Modeling and optimization of phosphogypsum transformation into calcium fluoride using experimental design methodology

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Abstract: In this work, the experimental design methodology has been used for the modeling and optimization of phosphogypsum transformation into calcium fluoride and sodium sulfate. For this reason a four factors box behnken design has been chosen to be used. The studied factors were reaction time (X_1), NaF/phosphogypsum ratio (X_2), mass of phosphogypsum (X_3) and stirring speed (X_4) while Y_1 (the calcium yield) and Y_2 (the purity of the formed precipitate) are selected as the responses variables. A compromise between the studied responses has been determined and the optimum conditions for this reaction have been fixed at a reaction time of 97.80 min, a NaF/phosphogypsum ratio equal to 2.06, with 8.13 g of phosphogypsum mass and a stirring speed of 506.39 rpm. At these experimental conditions the calcium yield is 95.61% and the purity of the formed precipitate is 98.86%.

Keywords: phosphogypsum; box behnken design; Response surface methodology; optimization

INTRODUCTION

Phosphogypsum is an industrial waste produced by phosphate industry [1]. The manufacturing 1 ton of phosphoric acid produces 5 tons of Phosphogypsum as a by-product. Accordingly, the annual word production of phosphogypsum exceeds 200 million tons [2]. This waste causes many environmental problems since it contains metals in high concentration [3]. Despite these drawbacks, it is accumulated in large stockpiles and occupies huge land areas. The phosphogypsum causes a very serious problem, especially when it is considered over production, for the damage that it causes to the environment due to its negative impact on water, air and soil [1]. Several efforts of valorization have been conducted by researchers in order to solve this environmental problem. Recently, many research works have studied the possibility of valorizing this waste and several commercial applications have been found [4]; its use as a fertilizer in agriculture, a building material, an amendment for soil stabilization and a coating pigment in the paper industry.

Today's priority is to try to find new applications of phosphogypsum in order to minimize its disposal and stockage [5] but there is a big problem in phosphogypsum because it contains many impurities [6]. Singh et all declared that they can solve this problem by washing phosphogypsum [7] or by treatment with ammonium hydroxide [8] or with aqueous ammonium sulfate [9] and a mixture of sulfuric acid and silica [10] before use.

Despite the purification of phosphogypsum and the previously- mentioned applications, problems caused by the stockage of phosphogypsum have not been completely solved. Therefore this work aim to study the transformation of phosphogypsum into CaF_2 and Na_2SO_4 by adopting the response surface methodology which is an efficient statistical method that has been successfully used in testing process parameters and their interactive effect [11-14].

Firstly, a box behnken experimental design was used to determine the most significant factors and the mathematical model that predict the response

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as function of factor variations. Then, the optimum conditions were determined using the model and its relative response surfaces [15]. Therefore, statistical design has been widely-employed for process characterization, modeling and optimization [16-17] in a reduced number of experiments [18]. In order to optimize the transformation of phosphogypsum into CaF_2 and Na_2SO_4, four factors were studied and two responses were evaluated.

EXPERIMENTAL DETAILS

1. Equipment and analysis methods

The studied transformation was carried out in a jacketed glass reactor (250 mL) in a batch way. Magnetic stirring was maintained during the reaction time. Solid and liquid samples were separated by centrifugation method.

Na^+ ions concentrations were analyzed by a flame photometer BWB Technologies. Ca^{2+} ions concentrations were determined by flame atomic absorption spectrometer (AAS Vario 6). The SO_4^{2-} ion concentration was determined by the gravimetric method. The ion meter (781-pH/Ion Meter, Metrohm) equipped with a crystalline membrane electrode 6.0502.150 was used to determine fluoride ion concentrations. Solid phases were characterized by XRD using a Philips PW 3040 generator, PW 3050/60 Θ/2Θ goniometer and PW 3373/00 copper cathode.

2. Calculation

Experimental designs setup and treatments of results were analyzed by NemrodW software. [19]

RESULTS AND DISCUSSION

1. Identification of significant factors

In order to determine the optimum conditions of conversion reaction (1), a box behnken matrix has been chosen.

$$CaSO_4.2H_2O + 2NaF \rightarrow CaF_2 + Na_2SO4 + 2H_2O \quad (1)$$

In this study Y_1 (the calcium yield) and Y_2 (the purity of the formed precipitate) are the responses variables. They were defined as below:

$$Y_1 = 100 * ({}^{n_{Ca}}/_{n_{Ca}^{initial}}) \quad (2)$$

$$Y_2 = 100 * (1 - (w_{SO_4^{2-}} + w_{Na+})) \quad (3)$$

When n_{Ca} and $n_{Ca}^{initial}$ are respectively, the mole number of calcium ions in formed precipitate and those initially introduced by phoshogypsum.

w_{SO4}^{2-} and w_{Na}^{+} are the mass fraction of sulfate and sodium ions respectively in formed precipitate.

While reaction time (X_1), ratio NaF/ phosphogypsum (X_2), mass of phosphogypsum (X_3) and stirring speed (X_4) were chosen as the four independent variables.

A total of thirty tests were determined including six experiments at the central point (ie the middle of interval of each factor). The design independent variables and their levels are given in table 1 and the experimental design matrix is summarized in table 2.

Data was analyzed by the full model as follows:

$$\mathbf{Y}=b_0+ b_1X_1+ b_2X_2+ b_3X_3+ b_4X_4+ b_{11}X_1^2+ b_{22}X_2^2+ b_{33}X_3^2+ b_{44}X_4^2+ b_{12}X_{12}+ b_{13}X_{13}+ b_{14}X_{14}+ b_{23}X_{23} + b_{24}X_{24}+ b_{34}X_{34} \quad (4)$$

b_i represents the coefficients of effects

b_{ij} represents the interaction effect of a two-factor interaction X_iX_j

The NemrodW logiciel was used for regression and graphical analysis of the data. The optimum values of the selected variables were obtained after solving the regression equations and analyzing the response surface. Then, we studied the responses of the statistical design, estimated the coefficients imputed in a mathematical model, predicted its response and validated its adequacy.

Table 3 and 4 summarize the estimation of the factor effects for the 2 responses Y_1 and Y_2 respectively. As it can be seen, for the first response Y_1, the significant factors are b_1 (reaction time) and the interaction term b_{23} (NaF/ phosphogypsum and mass of phosphogypsum).

While, for the second response Y_2, b_2 (NaF/ phosphogypsum), b_3(mass of phosphogypsum), the quadratic term b_{22} and the interaction b_{14} (between time reaction and stirring speed) are the significant factors.

Thus the obtained model is given through the following equations

$$Y_1=97.442-2.228X_1 +1.878X_{23} \quad (5)$$

$$Y_2=98.567-X_2+0.192X_3 +0.297X_2^2-0.185X_1X_4 \quad (6)$$

2. Analysis of residue

Residues are the difference between calculated and simulated responses. The graphical examination of residues is a common method

Table I: Independent variables and their levels

Coded variable	Normal variable	Factor	Levels	
			-1	+1
X_1	U_1	Reaction time (min)	30	120
X_2	U_2	Ratio NaF/phosphogypsum	1.5	3
X_3	U_3	Mass of phosphogypsum (g)	7	10
X_4	U_4	Stirring speed (rpm)	400	800

Table II: Box Behnken experimental design matrix for the four independent variables

Experiment no.	**U_1**	**U_2**	**U_3**	**U_4**	**Y_1**	**Y_2**
1	30.00	1.50	8.50	600.00	99.43	99.86
2	120.00	1.50	8.50	600.00	92.10	99.86
3	30.00	3.00	8.50	600.00	99.44	97.81
4	120.00	3.00	8.50	600.00	97.30	97.79
5	30.00	2.25	7.00	600.00	99.32	98.16
6	120.00	2.25	7.00	600.00	95.90	98.36
7	30.00	2.25	10.00	600.00	99.54	98.73
8	120.00	2.25	10.00	600.00	94.30	98.73
9	30.00	2.25	8.50	400.00	99.32	98.39
10	120.00	2.25	8.50	400.00	92.30	98.63
11	30.00	2.25	8.50	800.00	99.58	98.90
12	120.00	2.25	8.50	800.00	98.00	98.40
13	75.00	1.50	7.00	600.00	97.38	99.79
14	75.00	3.00	7.00	600.00	92.60	97.75
15	75.00	1.50	10.00	600.00	96.86	99.87
16	75.00	3.00	10.00	600.00	99.59	98.05
17	75.00	1.50	8.50	400.00	98.03	99.87
18	75.00	3.00	8.50	400.00	99.46	97.90
19	75.00	1.50	8.50	800.00	99.50	99.85
20	75.00	3.00	8.50	800.00	98.30	97.80
21	75.00	2.25	7.00	400.00	99.39	98.53
22	75.00	2.25	10.00	400.00	96.65	98.99
23	75.00	2.25	7.00	800.00	99.47	98.07
24	75.00	2.25	10.00	800.00	99.59	98.59
25*	75.00	2.25	8.50	600.00	99.74	98.51
26*	75.00	2.25	8.50	600.00	97.51	98.72
27*	75.00	2.25	8.50	600.00	95.50	98.63
28*	75.00	2.25	8.50	600.00	97.59	98.44
29*	75.00	2.25	8.50	600.00	95.91	98.46
30*	75.00	2.25	8.50	600.00	98.40	98.64

*: central points (to determine the experimental error)

Table III: Coefficients values and their statistical significance for Y_1

coefficient	Value	SE coef	t.exp.	Signif. %
b_0	97.442	0.677	144.02	***
b_1	-2.228	0.478	-4.66	***
b_2	0.282	0.478	0.59	57.0%
b_3	0.206	0.478	0.43	67.6%
b_4	0.774	0.478	1.62	12.3%
b_{11}	-0.544	0.633	-0.86	40.8%
b_{22}	-0.112	0.633	-0.18	85.7%
b_{33}	-0.037	0.633	-0.06	95.3%
b_{44}	1.088	0.633	1.72	10.3%
b_{12}	1.298	0.829	1.57	13.5%
b_{13}	-0.455	0.829	-0.55	59.7%
b_{23}	1.878	0.829	2.27	*
b_{14}	1.360	0.829	1.64	11.8%
b_{24}	-0.657	0.829	-0.79	44.5%
b_{34}	0.715	0.829	0.86	40.6%

Table IV: Coefficients values and their statistical significance for Y_2

coefficient	Value	SE.coef	t.exp.	Signif. %
b_0	98.567	0.061	1623.27	***
b_1	-0.007	0.043	-0.16	87.3%
b_2	-1.000	0.043	-23.29	***
b_3	0.192	0.043	4.46	***
b_4	-0.058	0.043	-1.36	19.2%
b_{11}	-0.026	0.057	-0.45	65.9%
b_{22}	0.297	0.057	5.22	***
b_{33}	-0.026	0.057	-0.45	65.9%
b_{44}	0.012	0.057	0.21	83.4%
b_{12}	-0.005	0.074	-0.07	94.6%
b_{13}	-0.050	0.074	-0.67	51.8%
b_{23}	0.055	0.074	0.74	47.7%
b_{14}	-0.185	0.074	-2.49	*
b_{24}	-0.020	0.074	-0.27	78.7%
b_{34}	0.015	0.074	0.20	83.7%

used to identify the suspect data, so we plot the value of residues versus the predicted responses (ie calculated) (figure 1 and figure 2) [20]. We note that the values of residue are very low for Y_2, which means that nothing of abnormal appears on these graphics. In fact, figure 2 shows a normality of residues, with a constant dispersion around zero.

Residue has an insignificant adjustment when it is greater than 2 in absolute value as seen in figure 1.

After preliminary examination of these Studentized residues, they will be then plotted as a function of calculated answers values in order

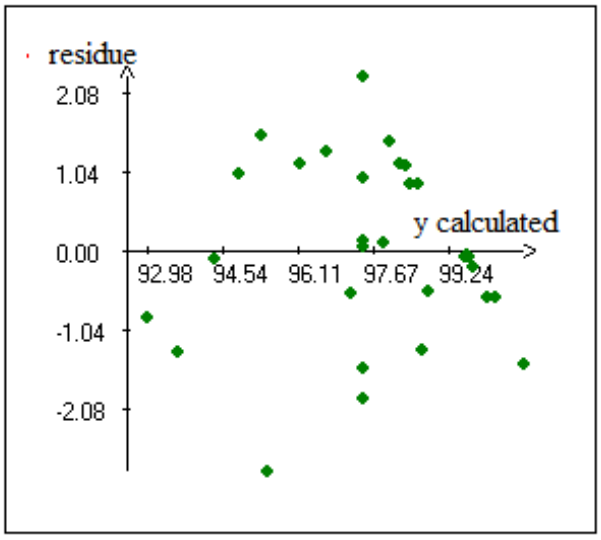

Figure 1: Observed yield versus predicted values for Y_1

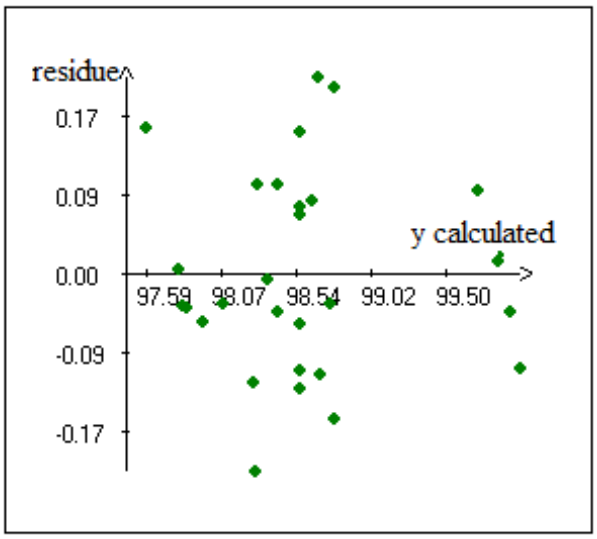

Figure 2: Observed yield versus predicted values for Y_2

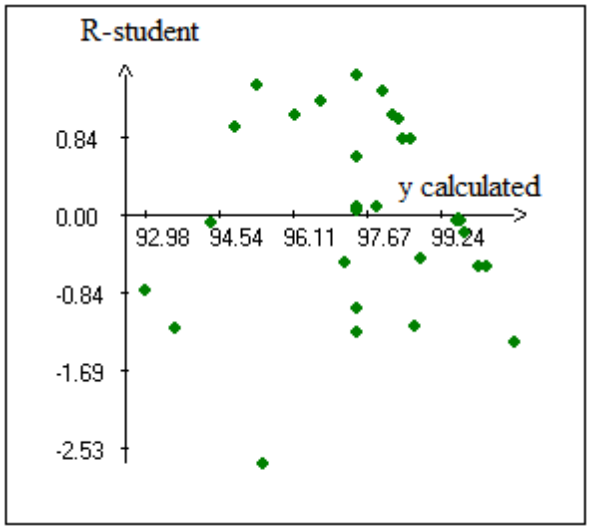

Figure 3: R-student versus the calculated for Y_2

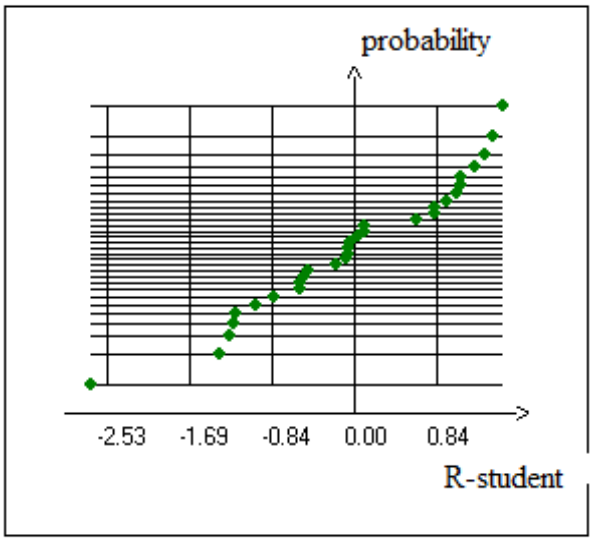

Figure 4: probability versus R-student for Y_2

to verify if the experimental variance remains constant for each value of the response. [21]
Residues should be randomly distributed around zero, and does not depend on the response value.
Figure 3 represents residue values based on responses studentized for Y_1. The graph shows a normality of experiments.
Residue values are very low; the variation interval is little so it's acceptable.
Generally the Henry graphical method is used, in order to explain the variation of responses.
Each point in this graph represent the value of the residue in the experiment's surface, the residues have a normal distribution if these points are almost aligned in a gauss-arithmetical graph.
So to assure the best results interpreted by Studentized residues, the exploitation of Henry line is required. Figure 4 shows the alignment of the points forming a straight line, which can be explained by the normality of errors.

3. Analysis of variance

Table 5 and 6 summarize the variance analysis of the two responses Y_1 and Y_2 respectively. We note that the ratio values of the mean square between the lack of fit and the pure error for response 1 and 2 (1.1689 and 2.1115) are inferior to

$$F_{10.5}^{0.05} = 4.75.$$

So we can conclude that the two models are valid. In addition, the ratio of the regression and residual mean square for Y_1 and Y_2 (2.9351 and 42. 9657) are superior to

$$F_{15.14}^{0.05} = 2.39.$$

Thus, the significant variables used in modeling have a significant effect on responses (Y_1 and Y_2). [22-23]

Table V: The analysis of variance for the first response Y_1

Source of variation	Sum of squares	Degrees of freedom	Mean square	ratio	Signification
Regression	112.8637	14	8.0617	**2.9351**	*
Residual	41.1997	15	2.7466		
Lack of fit	28.8562	10	2.8856	**1.1689**	45.7%
Pure error	12.3435	5	2.4687		
Total	154.0634	29			

Table VI: The analysis of variance for the first response Y_2

Source of variation	Sum of squares	Degrees of freedom	Mean square	Ratio	Signification
Regression	13.3070	14	0.9505	**42.9657**	***
Residual	0.3318	15	0.0221		
Lack of fit	0.2683	10	0.0268	**2.1115**	21.1%
Pure error	0.0635	5	0.0127		
Total	13.6388	29			

4. Optimization

We used the NemrodW software for the construction of isoresponses graph. These graphs are sections and projections that fixed levels of significant factors. The graphical analysis of the model consists essentially in converting the equation (the validate model) into iso-response curves. In fact, the study of the influence of operating conditions on the responses was performed by varying two factors and fixing the others.

For the first response Y_1 we plot isoresponses curves in the plan X_2/X_3 (NaF/phosphogypsum molar ratio; phosphogypsum mass) (figure 5) as mentioned in table 3 that the interaction between the second and the third factors is signifiacant and we fixed the reaction time at 75 min ($X_1 = 0$) and stirring speed at 600 tr/min ($X_4 = 0$).

Based on the graphical analysis (figure 5), we note that the first response Y_1 is maximum ($Y_1 = 99$ %) when X_2 and X_3 are close to level -1 it means that it is advantageous to work with low reactive ratio and low phosphogypsum mass. The next step is to study the effect of two factors $X_1$and X_4, so we must fix X_2 at the center point (2.25) and at the same level for X_3 (8.5g / 100mL). Graphics of figure 6, show a maximum yield $Y_1 = 99\%$ for X_1 Near to level 0 (75 min), while X_4 factor does not seem to affect the result (Y_1 still constant when we varied X_4 from levels -1 to 1) and this explains although the reason for which the X_4 factor was not significant on the model.

For the second response Y_2, we plot the isoresponse curves in X_1/X_4 plan (reaction time/ stirring speed) (figure 7). This response is maximum (99%) when X_1 (reaction time) is like the first response at 97 min and with 600 tr/min. After this, we should study the effect of the other significant factors, for this reason we plot the

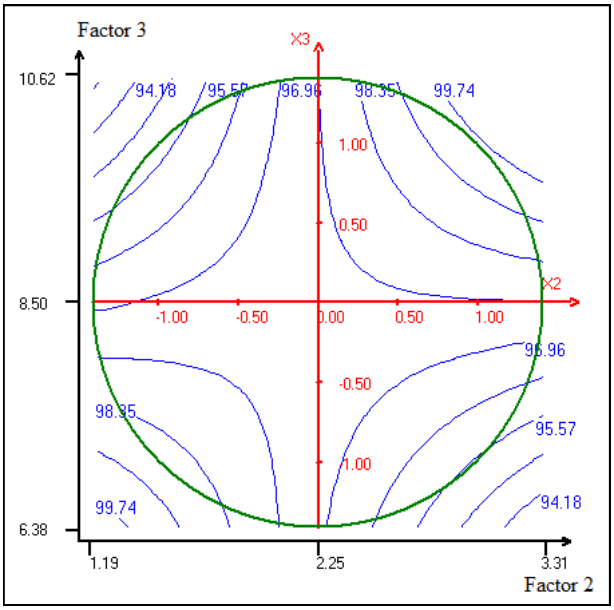

Figure 5 : Isoresponse curves in the plan X_2/X_3 for Y_1

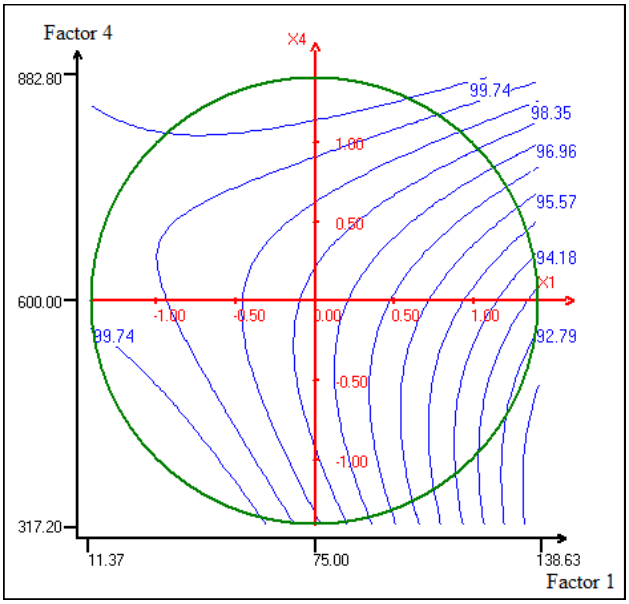

Figure 6: Isoresponse curves in the plan X_1/X_4 for Y_1

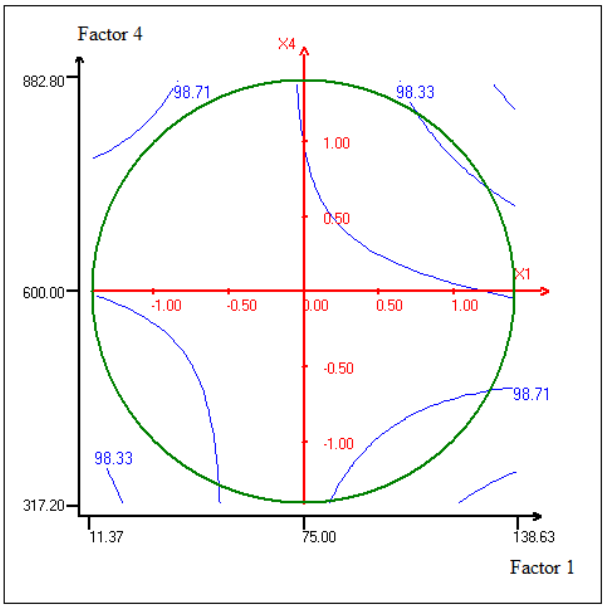

Figure 7: Isoresponse curves in the plan X_1/X_4 for Y_2

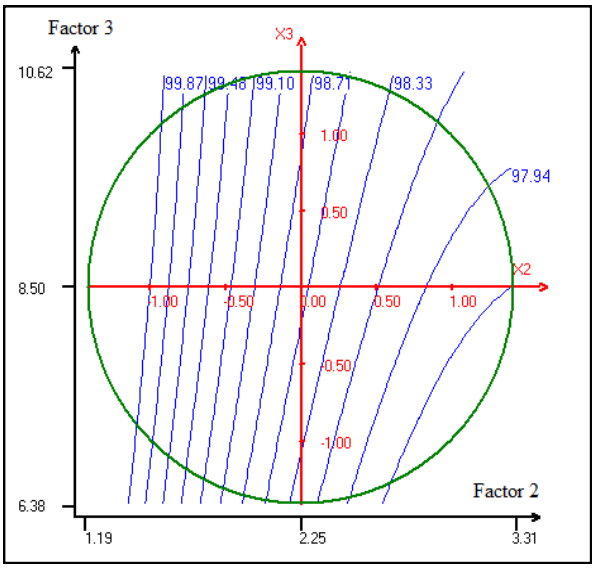

Figure 8: Isoresponse curves in the plan X_2/X_3 for Y_2

Table VII: Optimal conditions

Variable	Coded Value	Factor	Value
X_1	0.506639	Reaction time (min)	97.80
X_2	-0.250114	Ratio NaF/phosphogypsum	2.06
X_3	-0.249407	Mass phosphogypsum (g)	8.13
X_4	-0.468048	stirring speed(tr/min)	506.39

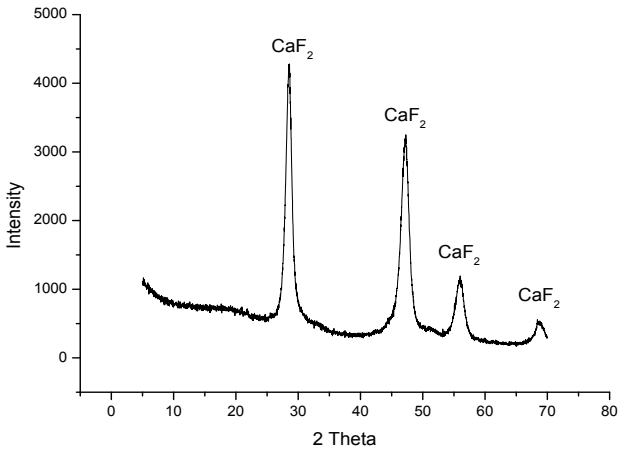

Figure 9: Diffractogramm of formed solid at optimal conditions

isoresponses curves in X_2/X_3 plan (figure 8). We note that Y_2 is maximizing when we use a NaF/ phosphogypsum ratio equal to 2.06 and at the central value of the phosphogypsum mass (8.5g).

5. Optimum characterization

A compromise between the two responses Y_1 and Y_2 allowed us to determine the optimal conditions which are summarized in table 7 and the correspondent values of responses (table 8).

If we compare the statistical (theoretical) results and the experimental ones (the optimum) it's found that there is a good agreement between them and the formed precipitate at these conditions is CaF_2 (figure 9).

CONCLUSION

Conversion of phosphogypsum into calcium fluoride (solid phase) and sodium sulfate (liquid phase) has been investigated using a small scale batch reactor. The application of experimental design methodology (box behnken matrix) was used in order to determine the optimum conditions that induce the maximization of the CaF_2 content in the precipitate. There is a good agreement

Table VIII: Optimal responses

Response	Name	Value (%)
Y_1	calcium yield	95.61
Y_2	purity of precipitate	98.86

between the predicted and the experimental results. This method has been very useful and advantageous; the conversion has been achieved with a percentage exceeding 96%.

REFERENCES

[1] Z. Kadirova, M. Hojamberdiev, L. Bo, R. Hojiyev, *J. of Cleaner Production*, **2014**, 83, 483-490.

[2] H. Zhao, L. Huiquan, B. Weijun, W. Chenye, L. Songgeng, L. Weigang, *J. of CO2 Utilization*, **2014**, 78 , 4-11.

[3] A. Carbonell-Barrachinaa, R.D. De Laune, A. Jugsujinda, *J. Waste Management*, **2002,** 22, 657–665.

[4] C. Papastefanou, S. Stoulos, A. Ioannidou, M. Manolopoulou, *J. of Environmental Radioactivity*, **2006**, 89, 188-198.

[5] M. Cavalcanti-Canuta, V. Feliciano-Jacomino, K. Bråtveit-Abdias, M. Gomes, M. Yoshida, *J. Materials characterization,* **2008**, 59, 365–373.

[6] S. Nakamori, Y. Mizuguchi, *Semento Gijutsu Nenpo*, **1996**, 21, 33 – 42.

[7] M. Singh, *Res. Ind*, 1982, 27, 167-169.

[8] M. Singh, M. Garg, S.S. Rehsi, *Constr. Build. Mater*, **1993**, 7, 3-7.

[9] M. Singh, Environ. *Health*, **1983**, 25, 300-306.

[10] M. Singh, S.S. Rehsi, C.A. Taneja, *Ind. J. Technol*, **1984**, 22, 28-32.

[11] C. Hong, W. Haiyun, *Bioresour Technol*, **2010**, 14, 5487-5493.

[12] H.M. Hamzah, A. Osman, C.P. Tan, F. Ghazali, *Postharvest Biol Technol*, **2013**, 75, 142-146.

[13] K. Murugesan, A. Dhamija, I.H. Nam, Y.M. Kim, Y.S. Chang, *Dyes Pigments*. **2007**, 75, 176-184.

[14] P. Kirmizakis, C. Tsamoutsoglou, B. Kayan, D. Kalderis, *Journal of Environmental Management*, **2014**, 146, 9-15.

[15] M. Asadollahzadeha, H. Tavakoli, M. Torab-Mostaedi, G. Hosseini, A. Hemmati, *Talanta*, **2014**, 123, 25–31.

[16] I.A. Alaton, G. Tureli, T.O. Hanci, *J. Photochem. Photobiol*, **2009**, 202, 142-153.

[17] R. Singh, R. Chadetrik, R. Kumar, K. Bishnoi, D. Bhatia, A. Kumar, N.R. Bishnoi, N. Singh, *J. Hazard Mater*, **2010**, 174, 623-634.

[18] S. Behij, K. Djebali, H. Hammi, A.H. Hamzaoui, A. M'nif, J. *Chemometrics*, **2011**, 25, 59-66.

[19] D. Mathieu, R. Phan Tan Luu, *Nemrod-W Software*, Aix-Marseille III University France **1999**.

[20] M. Khajeh, *Food Chem*, **2011**, 129, 1832-1838.

[21] Z. Zhang, H. Zheng, *J. Hazard. Mater*, **2009**, 172, 1388-1393.

[22] B. Kayan, B. Ozmen, *J. Hazard. Mater*, **2012**, 201-202, 100-106.

[23] K. Yetilmezsoy, S. Demirel, R.J. Vanderbei, *J. Hazard. Mater*, **2009,** 171, 551-562.