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Organophosphated Fertilizers Production in Humifert Process

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Humiphert process is an alternative process used for producing phosphated compound fertilizers with a slower solubilization when compared to other traditional fertilizers, resulting in a longer period of plant nutrition. During the process, phosphatic rocks are used along with some sort of limitation according to the normal development, both by their lower content percentage and by treatment of difficulties of industrial minerals, besides organic materials. In this paper, it was found operational conditions of the three-reactor compound system which produce the referred fertilizers under controlled system conditions. The nitric acid produced in the process promotes the attack and the partial dissolution of the apatite grains in the rock, liberating phosphorus (P) for various associations with the organic phase, generating the organophosphated fertilizer. In this experiment, the utilized compound had from 9.40% to 11.13% of P_2O_5 and, right after the attack under the controlled conditions, the product presented the following results of phosphorus (P) solubility expressed in P_2O_5 in the extractors used for evaluating the agronomic quality: from 0.10% to 1.41% of phosphorus (P) soluble in water (which represents P more promptly available to the plants), from 17.9% to 37.6% of phosphorus (P) soluble in citric acid at 2% (which evaluates phosphorus little soluble in water and it is able to become available when it is attacked by organic acids, thus representing a situation close to the real soil situation), and from 7.1% to 12.8% of phosphorus (P) soluble in neutral ammonium citrate (which represents phosphorus available in short and long term periods of time, contained in types not soluble in water).

Introduction

Based on Sternicha (1998), in the Humifert process, the phosphated compound fertilizers are preferentially produced by the reaction between a phosphatic rock mixture, organic material, humidity and nitric acid, whereas the later is synthesized by the contact between dinitrogen oxide (NO_2) and the humidity in the mixture of phosphatic rock and organic material in the reactor 3. On the other hand, dinitrogen oxide (NO_2) is obtained by the oxidation of ammonia with air in the reactors 1 and 2.

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Prior to this work Silverol (2010) studied the characterization of the organophosphated products in Institute of Geosciences, University of São Paulo. In this work, the effects of the estimated effects of the process variables (independent), temperature of Reactor 1, utilization of auxiliary air in Reactor 2, the porosity of the diffusing board in Reactor 3, the percentage of humidity of the mixture of phosphate rock with the organic material, and the agitation of the mixture in Reactor 3. The answers investigated were on the percentage of NO_2 expressed in terms of NO_2, and the solubilties of phosphorus in the extractors: water (P_{water}); neutral ammonium citrate (CNA) with water ($P_{CNA+water}$) and citric acid (solution at 2%) ($P_{citric\ acid}$). Theses answers about solubility of phosphorus are used to qualify the generated compound which is going to be used as a fertilizer. According to Oba (2004), the reaction between nitric acid and phosphate is variable, and the attack can be total (reaction 1); intermediate attack (reaction 2), which has as a feature the solubility in water; the partial attack (reaction 3), which has as a feature the solubility in citric acid at 2%. It may happen the phosphoric acid reactions with non-reacted apatita (reaction 4) during the maturation phase, or with the bicalcium phosphate (reaction 5).

$$Ca_{10}(PO_4)_6F_2 + 18\ HNO_3 \rightarrow 6\ H_3PO_4 + 9\ Ca(NO_3)_2 + CaF_2 \quad (1)$$
$$Ca_{10}(PO_4)_6F_2 + 12\ HNO_3 \rightarrow 3\ Ca(H_2PO_4)_2 + 6\ Ca(NO_3)_2 + CaF_2 \quad (2)$$
$$Ca_{10}(PO_4)_6F_2 + 6\ HNO_3 \rightarrow 6\ CaHPO_4 + 3\ Ca(NO_3)_2 + CaF_2 \quad (3)$$
$$Ca_{10}(PO_4)_6F_2 + 4\ H_3PO_4 \rightarrow 10\ CaHPO_4 + 2\ H_2O \quad (4)$$
$$CaHPO_4 + H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \quad (5)$$

In Ray and Johnston (1989) the essential reactions of the several phases of the process of HNO_3 production is found.

Materials and Methods

In order to produce the phosphate compound fertilizers, three reactors were required. In Reactor 1, the oxidation of ammonia creates NO (nitric oxide), which in the reactions of Reactors 1 and 2 are diffused through the mixture of phosphate rock, organic material and humidity. Temperatures were monitored inside Reactor 2, its exit gases, the ammonia flow and the auxiliary air. 200g of phosphate rock were used from the carbonatite complex, and 300g of organic material from the sewage treatment station. Both were previously sifted apart, in a sieve of 2mm, and the organic material was kept in a stove during 24 hours under 40º C. From this moment, the study was made by dividing the phosphate rock into a portion of thin ones that passed through the 2mm sieve (Thin) and the retained portion at the same sieve (Thick).

The collection of sample gases was made by a Gailard bulb, according to Paiva (1993). The solid sample (about 120g) was taken from the mixture of Reactor 3 by quartering, dried at 40ºC during 24 hours, and it was sent to analysis along with the extractors. The analysis methods employed to quantify phosphorus solubility were those previously developed by Laboratory of the Agriculture Superior School "Luiz de Queiroz" of the Department of Soil Science of the University of São Paulo.

Experimental Delimitation

The research on the influences of the process variables was made by employing factorial planning of the experiments, and its interpretation was made by using the surface answer methodology, according to Box et all (2005).

Two plans were developed. The first experimental planning, constituted by 14 essays, was a fractional factorial one, 2^{5-2}, with 6 central points, developed with the thins of phosphate rock, and the second one, constituted by 11 essays, was a fractional factorial planning, 2^{4-1}, with 3 central points, developed with the thicks of the phosphate rock, according to Table 2. The procedure of analysis and development of each planned essay was exactly the same both for the thins and the thicks of the phosphate rock. Due to the strong negative effect in the percentage of NO_x, resulting from the analysis of thins auxiliary air weren´t used in phosphate rock thicks. The codifications of the variables are presented in Table 1.

Table 1 – Codification of variables, Agitation (A), Temperature (B), Humidity in the Compound (C), Diffuser Plate (D) and Auxiliary Air (E).

Codified Variables: A, B, C, D e E	Agitation	Temp (ºC)	Humidity in the Compound (%)	Diffuser Plate	Auxiliary Air (L/h)
-1	Without	600	20	Low	0
0	Pulsating	640	30	Mean	75
1	Continuos	680	40	High	150

Table 2 – Results of 7 essays out of 14 for the thins and thicks of the phosphate rock, as well as the 11 essays planned and run for the thicks fo the phosphate rock.

Phosphate Rock Part	Pattern order	A	B	C	D	Average NO_2	P_{citric}	P_{water}	$P_{CNA + water}$	P_{total}
Thins	1	-1	-1	-1	1	5,72	2,87	0,10	0,11	9,40
Thins	2	1	-1	-1	-1	7,59	2,72	0,01	1,04	10,07
Thins	3	-1	1	-1	1	13,40	2,97	0,06	0,84	10,39
Thins	6	1	-1	1	1	10,93	2,53	0,10	1,07	10,01
Thins	7	-1	1	1	-1	5,33	3,02	0,04	1,25	9,76
Thins	10	0	0	0	0	9,21	2,78	0,07	1,15	9,73
Thins	13	0	0	0	0	9,19	3,65	0,07	1,04	9,72
Thicks	1	-1	-1	-1	-1	10,59	3,42	0,19	1,30	13,47
Thicks	2	1	-1	-1	1	10,93	2,44	0,08	1,24	12,42
Thicks	3	-1	1	-1	1	15,29	3,14	0,05	1,03	13,71
Thicks	4	1	1	-1	-1	14,04	2,35	0,07	0,99	12,67
Thicks	5	-1	-1	1	1	11,22	2,32	0,09	1,23	12,55
Thicks	6	1	-1	1	-1	11,08	2,44	0,05	1,27	12,48
Thicks	7	-1	1	1	-1	14,00	2,25	0,05	1,01	12,54
Thicks	8	1	1	1	1	13,39	2,93	0,05	0,97	13,63
Thicks	9	0	0	0	0	13,18	3,02	0,06	1,12	12,25
Thicks	10	0	0	0	0	11,82	3,70	0,10	1,25	12,26
Thicks	11	0	0	0	0	13,54	2,85	0,06	1,12	14,13

A, B, C and D are codified variables between -1 and +1.

Table 3 – Effects and coefficients of the regression to the model of percentage of NO_X, expressed as the percentage of NO_2 due to temperature and auxiliary air.

	Effect	ESE	t(3)	Value of p	Coeff.	CSE
Average	9,12	0,30	30,43	0,00008	9,12	0,30
(B) Temperature	0,58	0,72	0,81	0,47515	0,29	0,36
(E) Auxiliary Air	-6,18	0,72	-8,63	0,00327	-3,09	0,36
Inter. (B) and (E)	-1,89	0,72	-2,64	0,07798	-0,94	0,36

Subtitle: ESE = Effect Standard Error. CSE = Coefficient Standard Error

Table 4 - ANOVA of the regression to the model of percentage of NOx, expressed as a percentage of NO_2 due to temperature and auxiliary air.

Factor	SS	DF	SDA	Value of F	Value of p
(B)Temperature	0,39	1	0,39	0,66	0,47515
(E) Auxiliar Air	43,96	1	43,96	74,55	0,00327
Interaction between (B) and (E)	4,09	1	4,09	6,94	0,07798
Error	1,77	3	0,59		
Total Sum of Squares	49,00	6			

Subtitle: SS = Sum of Squares. DF= Degrees of Freedom. SDA = Squared Deviations Average. R^2 = 0,9639 R^2 adjusted = 0,92779.

Results and Discussion

The results taken from phosphorus solubility in the various extractors for the thins and thicks of the rock are presented on Table 2.

Since the obtaining of NO_x, (expressed in terms of NO_2) happens before Reactor 3, where the formation of organophosphate compounds occur, only the independent variables of auxiliary air and temperature can influence to the obtaining of those oxides. Seven essays made with the original planning permitted the generation of a factorial project 2^2. Data was statistically treated through the software called Statistic Version 8. Table 3 presents an estimate of the effects, coefficients and their standard error, as well as the value of p to these parameters. Table 4 presents the ANOVA of the regression. The analysis permits to affirm that the temperature and the flow of auxiliary air can be only interpreted simultaneously due to the interaction between them to a meaning level α =0,10. The best situation to produce NO_X is the auxiliary air in the minimum level (-1 = without air auxiliary) and the temperature in the maximum value (+1 = 680ºC). The analysis of Table 2 for the solubility of phosphorus in the extractor did not present results which could indicate meanings of any independent variable to the experiment with the thicks. Putting together all the essays (thins + thicks), and by using the strategy of tendencies from the graphic resources between the variables P_{citric} due to NO_2, it was possible to make an analysis of P_{citric} with all the coupled points of two plans, and then seven of them were excluded (thins: 1,7 and 13; thicks: 1, 4, 7 and 10),considering the other eleven as coherent. Tables 5 presents the ANOVA of the regression, to the solubility in P_{citric}, $P_{CNA+water}$, P_{water} expressed as % of P_2O_5, for coupled data. The statistics analyses indicated for the variables along with their respective interactions, through the Equations (1) and (4).

$$P_{Citric} = 2{,}8833 + 0{,}3062B - 0{,}0475C - 0{,}1971D \quad (1)$$

$$P_{CNA+H_2O} = 1{,}13 - 0{,}14B - 0{,}10\,CD \quad (2)$$

$$P_{H_2O} = 0{,}0633 - 0{,}0283A - 0{,}0162B + 0{,}0150C - 0{,}0087AB + 0{,}0246AD - 0{,}0050CD \quad (3)$$

By looking at Equations (1), (2) and (3), it is possible to notice that the agitation can only be interpreted along with the temperature and the diffuser plate, in case of formation of organophosphate soluble in water.

If there is the necessity of increasing the amount of organophosphate soluble in water, it will be necessary to operate with low agitation (-1), low temperature

(-1) and low porosity. In this situation, there is a relation for P_{water}, according Equation (4):

$$P_{H_2O} = 0{,}1399 + 0{,}0050C \qquad (4)$$

For P_{citric} and $P_{CNA+water}$, agitation has not been meaningful. For the variable temperature, it has been seen that lower temperatures favor formation of P_{water} and $P_{CNA+water}$, and disadvantage formation of P_{citric}. Therefore, the obtantion of P_{citric} is favored by higher temperatures. For the variable humidity, it has been noticed that P_{citric}, is favored by the low humidity and for $P_{CNA+water}$, the influence of humidity must be interpreted as a group with the porosity of the diffuser plate, due to the interaction between these two variables.

Table 5 - ANOVA of the regression, to the models of P_{citric}, $P_{CNA+water}$, P_{water}, expressed as % of P_2O_5 due to the agitation of reactor 3, the temperature of reactor 1, the humidity of the compound and the diffuser plate, as well as the interactions for coupled data.

Solubility	P_{ciric}				
	DF	SS	SDA	Value of F	Value of p
Main Effects	4	0,655	0,164	10,95	0,039
2-Way Interactions	3	0,058	0,019	1,30	0,417
Residual Error	3	0,045	0,015		
Pure Error	3	0,045	0,015		
Total	10				

Solubility	$P_{CNA+water}$				
	DF	SS	SDA	Value of F	Value of p
Main Effects	4	0,138	0,034	5,56	0,095
2-Way Interactions	3	0,049	0,016	2,64	0,223
Residual Error	3	0,019	0,006		
Pure Error	3	0,019	0,006		
Total	10				

Solubility	P_{water}				
	DF	SS	SDA	Value of F	Value of p
Main Effects	4	0,004	0,001	27,56	0,011
2-Way Interactions	3	0,001	0,000	10,52	0,042
Residual Error	3	0,000	0,000		
Pure Error	3	0,000	0,000		
Total	10				

Subtitle: DF = Degrees of Freedom. SS = Sum of Squares. SDA= Square Deviation Average. R^2_{citric} = 93,95% $R^2adjusted_{citric}$ = 79,82%. $R^2_{CNA+water}$ = 88,53%. $R^2adjusted_{CNA+ water}$ = 61,76%. R^2_{water} = 97,98% $R^2adjusted_{water}$ = 93,25%

Conclusions

Depending on the finality, the levels of the researched variables, can be manipulated to obtain the distribution of organophosphated required: P_{water} (P more promptly available to the plants), P_{citric} (P little soluble in water and it is able to become available when it is attacked by organic acids, representing a situation close to the real soil situation), and $P_{CNA+\ water}$ (P available in short and long term periods of time, contained in types not soluble in water).

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