

Determination of optimal conditions for obtaining phosphate fertilizer from cuban phosphoric rock

Determinación de las condiciones óptimas para la obtención de un fertilizante fosfatado a partir de la roca fosfórica cubana

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Resumen

Con la finalidad de lograr la seguridad alimentaria en el país, es necesario intensificar de manera sostenible la producción de fertilizantes para obtener incrementos de productividad y generar ganancias económicas, potenciando el uso de materias primas nacionales para disminuir las importaciones. Es por ello que, en este trabajo se realizó el estudio de la determinación de las condiciones óptimas del proceso de obtención de Superfosfato Sencillo (SFS) a escala de laboratorio, a partir de la roca fosfórica y el ácido sulfúrico y con ello determinar los valores de las variables que intervienen en el mismo, y que aseguren la máxima calidad del producto. Para la realización de la investigación se utilizó el diseño factorial centrado rotacional 2^2 con puntos estrellas en 13 corridas experimentales y se elaboró una matriz de experimentos con las variables independientes, relación ácido/roca y porcentaje de ácido sulfúrico, en el intervalo de 1.61-2.06 y 65%-75% respectivamente. Como resultado se obtuvo que los parámetros óptimos en el intervalo estudiado para la roca cubana beneficiada fueron: concentración de H_2SO_4 de 72% y la relación ácido/roca de 2.02. Los índices de calidad del Superfosfato Sencillo curado obtenido con los parámetros óptimos son: contenido de fósforo asimilable de 12.28%, humedad 8.21% y acidez libre 2.05%; cumpliendo de forma general con especificaciones internacionales del producto.

Palabras claves: Fertilizantes fosfatados, optimización, roca fosfórica, superfosfato sencillo.

Abstract

In order to reach food security in the country, it is necessary to intensify the production of fertilizers in a sustainable manner in order to obtain increases in productivity, generate economic profits, and increase the use of national raw materials to reduce imports. For these reasons it is necessary to determine the optimum conditions for the process of obtaining Single Superphosphate (SFS), from the phosphate rock and sulfuric acid at lab scale, and thus determine the values of the variables which intervene in that process and assure the maximum quality of the product. To carry out the research, the rotational centered factorial design 2^2 with star points was used in 13 experimental runs and an experiment matrix was elaborated with the independent variables, acid / rock ratio and percentage of sulfuric acid, in the range of 1.61-2.06 and 65% -75% respectively. As a result it was obtained that the optimum parameters in the range studied for the benefited Cuban rock are: H_2SO_4 concentration of 72% and acid / rock ratio of 2.02. The quality indexes of the Superphosphate Simple cured obtained with the optimum parameters are: assimilable phosphorus content of 12.28%, humidity 8.21% and free acidity 2.05%; acting in accordance with international product specifications.

Keywords: Optimization, phosphatic fertilizers, phosphate rock, single superphosphate.

1. Introduction

According to current projections the current world population of 6,000 million people would reach about 8,100 million by 2025 and about 9,600 million by 2050. At that time, the population of the developing world will probably be 8,200 million (1, 2). Approximately 50 percent of potentially arable land is currently under annual and permanent crops. In addition, an area of 2,000 million hectares is degraded and land degradation is progressing through a series of processes related mainly to the mismanagement of land by man (2, 3).

In this global context, many developing countries will face major challenges in achieving food security in a sustainable manner due to a number of reasons such as the land area available per inhabitant, the serious shortage of freshwater resources, and particular socio-economic conditions of the agricultural sector as well as their internal structures and conflicts (4).

That is why the significant increase in the world population in recent years has been demanding a constant challenge to agriculture to provide more food, both in quantity and quality.

Therefore, feeding a growing world population will be possible mainly if yields are increased by applying fertilizers, with rational application have been shown to produce higher quality products. However, increasing world production has brought an increase in the consumption of raw materials, among which phosphate resources, such as phosphoric rock, play a fundamental role.

Some countries do not have phosphate rock in their natural resources. The increase in prices in the world market, as well as the increase in demand in the last few years, has forced fertilizer producers to process several types of rocks available. These increases are causing technological difficulties some of which are due the different variables of operation that influence the process.

In Cuba, the situation of this phosphatic carrier for fertilizer production became even more acute

in 1991, when imports originating almost entirely from the former Soviet Union ceased to be supplied. This forced an acceleration in the search for national sources that satisfy at least a part of the needs of the agriculture. Phosphate rock is a source that can be used for the formulation of fertilizers with some kind of benefit, and are found mainly in Holguin, Matanzas, Havana, Pinar del Rio and Sancti Spiritus. Thus by using existing reserves of this mineral throughout the country, a decrease in imports is achieved.

Single Superphosphate (SFS) is the oldest source of phosphorus for the manufacture of fertilizers. The first objective in producing it is the conversion of the phosphorus contained in the mineral to a more soluble form that is used by the plants, which contains between a 14% and 20% of P_2O_5 assimilable, this being largely dependent on the composition and characteristics of its fundamental raw material, which is phosphoric rock.

In Cuba a plant for the production of SFS by the carriage system DEN, discontinuous production method, was designed and built to work with phosphoric rock from the "La Pimienta" deposit in Pinar del Rio, as well as rock from other places, such as, Florida, Morocco and Algeria. The plant stopped producing due the problems of aging and deterioration.

The Trinidad de Guedes field, in Matanzas, offers the greatest prospects for the production of fertilizers, as it presents areas of clayey granular phosphorites with P_2O_5 contents that meet the minimum requirements for this industry (5-7).

This is why it is necessary to carry out the study of the determination of the optimal conditions of the process of obtaining SFS from the knowledge of the main characteristics of the Cuban phosphate raw material in order to determine the parameters or variables of operation that ensure the highest quality of the product. The need on the behalf of Chemical Industry to develop projects for the recovery of the Fertilizer Industry is the fundamental objective of the present work.

2. Methodology

The physical chemical characterization of the phosphoric rock was performed according to the following standards and / or methods shown in Table 1.

Table 1. Methods and norms for the physical-chemical characterization of Cuban phosphoric rock.

Determination	Method	Rule
P ₂ O ₅ Total	Volumetric	NRIB 350: 81*
P ₂ O ₅ insoluble	Volumetric	NRIB 350: 81
CaO	Volumetric	NRIB 350: 81
SiO ₂	Volumetric	NRIB 350: 81
MgO	Volumetric	NRIB 350: 81
R ₂ O ₃	Gravimetric	NRIB 350: 81
Fe ₂ O ₃	Colorimetric	NRIB 350: 81
CO ₂	Volumetric	NRIB 350: 81
F	Colorimetric	NRIB 350: 81
Cl	Volumetric	NC 1118: 2016**
Mn	Colorimetric	NRIB 350: 81
Na ₂ O	Potentiometric	NRIB 350: 81
K ₂ O	Potentiometric	NRIB 350: 81
SO ₄	Gravimetric	NRIB 350: 81
H ₂ O	Gravimetric	NC 1119: 2016***
Granulometry	Gravimetric	NC 631: 2008****

* Standard Branch of the Basic Industry. Phosphoric Rock. Chemical analysis.

** Cuban Standard. Fertilizers. Determination of Chlorides. Volumetric Method.

*** Cuban Standard. Fertilizers. Determination of Humidity. Gravimetric Method.

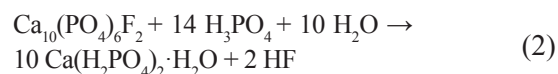
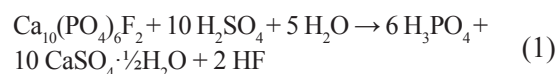
**** Cuban Standard. Minerals. Sieve analysis. General requirements.

Due to the simplicity of the process, the SFS can be produced in small and inexpensive plants. Its manufacture comprises the steps of mixing the phosphorite with the acid, then drying it to obtain a solid product in a reactor and finally a curing, which

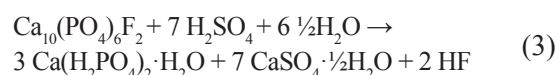
consists of stacking the product and allowing the acidification reaction to complete (8).

There are many variables that influence the process of obtaining SFS such as reaction time, sulfuric acid temperature and concentration, rock granulometry, setting time and temperature, curing time and acid/rock ratio (9, 10). It is known from studies with rocks previously evaluated that in the intervals studied, which are relatively large, only the concentration of sulfuric acid and acid / rock ratio exert a significant influence in the process; therefore the execution of the laboratory tests was focused only on these two variables. Since these variables are independent of the process and were taken at the minimum allowable values, the product was obtained with minimal cost (4, 9, 11).

The chemical equations that predominate in the production process appear according to equations (1)-(2):



The overall result of the process can be synthesized in equation (3):



In addition to this fundamental reaction, other series of secondary reactions occur due to the presence of impurities in the phosphate ore. It follows that the amount of acid required for 100% acidification is difficult to predict by the effects of consumption and acid production due to the other constituents. In practice, estimates of stoichiometric requirements are made based on certain theoretical assumptions, which must necessarily be confronted in experiences derived from the acidification of the study source. In the case of the acid/rock ratio, the stoichiometric ratio (1.61) and higher were

calculated on the basis of the impurities in the rock which consumed a certain amount of sulfuric acid (2.06) as explained previously.

The process-dependent variables were taken according to the quality indexes used in super-phosphate manufactures, such as the assimilable phosphorus content, free acidity and humidity.

Apart from these quantitative determinations, the need to measure qualitative parameters of the reaction products was established, which is

understood as the ease or difficulty of materials to form cakes or “cheeses”, and friability as the ease of shredding of the “cheese” formed. For the latter, specific techniques are not determined, only visual inspection being used for their determination.

Table 2 shows the distribution or experimental plan used, the different levels for the variables studied and the volumes of sulfuric acid for the test concentrations, calculated on the basis of 100 g of phosphate resource.

Table 2. Experimental distribution and levels of variables.

No. Exp.	Distribution % H ₂ SO ₄	Experiment acid/rock Ratio	Concentrate of H ₂ SO ₄ (%)	acid/rock Ratio	Volume of H ₂ SO ₄ required (mL)
1	-1	-1	65	1.61	43
2	+1	-1	75	1.61	35
3	-1	+1	65	2.06	55
4	+1	+1	75	2.06	45
5	+α	0	77	1.83	38
6	-α	0	63	1.83	47
7	0	+α	70	2.15	52
8	0	-α	70	1.51	36
9	0	0	70	1.83	44
10	0	0	70	1.83	44
11	0	0	70	1.83	44
12	0	0	70	1.83	44
13	0	0	70	1.83	44

For the processing of the results the data were adjusted to a rotational centered design 2² with stars in which the effects of 2 factors in 13 experimental runs were studied, based on the uniformity of the precision, by the use of Statgraphics Centurion XVI. A Variance Analysis (ANOVA) was performed to verify if the variables in study were statistically significant and then we proceeded to search for mathematical expressions or models,

which represent the relation of functionality between the dependent and independent variables, looking in all cases that this relationship is as appropriate as possible. For this, statistical methods based on multiple regression are used, applying their respective analysis of variance to the models obtained in order to evaluate their correlation coefficients and to certify with them the degree of correlation between the experimental

data and the data calculated by the Model, in order to finally optimize the results (12).

2.1 Obtaining SFS at laboratory scale

The finely ground phosphate rock (85% <0.15 mm) is weighed so that 100 g of sample can be obtained and emptied into a reaction vessel. Similarly sulfuric acid, previously prepared at the concentration (65% to 75%) and required temperature (30°C) and specified by experience, is measured volumetrically so as to obtain the amount calculated from the acid / rock reaction To use (1.61 to 2.06). It is then poured onto the phosphate sample by applying a manual stirring for one minute to homogenize the sample; This process was carried out inside a hood due to the evolution of gases during the reaction.

Once the mixing time is reached, the maximum reaction temperature is measured and then the reaction vessel is placed inside a stove, inside which the sample continues its reactions that started in the previous step. There it remains for 30 minutes, and is then extracted and cooled to room temperature. So far the process allows us to have a product called crude superphosphate, and it is necessary to follow its reaction process. At this stage, the physical characteristics of the product

obtained are analyzed visually, with a view to having a global idea of the differences to which they give rise, depending on the variables used. Likewise, the percentages of loss produced in the reaction processes are determined by removing gases and water vapor by weighing the sample obtained before and after setting.

The product obtained is emptied into suitable containers, leaving it under normal laboratory conditions for a period of twenty-one days to complete its reactions, at which time a totally stationary state is not reached but is very close to it.

Sampling in order to characterize them chemically is verified in two stages, one after the setting, which is taken as day zero and another after the cure time, at 21 days, proceeding in each case to the analytical determination of the quality parameters of interest in duplicate, with the aim of obtaining a reliable result. (9, 13)

2.2 Process constants

The operational parameters were taken constant for the experiment. In this way, the fixed parameters of these variables are established the normal operational data that is reported in the bibliography is consulted, and the specific technology that is analyzed is adjusted (table 3).

Table 3. Constant operational parameters.

Operational parameter	Set level	Observations
Granulometry of the rock	85% < 0.15 mm	Determined by the "Wet Mesh Analysis"
Sulfuric acid temperature	30°C	Room temperature
Setting temperature	105°C	In stove
Mixing time	60 s	Manual operation
Setting time	30 min	In stove
Curing time	21 days	Outdoor piles
R ₂ O ₃ /P ₂ O ₅ ratio in the rock	31.8%	Permissible until 35% (5)

3. Results and Discussion

The results obtained by analyzing the sample in duplicate are shown below in table 4.

Table 4. Average results of the physical chemical characterization of the Cuban phosphate rock benefited.

Determination	Average values
P ₂ O ₅ Total	26.78
P ₂ O ₅ Insoluble	23.30
CaO	38.92
MgO	0.49
SiO ₂	7.58
R ₂ O ₃	8.92
Fe ₂ O ₃	3.09
CO ₂	1.94
F	1.57
Cl	0.16
Mn	0.06
Na ₂ O	0.96
K ₂ O	1.36
SO ₄	0.11
H ₂ O	5.26
Granulometry	
> 0.5 mm	5.0
0.5 – 0.3 mm	16.5
0.3 – 0.15 mm	39.0
< 0.15 mm	39.5

As can be seen, phosphoric rock has a lower total P₂O₅ content than rocks traditionally used in the fertilizer industry, presenting a percentage of it in an insoluble form (7). The presence of a considerable amount of clays is highlighted in the sample, which is demonstrated by the iron, aluminum, magnesium, silica, sodium and potassium contents, which corroborates the results of mineralogical analysis. Also the presence of fluorine and carbonate reaffirm that the fundamental component of the granular

granular rock is the apatite fluorocarbon.

As for the granulometric composition, it is possible to be detected by means of its analysis as the benefit process that is carried out with the fundamental objective of decreasing the clay content has been quite effective, since originally the sample from the deposit has about 70% under 0.15 mm mesh. To perform a cut in the wash at a larger particle size implies a decrease of the clay content, but higher losses of P₂O₅, so that the value of 0.15 mm was established to obtain a compromise between both variables (14).

The CaO/P₂O₅ ratio was 1.45 which is adequate for the acidification of the phosphoric rock to be an economically profitable industrial scale process, since when this ratio is greater than 1.6 a large excess of sulfuric acid is required to guarantee a good conversion of calcium phosphate to SFS (15).

Table 5. Qualitative appraisals.

Experiment	Consistency of the mixture	Property analyzed		
		Degree of porosity	Friability	Gas evolution
1	Compact	Micropore	high	Little
2	Little. Liquid phase	Micropore	Half	Little
3	Fluid liquid	Micropore	Half	Good
4	Compact	Micropore	high	Good
5	Compact	Micropore	Half	Good
6	Fluid liquid	Micropore	Half	Little
7	Compact	Micropore	high	Good
8	Little. Liquid phase	Micropore	Half	Little
9	Compact	Micropore	high	Good
10	Compact	Micropore	high	Good
11	Compact	Micropore	high	Good
12	Compact	Micropore	high	Good
13	Compact	Micropore	high	Good

Table 6. Experimental results.

Exp.	Independent variables			0 day		21 days			
	H ₂ SO ₄ (%)	acid/rock Ratio	T (°C)	P ₂ O ₅ Assim.	Acidity Free	Humidity	P ₂ O ₅ Assim.	Acidity Free	Humidity
1	65	1.61	70	10.98	6.58	15.14	11.52	3.45	9.88
2	75	1.61	73	9.81	3.21	15.11	11.90	2.95	9.26
3	65	2.06	74	11.79	6.18	14.50	12.06	2.90	8.97
4	75	2.06	75	11.73	4.43	15.08	12.39	2.02	8.09
5	77	1.83	99	10.21	7.46	13.80	12.21	2.84	9.11
6	63	1.83	70	9.73	6.37	14.26	11.75	3.28	9.76
7	70	2.15	76	11.11	7.28	15.71	12.16	2.21	8.64
8	70	1.51	78	8.97	4.72	11.26	11.59	3.31	9.23
9	70	1.83	79	9.56	5.06	13.41	11.95	2.53	8.31
10	70	1.83	79	9.59	5.19	13.53	12.03	2.26	8.28
11	70	1.83	78	10.80	6.18	14.50	12.12	2.14	8.52
12	70	1.83	79	9.85	5.39	13.70	12.27	2.12	8.32
13	70	1.83	78	9.85	5.70	13.81	12.25	2.10	8.43

On the other hand, the results obtained are shown in tables 5 and 6, which describe the analytical results obtained during all the experiments, including measurements of the maximum reaction temperature and percentage losses, which originate during the reaction and the Setting of the fertilizer. In table 5, it was possible to conclude that the qualitative characteristics evaluated show that from the phosphoric rock beneficiation used in this work, it is possible to obtain SFS. It should be noted that those experimental points where an excess of liquid phase is observed can not be processed by the simulated DEN carriage technology, since this prevents the formation of the “cheese” described above.

Table 6 shows the influence of the studied parameters, such as concentration and acid/rock ratio, on the experimental results, varying the reaction temperature between 70°C and 99°C and the analytical determinations carried out to characterize the crude product and cured.

In this case, it was also possible to observe that in some experimental runs the free acidity at 21

days maintained high values in some cases greater than 2.4%, so that the possibility of increasing the curing period for a few more days could be taken into account. In order to determine whether the relevant reactions in superphosphate continue to occur in order to increase the assimilable phosphorus and therefore the conversion rate, by continuing to interact the free acidity present with the insoluble phosphorus of the product. Likewise, moisture in all experiments was greater than 8%, a standard value according to international quality specifications. For this reason, it is also considered to carry out a more in-depth study of the kinetics of the reaction, since it plays a decisive role in the quality of the final product obtained, as well as in the overall technical-economic efficiency of the system, despite being considered the Cuban phosphoric rock as a reactive material.

It should be noted that the assimilable phosphorus obtained at all experimental points yield results lower than those reported internationally. This is due to the fact that it is part of a mineral considered of low

law, since the phosphoric materials recommended for this production present at least 32% of P_2O_5 . During the curing period an increase of this parameter is observed, which causes an increase of the conversion close to 80%, similar to that reported by other international rocks (16), (17).

However, there are references from other countries that also follow the current tendency to take ad-

vantage of national resources and from them produce and market lower-grade fertilizers (18), (19).

When performing the ANOVA, the following results are obtained, as shown in figures 1, 2 and 3 and in tables 7, 8 and 9.

P₂O₅ assimilable (21 days)

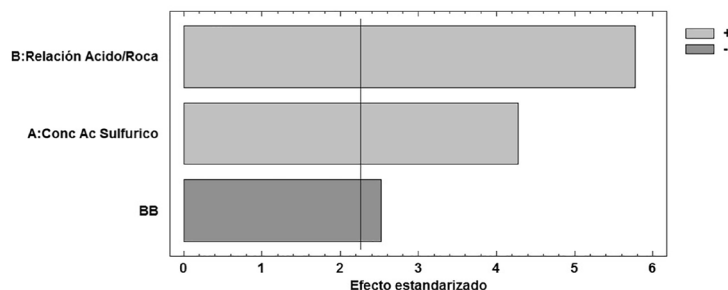


Figure 1. Standardized Pareto Diagram for % P_2O_5 Assimilable.

Table 7. Analysis of Variance for % P_2O_5 Assimilable.

Source	Sum of squares	Gl	Middle Square	Reason-F	P-value
A: Concentration Sulfuric Acid	0.231383	1	0.231383	18.33	0.0020
B: Acid / Rock Ratio	0.421408	1	0.421408	33.39	0.0003
BB	0.0801371	1	0.0801371	6.35	0.0328
Total error	0.113595	9	0.0126216		
Total (corr.)	0.846523	12			

R-square = 86.581 percent
 R-squared (adjusted by g.l.) = 82.1081 percent
 Standard error of est. = 0.112346
 Mean Absolute Error = 0.0747679
 Durbin-Watson Statistic = 0.764387 (P = 0.0025)

Free acidity (21 days)

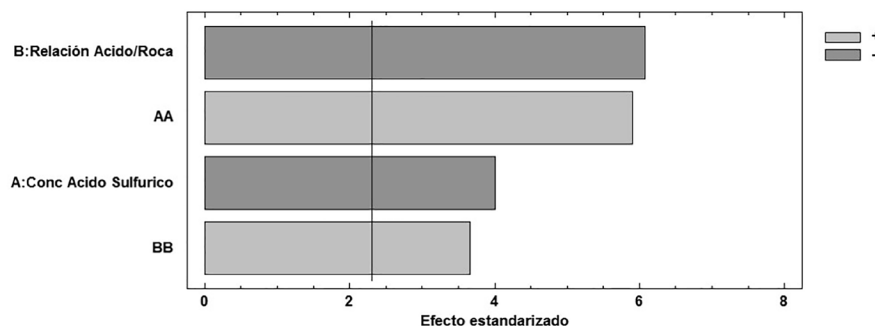


Figure 2. Standardized Pareto Diagram for Free Acidity.

Table 8. Analysis of Variance for Free Acidity.

Source	Sum of squares	Gl	Middle Square	Reason-F	P-value
A: Concentration Sulfuric Acid	0.731589	1	0.731589	17.75	0.0029
B: Acid / Rock Ratio	1.0617	1	1.0617	25.76	0.0010
AA	1.72352	1	1.72352	41.82	0.0002
BB	0.426997	1	0.426997	10.36	0.0123
Total error	0.329734	8	0.0412168		
Total (corr.)	4.08309	12			

R-square = 92.333 percent
 R-squared (adjusted by g.l.) = 88.4995 percent
 Standard error of est. = 0.176559
 Mean Absolute Error = 0.114326
 Durbin-Watson Statistic = 1.32562 (P = 0.0570)

Humidity (21 days)

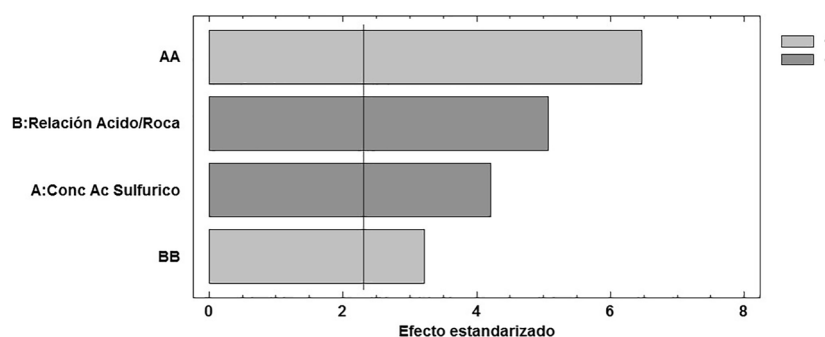


Figure 3. Standardized Pareto Diagram for Humidity.

Table 9. Analysis of Variance for Humidity.

Source	Sum of squares	Gl	Middle Square	Reason-F	P-value
A: Concentration Sulfuric Acid	0.501127	1	0.501127	16.08	0.0039
B: Acid / Rock Ratio	1.15189	1	1.15189	36.95	0.0003
AA	1.0854	1	1.0854	34.82	0.0004
BB	0.417569	1	0.417569	13.40	0.0064
Total error	0.249386	8	0.0311733		
Total (corr.)	3.25271	12			

R-square = 91.9244 percent
 R-squared (adjusted by g.l.) = 87.8866 percent
 Standard error of est. = 0.203019
 Mean absolute error = 0.129272
 Durbin-Watson Statistic = 2.34862 (P = 0.6578)

As can be observed, in all cases it is observed that the variables acid/rock ratio and sulfuric acid concentration, have a statistically significant effect on the studied variables % P₂O₅, Free Acidity and Humidity, since the P-value is less than 0.05 with a confidence level of 95.0%. As it is known, an increase of the latter two variables is negative in the quality of the product, since they constitute restrictions to be fulfilled in its quality specifications.

Tables 7, 8 and 9 show that the R-square statistic reflects that the obtained model describes a suitable behavior of the % P₂O₅, Free Acidity and Humidity of the process, respectively. The Durbin-Watson (DW) statistic examines the residuals to determine if there is any significant correlation based on the order in which the experimental data are presented. This is shown in figures 4, 5 and 6 as shown below.

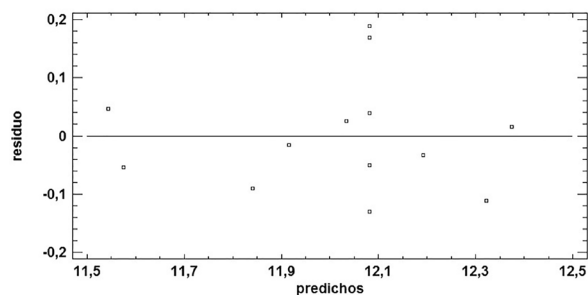


Figure 4. Graph of waste for the % P₂O₅ Assimilable.

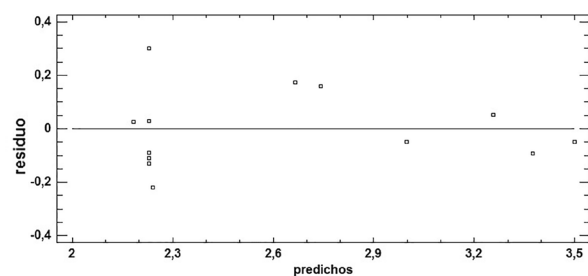


Figure 5. Graph of waste for % Free Acidity.

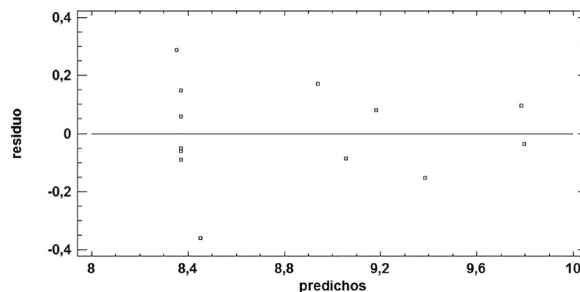


Figure 6. Graph of waste for % Humidity.

The models obtained are the following:

P₂O₅ assimilable (21 days)

$$\% P_2O_5 \text{ assimilable} = 0.750347 + 0.0340134 \cdot A + 8.73426 \cdot B - 2.10196 \cdot B^2 \quad (4)$$

Free Acidity (21 days)

$$\text{Free Acidity} = 102.544 - 2.2605 \cdot A - 19.4474 \cdot B + 0.0157999 \cdot A^2 + 4.83949 \cdot B^2 \quad (5)$$

Humidity (21 days)

$$\text{Humidity} = 129.614 - 2.84787 \cdot A - 19.5794 \cdot B + 0.0199099 \cdot A^2 + 4.89381 \cdot B^2 \quad (6)$$

When the optimization process is carried out, the maximum assimilable phosphorus of 12.28% is reached when the sulfuric acid concentration is 72% and the acid/rock ratio is 2.02. This result is considered acceptable, since the Cuban phosphate rock is low phosphorus content, but high reactivity. With this result, a minimum humidity of 8.21% and a minimum free acidity of 2.05% are obtained, the latter complying with international product specifications of less than 2.4%, but not for moisture, which exceeds 8%. In order to achieve greater concentration in the SFS, it is recommended to study the possibility of mixing with other imported rocks of higher concentration.

Figure 7 shows the combination of factor levels that maximizes the desirability function in the indicated region, in addition to the combination of factors at which the optimum is reached, where the value at which the above results are obtained is 0.87.

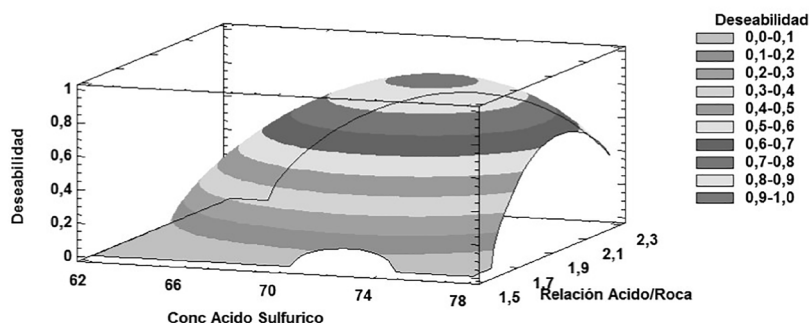


Figure 7. Surface Estimated Response.

4. Conclusions

The optimum parameters were reached in the interval studied for the beneficiated cuban rock, determining that it is possible to obtain SFS from the Trinidad de Guedes deposit, despite not being as high % P_2O_5 as in the case of other international rocks that are processed for this purpose.

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