factors: amount of natural material (Q), temperature (T) and time (t) needed for desulphation. For an efficient removal of sulphates, full factorial design methodology has afforded a statistically validated model (R^2 = 99.94%) able to predict the optimal conditions (Q, T, t) and taking in consideration the initial amount of sulphate in the phosphoric acid to be pretreated.

KEYWORDS: phosphoric acid, natural material, desulphation, protocol modeling, full factorial design.

1. INTRODUCTION
The production of phosphoric acid from phosphate rock by sulfuric acid attack generates inevitably impurities such as sulphates, fluorine, organic matter and heavy metals. The rate of sulfate ions, in particular, is about 2% (w/w), which undoubtedly affects the efficiency of 29% P_2O_5 phosphoric acid concentration. Consequently, the formed solid (deposit) generates premature clogging of the production chain, and therefore 20% decrease of productivity and 30% if washing downtimes is taken into account. Moreover, this solid generates equipment degradation due to the increase of pressure. The physicochemical characterization of the formed deposit showed that it is mainly gypsum. Following studies carried out by Y. Bounou et al.[1-3] for the pretreatment of the 54% P_2O_5 phosphoric acid with a natural material, we propose in this work to study the effect of this material on the pretreatment of the 29% P_2O_5 phosphoric acid and especially for the reduction of sulphate ions rate.

2. MATERIALS AND METHODS

Natural material
This natural material is yellowish, with very fine grains, 3% of moisture content and 42.2% of loss on ignition (LOI). Its preparation is limited to a simple grinding. The physicochemical characterization showed that it contains 20% clay fraction (illite) and 80% coarse fraction (72.4% dolomite and 7.6% quartz). Pretreatment tests of 54% P_2O_5 phosphoric acid allowed to choose this material among others by the use of principal component analysis (PCA) methodology, this materiel shown clear quality improvement of the pretreated phosphoric acid [4].

Phosphoric acid
Phosphoric acid was produced from Moroccan fluoroapatite by wet process according to the following equation [5-6]:

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 10\ x\ H_2O \rightarrow 6H_3PO_4 + 10\ CaSO_4,\ x\ H_2O \downarrow + 2HF \uparrow$$
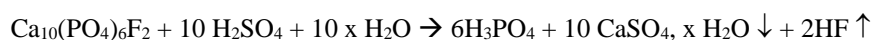
Depending on the process conditions, such as the temperature, either calcium sulfate hemihydrates (x=1/2, HH) or dehydrate (x=2, DH or phospho-gypsum) is formed. In the dihydrate process (DH), the temperature of the

reactor is maintained less than 80°C. The obtained phosphoric acid (26 to 29 % P_2O_5) contains mainly the impurities shown in table 1.

Table 1. Rate of impurities in the phosphoric acid 27 % before treatment.

P_2O_5	Density	Solid rate	SO_4^{2-}	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2	F^-	Na_2O	K_2O
27.12%	1267	0.05%	1.73%	1.62%	0.30%	0 .27%	0.16%	0.42%	0.73%	0.06%	0.06%

Deposit solid characterization

The physicochemical characterization of the deposited solid during of the 29% P_2O_5 phosphoric acid concentration is performed using X-ray diffraction and Inductively Coupled Plasma coupled to Optical Emission Spectrometry (ICP-OES). The X-ray diffractogram (Figure 1) shows that the solid is formed mainly by gypsum and sodium fluorosilicate. ICP-OES (Table 2) confirmed that the major component is gypsum [7], with the presence of fluosilicate [8] as a minor component. In light of these results, it is advisable to study the possibility of avoiding gypsum deposition by reducing the sulfate rate before the concentration step. For this purpose, we used this natural material rich in calcium.
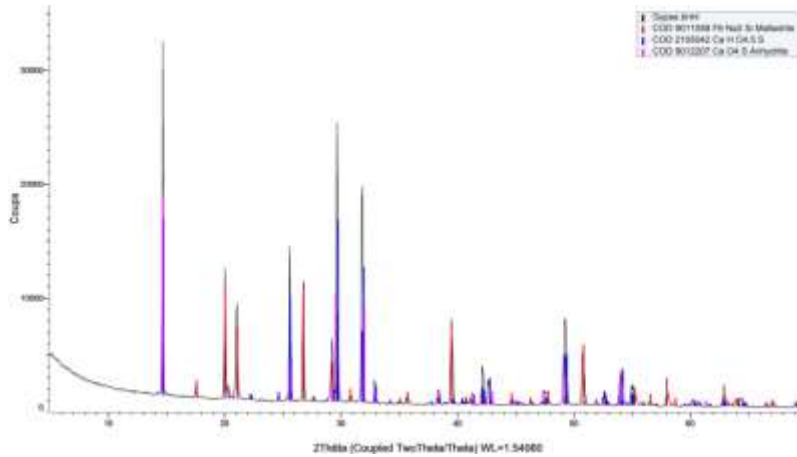

Figure 1. X-ray diffraction (XRD) for the deposit solid

Table 2. Results analysis of deposit solid by ICP-OES (% w)

SO_4^{2-}	CaO	Al_2O_3	F	MgO	Na_2O	SiO_2	K_2O	Fe_2O_3
46.9	32.75	0.7	0.66	0.16	0.41	0.88	0.25	0.02

Experimental apparatus

The experimental set-up is soundly chosen to be easily integrated in the phosphoric acid manufacturing process (Figure 2). 100 ml of phosphoric acid is heated (refluxed), in stirred reactor (flask) to the desired temperature (T), then the amount of material is added (Q), and the mixture is filtered after a period of time (t), then the filtrate is titrated to determine the residual mass of H_2SO_4 (Y).
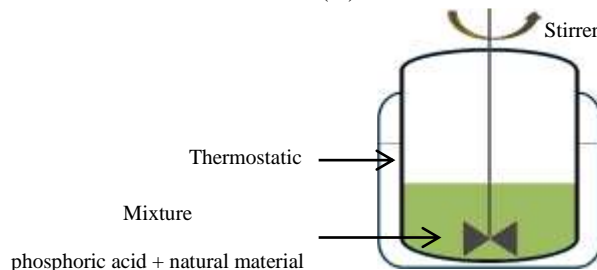

Figure 2. The scheme of a laboratory pre-treatment unit

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 baryum chloride and sulfonazo-3 ($C_{22}H_{12}N_4Na_4O_{14}S_4$) as an indicator. The determination of rate of phosphoric acid impurities was carried out by ICP-OES (JobinYvon ULTIMA2).

3. RESULTS AND DISCUSSION

Modeling by full factorial design

In order to model the desulphation process, we used two-levels full factorial desing where the average response can be adjusted properly using a linear model. This methodology uses less number of tests to determine the main effects of each factor and their interactions and avoids alias phenomenon [9]. In this study, four factors were studied to determine their effects on the desulphation process, namely the amount of natural material (X_1 in g/l), the initial amount of H_2SO_4 (X_2 g/l), temperature (X_3 in °C) and time (X_4 min). The target gol is to minimize the residual rate of H_2SO_4 (Y in g/l) in the pretreated phosphoric acid. The adjustment of the sulphate ratefor the factor (X_2) is ensured by addition of H_2SO_4 (d = 1.82, 98%). The amount of phosphoric acid to be treated is kept constant at 100 ml for all tests. Factors intervals variation (Table 3) is fixed taking into account the different grades of phosphoric acid (X_2), and operating conditions available industrial site to meet the technical and economic aspects of phosphoric acid manifacturing.

Table 3. Experimental variation of each factor

Factor	amount of natural material (g/l): X_1	initial amount of H_2SO_4 (g/l): X_2	Temperature (°C) : X_3	Time (min) : X_4
Niveau (-1)	25.0	17.0	40	25
Niveau (+1)	70.0	29.4	74	60

Two-levels full factorial desing methodology sets all operating conditions for four factors (2^4 = 16 tests) and the obtained results are summarized in Table 4. The coded mathematical model is presented by the equation 1.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 + b_{134}X_1X_3X_4 + b_{234}X_2X_3X_4 + b_{1234}X_1X_2X_3X_4 + \varepsilon \tag{1}$$

Table 4. Results of conducted experiments

N°	Codified values				True values				removal H_2SO_4 (g/l)		
	X_1	X_2	X_3	X_4	Dose	H_2SO_4	T(°C)	Time	Obs.	Pred.	Res.
1	-1	-1	-1	-1	25	17	40	25	13.23	13.2147	0.0153
2	1	-1	-1	-1	70	17	40	25	0.98	1.1791	- 0.1991
3	-1	1	-1	-1	25	29.4	40	25	18.865	18.7272	0.1378
4	1	1	-1	-1	70	29.4	40	25	5.635	5.6503	- 0.0153
5	-1	-1	1	-1	25	17	74	25	14.7	14.9297	- 0.2297
6	1	-1	1	-1	70	17	74	25	0.98	0.9341	0.0459
7	-1	1	1	-1	25	29.4	74	25	21.07	21.1159	- 0.0459
8	1	1	1	-1	70	29.4	74	25	7.84	7.6716	0.1684
9	-1	-1	-1	1	25	17	40	60	11.025	11.0709	- 0.0459
10	1	-1	-1	1	70	17	40	60	0.98	0.8116	0.1684
11	-1	1	-1	1	25	29.4	40	60	17.15	17.3184	- 0.1684
12	1	1	-1	1	70	29.4	40	60	2.45	2.4653	- 0.0153
13	-1	-1	1	1	25	17	74	60	13.475	13.2759	0.1991
14	1	-1	1	1	70	17	74	60	0.98	1.0566	- 0.0766
15	-1	1	1	1	25	2.94	74	60	22.295	22.2797	0.0153
16	1	1	1	1	70	2.94	40	60	6.86	7.0591	- 0.1991
17	0	0	0	0	47.5	23.2	57	42.5	9.8	9.9225	- 0.1225
18	0	0	0	0	47.5	23.2	57	42.5	10.045	9.9225	0.1225
19	0	0	0	0	47.5	23.2	57	42.5	10.29	9.9225	0.3675
20	0	0	0	0	47.5	23.2	57	42.5	9.8	9.9225	- 0.1225

| 21 | 0 | 0 | 0 | 0 | 47.5 | 23.2 | 57 | 42.5 | 10.045 | 9.9225 | 0.1225 |
| 22 | 0 | 0 | 0 | 0 | 47.5 | 23.2 | 57 | 42.5 | 9.8 | 9.9225 | - 0.1225 |

Obs.: observed, Pred.: predicted, Res.: residual. OM: organic matt

Where Y is the amount of residual sulfate (response to be fitted and be optimized). X_1, X_2, X_3 and X_4 is factors in codified units, b0 is the global mean, bi are the main and interaction effects and ε is the random error associated with the response. The results in Table 4 are processed by JMP-SAS software to determine the effects bi on the residual amount of H_2SO_4 (Y g/l) and validate statisticaly the model. Statistical analysis by Student test with a risk of 5% identifies the factors with significant influence on the observed response (Y g/l) [10]. Table 5 sumerizes effects, t-ratio and p-value of each factor. According to the p-value, the interactions X_1*X_4, X_2*X_4, $X_1*X_3*X_4$, $X_1*X_2*X_3*X_4$ are not statistically significant on desulphation (p-value> 0.05).

Table 5. Analysis of the effects of variables

Term	Scaled Estimate	Plot Estimate	Std Error	t Ratio	Prob>|t|
Intercept	9.9225		0.040249	246.53	<.0001
X_1	-6.5691		0.047196	-139.19	<.0001
X_2	2.8634		0.047196	60.67	<.0001
X_3	1.1178		0.047196	23.68	<.0001
X_4	-0.5053		0.047196	-10.71	<.0001
X_1*X_2	-0.5053		0.047196	-10.71	<.0001
X_1*X_3	-0.2909		0.047196	-6.16	0.0008
X_1*X_4	-0.0153		0.047196	-0.32	0.7566
X_2*X_3	0.6278		0.047196	13.30	<.0001
X_2*X_4	-0.0766		0.047196	-1.62	0.1559
X_3*X_4	0.3828		0.047196	8.11	0.0002
$X_1*X_2*X_3$	0.1991		0.047196	4.22	0.0056
$X_1*X_2*X_4$	-0.4441		0.047196	-9.41	<.0001
$X_1*X_3*X_4$	-0.1072		0.047196	-2.27	0.0636
$X_2*X_3*X_4$	0.2603		0.047196	5.52	0.0015
$X_1*X_2*X_3*X_4$	0.0153		0.047196	0.32	0.7566

The effects of each factor are represented in Figure3. Considering t-ratio values and the graph of the effects of each factor, (Table 5 and Figure 3), we observed that the natural material amount (X_1) and the initial sulfates (X_2) have a significant and an antagonistic effect on the residual sulphate content (Y), while the temperature (X_3) and the time (X_4) have no significant effect on the process of desulphation. The mathematical model is therefore written (Equation 2):

$$Y= 9.9225 - 6.5691*X_1 + 2.8634*X_2 + 1.1178*X_3 - 0.5053*X_4 - 0.5053*X_1*X_2 - 0.2909*X_1*X_3 + 0.6278*X_2*X_3 + 0.3828*X_3*X_4 + 0.1991*X_1*X_2*X_3 - 0.4441*X_1*X_2*X_4 + 0.2603*X_2*X_3*X_4 \quad (2)$$
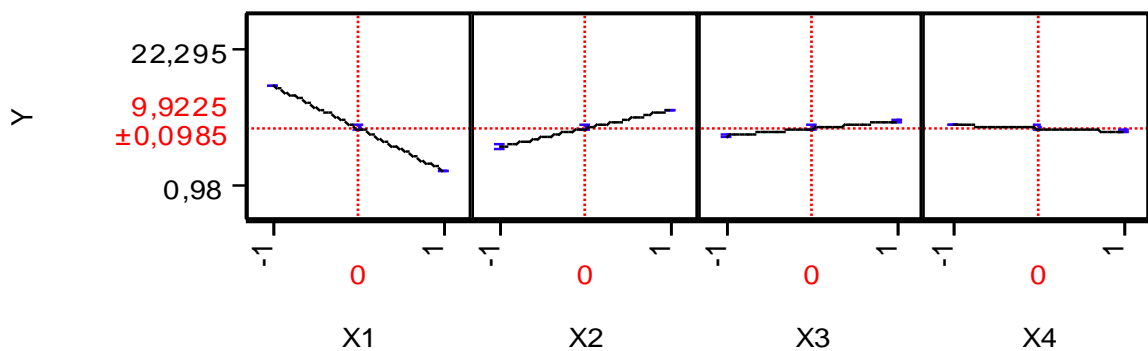

Figure 3. Effects of four factors on the sulphation phosphoric acid 29% P_2O_5

Table 6 shows the Analysis of variance (ANOVA) which confirms the statistical validity of the mathematical model (Equation 2) with R^2 factor of 99.94%. Indeed, figure 4 shows the graphical adjustment of the model and confirms the accuracy of the modelling of the estimated responses (Y_{est}) by the experimental results. Hence, the residuals analysis (difference between $Y_{obs}-Y_{est}$) shows that the residuals are randomly distributed around zero with no particular form. To confirm the modelling validation, additional tests were conducted within the experimental area and using experiments not tested in the full factorial design matrix (Table 4). Table 7 shows that the differences between the experimental results (Y_{obs}) and the estimated results (Y_{est}) are not significant. Therefore, the desulphation protocol can be modeled by Equation 2 to set the optimal operating conditions for effective reduction of sulphates from phosphoric acid.

Table 6. Analysis of variance (ANOVA)

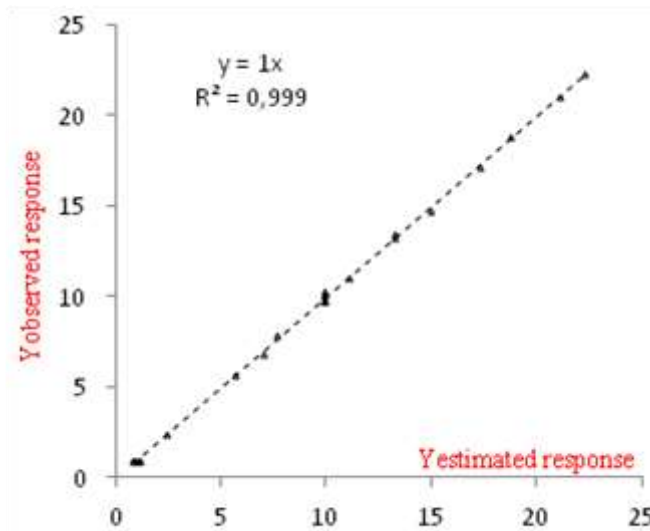| Source	DF	Sum of Squares	Mean Square	F Ratio
Model	11	864.671	78.606	1575.414
Error	10	0.499	0.050	Prob > F
C. Total	21	865.170		<.0001

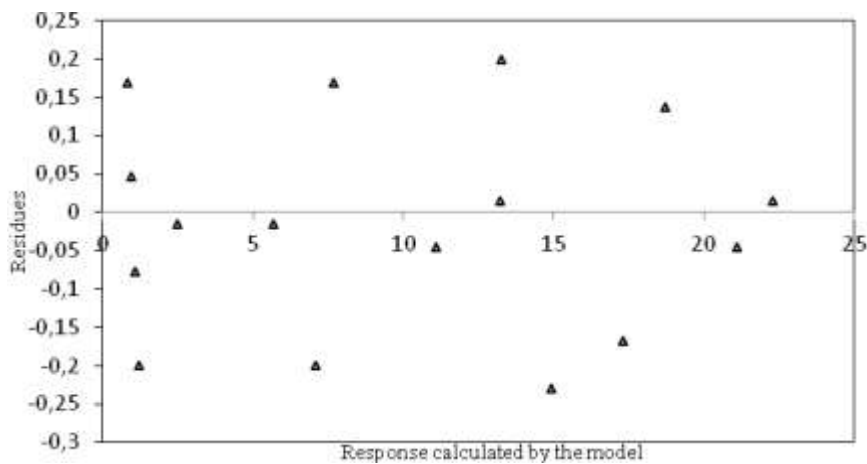*Figure 4. Adjustment graph*

Figure 5. Residuals graph

Table 7. Additional tests

test	the amount of the natural material (in g/l): X_1	Amount of H_2SO_4 (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
1	45.6	17	74	60	7.84	7.683	0.158
2	35	17	56	42	10.535	10.405	0.135
3	60	27	40	60	5.39	5.248	0.142

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 (X_2), the amount of the natural material is determined using equation 3.

$$X_1 = \frac{10.918 - Y_{tolerated} + 3.751X_2}{6.86 + 0.75X_2} \qquad (3)$$

$Y_{tolerated}$ is the maximum residual amount of H_2SO_4 having no effect on the formation of deposit solid during the phosphoric acid concentration step. The value of $Y_{tolerated}$ is determined using the solubility product of calcium sulfate in 54% P_2O_5 phosphoric acid ($Ks = 0.105$) [11]. In this case, the calcium intake of the natural reagent must be taken into account. Indeed, the mass of calcium ions remaining in the 29% acid after desulphation is:

$$m(Ca_{unreacted})_{29\%} = m(Ca_{initial})_{29\%} + 0.214m_M - (m(SO_4^{2-})_{29\%} - Y_{tolerated})\frac{40}{96}$$

$$m(Ca_{unreacted})_{29\%} = m(Ca_{initial})_{29\%} + 4.821X_1 - 2.531X_2 + 0.408Y_{tolerated} + 0.709$$

with m_M: mass of natural material (g) for one liter of phosphoric acid.
The volume of 54% phosphoric acid obtained after concentration of one liter of phosphoric acid 29% is $V_{54\%} = 0.3825$ liter. Therefore, the concentration of calcium ion in the 54% P_2O_5 phosphoric acid will be:

$$[Ca]_{54\%} = \frac{m(Ca_{unreacted})_{29\%}}{40V_{54\%}}$$

From where:

$$[Ca]_{54\%} = 0.065m(Ca_{initial})_{29\%} + 0.315X_1 - 0.165X_2 + 0.027Y_{tolerated} + 0.046$$

Similarly, the concentration of sulphate in 54% P_2O_5 phosphoric acid is:

$$[SO_4]_{54\%} = \frac{Y_{tolerated}}{96V_{54\%}} = 0.027Y_{tolerated}$$

So, the solubility product is written:

$$Ks = [Ca]_{54\%}[SO_4]_{54\%} = 0.105$$

From where:

$$[7.12\ 10^{-4}Y_{tolerated} + 1.74\ 10^{-3}m(Ca_{initial})_{29\%} + 8.41\ 10^{-3}X_1 - 4.41\ 10^{-3}X_2 + 1.24\ 10^{-3}]Y_{tolerated} = 0.105 \qquad (4)$$

We obtain a system with two equations (3) and (4). Knowing the initial quality of the 29% acid (X_2), the first equation determines the relationship between X_1 and $Y_{tolerated}$ that will be inserted into equation (4) in order to determine the value of $Y_{tolerated}$ and thereafter the amount of natural material to be used (X_1).
For example, for a 29% acid containing 6.6 g/l of calcium and 22 g/l of H_2SO_4:

$$X_1 = 1,518 - 0,149Y_{tolerated} \qquad (5)$$

Equation (4) is written as (6):

$$[7.12 \ 10^{-4}Y_{tolerated} + 8.41 \ 10^{-3}(1{,}518 - 0{,}149Y_{tolerated}) + 1.36 \ 10^{-2}]Y_{tolerated} = 0.105 \tag{6}$$

The values of $Y_{tolerated}$ and X_1 will therefore be 4.376 g/l and 0.8662 respectively.
The optimum mass of the natural material to be used to desulphate one liter of 29% phosphoric acid and to avoid the formation of the solid during the concentration step is $m_M = 66.99$ g.

4. CONCLUSION

Solid deposition during the 29% P_2O_5 phosphoric acid concentration is a real problem for industrial processing of 54% P_2O_5 phosphoric acid. Physicochemical characterization, by ICP-OES and X-ray diffraction, showed that this deposit is mainly composed of gypsum and sodium fluosilicate. To avoid gypsum deposition in the concentrators and increase life cycle of production chain, we suggest the use of natural material based on dolomite for desulphation of 29% P_2O_5 phosphoric acid with a simple protocol that can be easily inserted in the industrial scale. Desulphation process is limited to a simple addition of the natural material to the preheated phosphoric acid under stirring. Full factorial design based on tow-levels strategy allowed the desulphation modeling, taking into account four factors (quantity of natural material, initial quantity of sulphates, temperature and desulphation time). The validated model ($R^2 = 99.94\%$) ensures the determination of the natural material amount according to the phosphoric acid quality and regarding the availability of industrial conditions.

5. ACKNOWLEDGEMENTS

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