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Application of Plackett-Burman Design in the Screening of Factors Acting on the Sulfuric Leaching Process of Rare Earths from Moroccan Phosphogypsum



Abstract: - As the main waste of the phosphates industry (200–300 million tons per annum produced globally), phosphogypsum (PG) is a major environmental concern (85% of PG is disposed of on land or at sea). The valorization of PG as a secondary source of rare earth elements (REE) is one of the most recent valorization options under investigation. This study investigated the sulfuric acid leaching process of REE from a Moroccan PG. Plackett -Burman design was used to statistically screen significant factors affecting the leaching efficiency of REE named the studied response (Y). Seven factors considered potentially influential were studied as the model variables : Sulfuric acid concentration (X1); Solid to liquid ratio (X2); Drying temperature (X3); Leaching time (X4); Stirring speed (X5); Temperature (X6). Particle size (X7). According to the results, the predicted values of the fitted model were in good agreement with the experimental values by a coefficient of determination (R²) equal to (99 %). drying temperature has a statistically insignificant effect with $p=0.336 > 0.05$. All the other six variables have significant effects ($p < 0.05$), but 97,91 % of Y was affected only by the following four factors: X1 (63.71%), X4 (17.94%), X2 (9.98%) , X5 (6.24%).

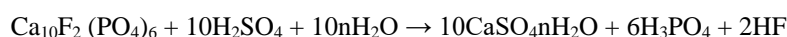
Keywords: Phosphogypsum, Plackett -Burman design, Rare earth elements, Sulfuric acid leaching.

1. Introduction

Rare earth elements (REE) is a term that corresponds to 17 chemically similar metallic elements (15 lanthanides, plus scandium and yttrium). Thanks to their unique properties, their application has gone beyond the classical use as basic materials in many technologically advanced products (satellite, automotive, defense ...). Today, they are becoming increasingly important in the transition to a low-carbon circular economy, given their essential role in permanent magnets, lamp phosphors, rechargeable nickel-metal hydride batteries, catalysts and other green economy applications [1]. As a result, demand for REE has grown significantly, from 75,500 tonnes of rare earth oxides (REO) in 2000 to 123,100 tonnes of REO in 2016 [2]. Moreover, the European Commission considers rare earths as the most critical group of raw materials with the highest supply risk [3]. Thus, the recovery of these strategic elements from secondary sources is a mandatory option.

Bastnasite, monazite and xenotime are the three most frequently mined rare earth minerals (primary sources of REE) [4]. The lack of economically viable and operational primary deposits is driving many countries towards the exploitation of secondary sources such as end-of-life products (permanent magnets, fluorescent lamps, nickel-metal hydride batteries) [5]. In parallel, researchers are obliged to test the recovery potential from other likely secondary sources such as phosphogypsum.

Phosphogypsum (PG) is the main by-product of phosphoric acid production resulting from the digestion of phosphate rock by sulphuric acid according to the reaction below [6]:



Where $n = 0, 1/2$ or 2 , depending on whether the calcium sulphate crystallises in a more or less hydrated form. Unlike end-of-life products, this mine tailings has a low concentration of rare earths (about 0.035 to 1.335% (w/w) [7] (Habashi., 1985), yet it can become a secondary source of significant amounts of these elements, especially considering its annual world production of about 100 to 280 million tonnes [8,9].

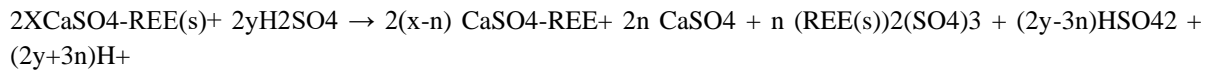
Leaching is an essential primary phase in the process

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of rare earth recovery from phosphogypsum. Although this reaction can be carried out with a number of different acids [10], sulphuric acid is the most readily available on-site and the most easily integrated into the existing infrastructure of phosphoric acid plants [11]. The sulphuric leaching of rare earths from phosphogypsum proceeds according to the following reaction [12]:



Several research studies have been conducted to understand and improve this critical phase in the hydrometallurgical process of rare earth recovery from phosphogypsum [10,11 13,14,15]. However, the lack of statistical approaches and process modelling is a shortcoming that should not be overlooked in future studies. In this sense, the

objective of the present work was to screen the main factors (variables) acting on the leaching reaction studied using reliable statistical techniques. This type of screening design is generally the most used in similar studies for two reasons: the first is the economic feature of this design. In general, Plackett-Burman proposes very few experimental trials (as few as 12). Since experimental trials and analyses can be expensive to conduct, this makes its models more economical. The second reason is the proper assessment of main effects because confounding between main effects and two-factor interactions is only partial (or fractional) [16]. Thus, thanks to this study, we will be able to determine the "weight" of the main effect of each factor of all the seven studied factors, test their statistical significance and rank them based on their contribution to the leaching efficiency of REE.

2. Materials and methods

2.1. Materials

The Moroccan phosphogypsum sample in this study is from Jorf Lasfar, one of two phosphate treatment plants of the OCP group. The chemical components in this by-product sample are presented in Table 1. A Sulphuric acid of technical grade (98%) was used for the preparation of leach solutions.

2.2. Leaching reaction

The pre-treatment step of the raw PG is controlled by two factors: Drying temperature X_3 and particle size X_7 . The PG was then leached by a sulphuric acid solution with a molar concentration X_1 . The course of the experimental leaching reaction respects the temperature X_6 and the stirring speed X_5 . After the leaching time X_4 , the pregnant leach solutions (PLS) were separated from the solid by a vacuum filtration before being analyzed by ICP-MS to determine its REE content. The values of the seven investigated factors (X_1 through X_7) and the conditions of each run are presented in table 2 and table 3.

The calculation of REE leaching efficiency expressed in (%) was carried out using the following equation:

$$Y_{REE}(\%) = \frac{[REE]_L \times V}{m_s \times [REE]_T} \times 100$$

where $[Y_{REE}]_L$, V , m_s , and $[Y_{REE}]_T$ represent leached metal REE ions concentration in $\text{g}\cdot\text{L}^{-1}$ in the PLS, the pregnant leach solution (PLS) volume in liters, the mass of sample PG in ton, and the REE content in g/t respectively.

2.3. Design of Experiment (DoE)

The Plackett - Burman design is a fractional factorial experimental plan based on a Hadamard matrix. Using this low-cost experimental design, we studied the main effect of seven factors only by 16 experimental runs (eight base runs and two replicates were carried out). Our experimental design of leaching REE from PG with measured response (REE leaching efficiency) was presented in Table 3. The experimental values of this response was analyzed using NemrodW statistical software. The resulting mathematical model is a polynomial of the first order given as:

$$\hat{Y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 + b_6X_6 + b_7X_7 + \varepsilon$$

Where \hat{y} and ε denote the response function and the error constant. X_1, X_2, \dots, X_7 are term factors. $b_0, b_1, b_2, \dots, b_7$ represent multivariate regression coefficients. Validity of the RSM model was based on the analysis of variance (ANOVA). The factor coefficients are considered statistically significant when their p-value < 0.05 .

Strong relationship with the model is observed when the correlation coefficient R^2 approach unity.

3. Results and Discussions

3.1. Experimental design and dosed responses.

The value of the experimental (observed) response Y that corresponds to each combination of the seven studied variables is shown in Table 3.

3.2. Computation of model coefficients.

Once we add the experimental responses (y_i) to the experimental design, the calculation was done automatically with the NemrodW software. The results are shown in Table 4 and Table 5.

Table 1 Main chemical components and rare earth elements in the phosphogypsum sample

Component Content (%)	CaO	P ₂ O ₅	SO ₃	MgO	Al ₂ O ₃	K ₂ O
	31.15	1.1	42.1	<0.10	<0.10	0,75
Component Content (ppm)	Y	La	Nd	Ce	Dy	ΣREE
	128.1	64.52	49.08	42.48	13.16	359

Table 2 Factors and their actual and coded levels.

Factors (variables)	Levels (values)	Coded levels	Units	Coded variables
[sulfuric acid]	2.2	-1	M	X ₁
	4.4	1		
Ratio S/L	1/6	-1		X ₂
	1/3	1		
Drying Temperature	70	-1	°C	X ₃
	RT	1		
Leaching Time	20	-1	min	X ₄
	40	1		
Stirring speed	300	-1	rpm	X ₅
	600	1		
Temperature	40	-1	°C	X ₆
	80	1		
Particle size]200-600]	-1	µm	X ₇
	≤100	1		

Table 3 Experimental design of the leaching process of REE from PG with recorded responses.

Base runs	Tests	Factors (X)							Response y (%)	
		X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	X ₇	Y /Test	Average
		M		°C	min	rpm	°C	µm		
1	1	4.4	0.333	RT	20	600	40]200-600]	2.24	2.66
	2	4.4	0.333	RT	20	600	40]200-600]	3.08	
2	3	2.2	0.333	RT	40	300	80]200-600]	35.79	34.55
	4	2.2	0.333	RT	40	300	80]200-600]	33.31	
3	5	2.2	0.166	RT	40	600	40	ø ≤ 100	53.12	52.105
	6	2.2	0.166	RT	40	600	40	ø ≤ 100	51.09	
4	7	4.4	0.166	70	40	600	80]200-600]	27.49	28.6
	8	4.4	0.166	70	40	600	80]200-600]	29.71	
5	9	2.2	0.333	70	20	600	80	ø ≤ 100	34.20	33.13
	10	2.2	0.333	70	20	600	80	ø ≤ 100	32.06	
6	11	4.4	0.166	RT	20	300	80	ø ≤ 100	11.15	10.755
	12	4.4	0.166	RT	20	300	80	ø ≤ 100	10.36	
7	13	4.4	0.333	70	40	300	40	ø ≤ 100	11.33	11.79
	14	4.4	0.333	70	40	300	40	ø ≤ 100	12.25	
8	15	2.2	0.166	70	20	300	40]200-600]	29.68	29.095
	16	2.2	0.166	70	20	300	40]200-600]	28.51	

Table 4 Analysis of variance

Source of variation	Sum of squares	df	Medium Square	Ratio F	Significance	R ²
Regression	3594.62	7	513.517	352.2620	***	99 %
Residue	11.66	8	1.457			
Total	3606.28	15				

Table 5 Statistical evaluation of the model

Factor	coefficient bi		Standard Deviation 'σ'	Significance	
	code	value		Ti = bi/σ	P-Value
Constant	b ₀	25.336	0.3018	83.94	***
[sulfuric acid]	b ₁	-11.884	0.3018	-39.37	***
Ratio S/L	b ₂	-4.803	0.3018	-15.91	***
Drying temperature	b ₃	-0.318	0.3018	-1.05	0.323

Leaching Time	b ₄	6.426	0.3018	21.29	***
Stirring speed	b ₅	3.788	0.3018	12.55	***
Temperature	b ₆	1.423	0.3018	4.71	0.0015
Particle size	b ₇	1.609	0.3018	5.33	0.0007

*** : P-Value < 0.0001

3.3. Model validation.

Based on the results of table 5, the postulated model that must be validated is:

$$\hat{Y} (\%) = 25.336 - 11.884 X_1 - 4.803 X_2 - 0.318 X_3 + 6.426 X_4 + 3.788 X_5 + 1.423 X_6 + 1.609 X_7 + 1.2$$

The experimental error (ε) is calculated from the standard deviations of the experiment replications and was found to be 1.2. As stated in the Fisher-Snedecor (R_x) table, the value of $F(0.05;7,8) = 3.50$. From the analysis of the variance table (Table 4), we can deduce that our model has F Ratio (R/r) able to satisfy the condition

$$F_{(R/r)} > (F_{(0.05;7,8)})^*5$$

Thus, the model is statistically significant and did not show a poor fit [17]. This is well confirmed by the obtained correlation coefficient R^2 (99%). Its high value demonstrates a good agreement between the measured experimental values "Y_{exp}" and the predicted responses of the fitted models " \hat{Y} ".

3.4. Study of Main Effects

The main effects of the seven variables are presented in table 5. Each coefficient is associated with t.exp. and a p-value. A graphical illustration of these results is provided in Fig.1 and Fig.2.

3.4.1. Statistically significant parameters (factors)

Except X_3 (drying temperature), all the other six factors have significant effects on the response (table 5 and fig.1). Sulfuric acid concentration is the most influential factor in leaching efficiency with a coefficient of (-11.884). The negative sign of this coefficient shows that the change in concentration from 2.2 M (level -1) to 4.4 M (level +1) leads to a remarkable reduction in the studied response.

This decrease can be explained by the fact that high concentrations of the sulfuric acid solution like 4.4M increase the availability of additional SO_4^{2-} in the solution (a common ion between the two reactants). This has a negative influence on the phosphogypsum solubility which is a determining factor for the leaching rate of REE. Thus the REE remain trapped in the undissolved PG particles [13,15]. This result is consistent with a set of studies carried out on the sulfuric leaching of rare earths from phosphogypsum and which have all opted for the use of low concentrations of sulfuric acid to guarantee a good yield of leached rare earths [13-17].

The leaching time is the second most important factor affecting the response with a positive sign coefficient (+6.426). This proves that the performance has known a strong increase from 20 min to 40 min. Thus our results are in agreement with a set of studies [11]-[18]-[19] which propose long leaching times (of an hour or more) compared to the research carried out by walawalkar which sets 20 min as quite enough leaching time for the leaching reaction of REE [13]. The ratio S/L comes in third place with a coefficient (-4.803). This indicates that the lower the ratio is the efficiency becomes greater (going from 1/3 to 1/6 in our case) (see fig1). Thus, the leaching efficiency increases with the decrease in the S/L ratio. Our result can be explained by the dependence of REE leaching on the solubility of gypsum, which quickly reaches its limit with the ratio 1/3 [11]. Yet economically weak ratios should be avoided as they increase the size and cost of downstream processes [20]. The coefficient (+3.788) of stirring speed indicates that the high stirring speed of 600 rpm has allowed a good mixing and dispersion of PG particles in the sulfuric acid solution. In general, this factor has not been taken into account in all previous studies. It was merely set or not even determined.

3.4.2. Statistically negligible parameters (factors)

The table 5 illustrates clearly that drying temperature has a P-value = 0.323 that is too higher than 0.05. The effect of this factor is the closest one to zero (fig.1). This shows how low the variation of This factor values had no effect on the response. This result directs us to the fact that the majority of the research carried out on the leaching REE from PG has been carried out in ambient temperatures [16].

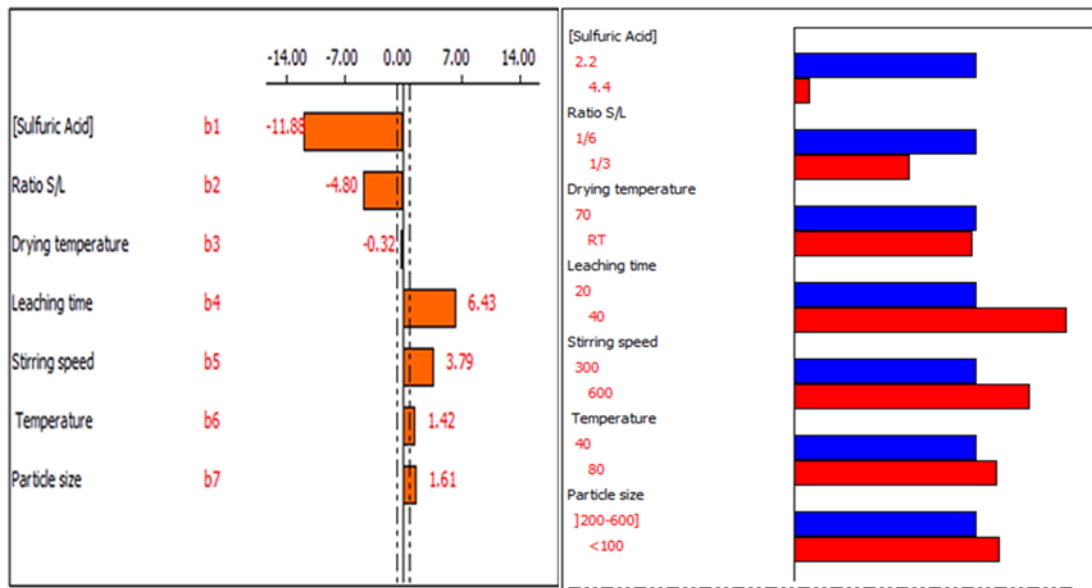


Figure 1: On the left is a graphical presentation of the effect of each factors on leaching performance, on the right is the variation of the response (Y) with the variation of each parameter.

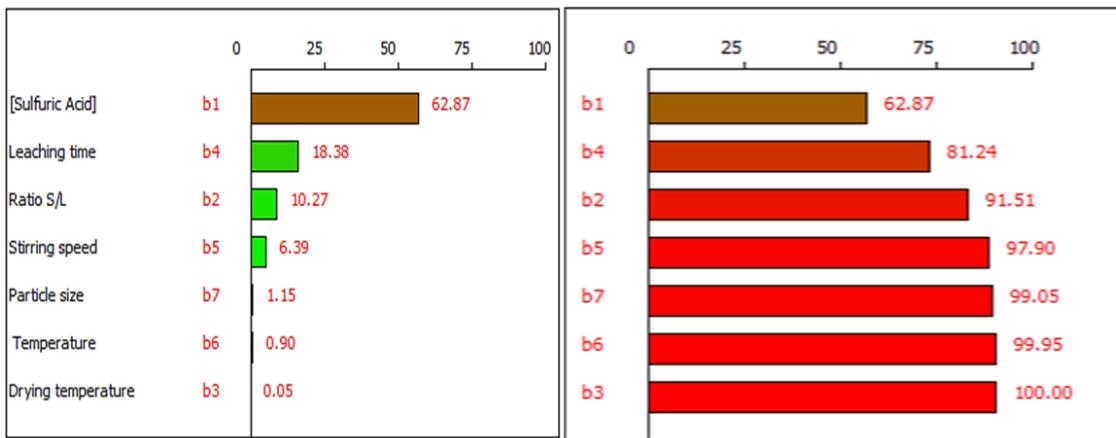


Figure 2: On the Left: Individual Pareto effects (the percentage contribution of each factor in the variation of the response studied), on the right: Cumulative Pareto effects.

3.5. Simplified fitted models

Based on the results, the X_3 effect (b3) has no significant influence on the leaching efficiency of rare earth elements from PG. Thus, the simplified model to be adopted is as follows:

$$\hat{Y} (\%) = 25.336 - 11.884 X_1 - 4.803 X_2 + 6.426 X_4 + 3.788 X_5 + 1.423 X_6 + 1.609 X_7$$

4. Conclusion

The Plackett-Burman design (PBD) method was used to screen the main seven influencing factors on leaching REE from PG and a regression equation (model) was developed to predict the studied response (REE leaching efficiency). According to their coefficients and contributions to the response, the six factors having a significant effects (p-value > 0.05) could be ranked as follows:

X_1 (62.87%) > X_4 (18.38%) > X_2 (10.27%) > X_5 (6.39%) > X_7 (1.15 %) > X_6 (0.90%)

The cumulative Pareto effect of sulfuric acid concentration (X_1), leaching time (X_4), ratio S/L (X_2) and, stirring speed (X_5) presents 97,91 % of REE leaching efficiency from PG. The value of response depends mainly on these four highly significant variables. Then, particle size and Temperature have a negligible contribution (less than 2%). That's why it is better to set them at their economic values, in other words, to use a raw PG only dried at room temperature without grinding and 40°C as a leaching temperature. Experimental results indicated that REE leaching efficiency reached a maximum of 52.1% at experimental conditions of a sulfuric acid concentration 2.2 M; a solid-to-liquid ratio of 1/6; a leaching time of 40 min; and a stirring speed of 600 rpm.

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