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Study of the Decomposition of Mussoorie Rockphosphate with Nitric Acid as related to the Time and Method of Acidulation*

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Ground (minus 100 mesh) Mussoorie rockphosphate (RP) was acidulated with graded levels of HNO_3 by using concentrated acid (Method 'A') or diluted acid (Method 'B'). The magnitude of all the P forms except total phosphate, was observed to be higher at almost all the comparable levels of acidulation, with the former than with the latter procedure. The superiority of Method 'A' over Method 'B' in solubilizing RP was ascribed to a relatively more intense chemical reaction of concentrated acid than that possible with diluted acid. The effect of time of curing (0 to 144 hrs) on the contents of total and citrate soluble phosphates was non-significant, while it was significant and positive on water soluble and available phosphate content. In general, maximum decomposition of RP was observed at 24 hours duration of curing.

Key Words: Rock phosphate decomposition, Nitric acid, Time and method of acidulation

Introduction

Partial acidulation of rock phosphate is one of the most promising means of increasing its agronomic effectiveness for direct applications (Ashby et al. 1966, Panda & Mishra 1970, Shinde et al. 1978, Anonymous 1982). In this process various acids have been tried with varying degrees of success. Nonetheless, interest in processes involving acidulation of R P with HNO_3 has been greatly stimulated by a rising sulphur shortage and an expanding capacity for HNO_3 production in the world including India. The fact that the agronomic effectiveness of HNO_3 acidulated products is comparable to the best acidulant i.e., H_3PO_4 (Marwaha et al. 1983), further favour the use of HNO_3 as an acidulant of RP. The rate of chemical reaction of an acid with RP powder depends upon various factors

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such as the intrinsic property of phosphate rock, acidity of the liquid phase, acid to rock ratio, acidulation time etc. However, there does not seem to be an agreement among the scientists about the suitable method of acidulation as well as about the time of acidulation (Terman et al. 1964, Panda & Mishra 1970, Shinde et al. 1978). To utilise Mussoorie R P for partial acidulation, it was found necessary to study its solubilization with graded levels of HNO_3 as related to the method of acidulation and the time of curing of acidulated products.

Materials and Methods

Acidulated samples of ground (minus 100 mesh) Mussoorie rock phosphate (possessing 17.8% total P_2O_5, 4.8% of total P_2O_5 in available form, CO_2 4.2%, organic matter 7.8% and CaO/P_2O_5 ratio 2.2) (RP) were prepared by using two acidulation procedures. In one instance, concentrated HNO_3 was added slowly to RP with continuous mixing of the ingredients (Method 'A'). Five degrees of acidulation (0, 12.5, 25, 50 and 75%) were obtained by adding 0, 17.9, 35.8, 71.6 and 107.3 ml of the concentrated (70%) HNO_3, per 100 g of RP. In another procedure (Method 'B'), however, all the 5 degrees of acidulation of RP were achieved by adding the indicated amounts of concentrated HNO_3 which was diluted with sufficient water (so that total volume of diluted acid in each case was 100 ml as determined by a preliminary test), to wet all the RP dust to a consistency of thin paste. The diluted acid was added rapidly with constant stirring to ensure contact with all the RP particles.

All the samples were cured for 0, 2, 4, 6, 8, 12, 24, 48, 96 and 144 hours alongwith a blank treatment, that is, RP + water. Then they were dried in a hot air oven at 78°C. The dried samples were ground to pass through 100 mesh sieve and stored in air tight stoppered bottles.

Finally, all the prepared samples were analysed for total, water soluble, citrate soluble and available phosphate according to AOAC procedures (AOAC 1982).

Results and Discussion

Effect of Levels and Methods of Acidulation

The content of water soluble, citrate soluble and available phosphate was observed to increase invariably with successive increase in the degree of acidulation (table 1). This finding is in close proximity to those of Ashby et al. (1966), Panda and Misra (1970) and Shinde et al. (1978). Nevertheless, it is of interest to note that the amount of citrate soluble phosphate was relatively much higher than that of water soluble phosphate at all the comparable levels of acidulation, irrespective of the method of acidulation tried. This evidently suggests that HNO_3 was relatively more effective in dissolving rock phosphate leading to the formation of dicalcium phosphate and further break down of the apatite into monocalcium phosphate was slow. In other words, HNO_3 was a relatively mild acidulant leading to a slower breakdown of the apatite bond of phosphate rock depending upon of course on the degree of acidulation. This observation is in line with the conclusion drawn by Marwaha et al. (1982) while evaluating the efficiency of HNO_3 relative to H_3PO_4 as an acidulant of several Indian rock phosphates, and of Panda and Misra (1970) pertaining to Florida RP.

Table 1 *Effect of levels and methods of acidulation on the total, water soluble and citrate soluble phosphate contents of Mussoorie RP*

Levels of acidulation (%)	Total P_2O_5 (%)	Water soluble P_2O_5 (%)*			Citrate soluble P_2O_5 (%)*		
		Method A	Method B	Mean	Method A	Method B	Mean
0	22.90	1.15	1.28	1.22	4.38	4.42	4.40
12.5	17.44	2.95	1.96	2.46	11.84	9.63	10.33
25.0	15.37	9.40	6.46	7.93	18.61	15.88	17.24
50.0	12.16	26.50	17.92	22.21	33.19	25.34	29.36
75.0	11.67	34.43	32.43	33.43	55.59	45.30	48.46
Mean	15.91		12.01			28.11	
S Em±	0.12						
LSD 5%	0.33						

	S Em±		LSD 5%	
	Water soluble phosphate	Citrate soluble phosphate	Water soluble phosphate	Citrate soluble phosphate
Methods of acidulation	0.29	0.56	0.82	1.59
Levels of acidulation	0.46	0.89	1.30	2.52
Methods × levels of acidulation interaction	0.65	1.26	1.84	3.56

*Expressed as percentage of the total phosphate

The differences in the magnitude of water and citrate soluble phosphate contents at a given level of acidulation widened further depending upon the method of acidulation. In general, samples acidulated with concentrated acid (Method 'A') resulted in greater formation of both water soluble and citrate soluble phosphate than that obtained with the use of diluted acid (Method 'B'). The superiority of former procedure over the latter was especially marked at the 50% level of acidulation, thereby indicating that the initial rate of chemical reaction of HNO_3 with RP particles was slow which picked up gradually to reach the satisfactory rate at the level of 50% or above in general and with concentrated acid (Method 'A') in particular.

Effect of Levels of Acidulation and Times of Curing

The effect of time of curing on the contents of total (table 2) and citrate soluble phosphate was found to be non-significant, while it was significant and positive on the contents of water soluble phosphate (table 3).

In relation to the levels of acidulation, time of curing failed to cause any significant changes in the content of water soluble phosphate of 12.5% acidulated RP samples. However, the effect of 25, 50 and 75% acidulation levels over their respective preceding levels, at all the respective times of curing, was significant up to the maximum duration of 144 hours of curing tried. Nevertheless, when the effect of curing times, irrespec-

Table 2 *Effect of methods of acidulation and the times of curing on the total phosphate content of rock phosphate*

Time of curing (hours)	P_2O_5 (%)		
	Method A	Method B	Mean
0	16.76	16.07	16.41
2	16.31	16.26	16.28
4	16.04	15.64	15.84
5	15.96	15.58	15.77
8	15.65	15.91	15.78
12	15.55	16.04	15.79
24	15.80	15.81	15.80
48	15.51	16.09	15.80
96	15.72	15.85	15.78
144	15.72	15.85	15.79
Mean	15.90	15.91	
		S. Em+	LSD 5%
	Methods of acidulation	0.17	N S
	Time of curing	0.07	N S

NS: Non-significant.

Table 3 *Effect of levels of acidulation and the time of curing on water soluble and citrate phosphate content of rock phosphate*

Time of curing (hours)	Water soluble phosphate (%) at different levels of acidulation						Citrate soluble phosphate (%)	Available phosphate (%)
	0	12.5	25	50	75	Mean		
0	1.15	3.2	6.8	17.8	18.7	9.51	21.6	31.9
2	1.22	2.1	6.3	20.8	34.5	13.0	20.1	33.0
4	1.22	2.7	10.6	23.3	30.9	13.7	19.4	33.7
6	1.22	2.5	11.3	25.9	34.6	15.1	20.5	35.6
8	1.22	2.4	10.1	23.0	31.0	13.5	21.5	35.0
12	1.22	1.9	6.6	22.7	34.0	13.3	23.0	36.2
24	1.22	3.0	7.2	22.5	36.1	14.0	24.8	38.2
48	1.22	2.5	6.4	20.3	35.8	13.3	22.3	35.6
96	1.22	2.5	6.6	21.2	40.4	14.4	22.2	36.6
144	1.22	1.9	7.5	24.6	38.3	14.7	23.5	38.2
Mean	1.21	2.5	7.9	22.2	33.4			
		S Em±		LSD 5%		S. Em±		LSD (5%)
Time of curing		0.7		1.9		1.3		3.7
Levels of acidulation		0.5		1.3				1.6
Time of curing × levels of acidulation interaction		1.5		4.1				5.2

N.B.: Content of water and citrate soluble phosphate is expressed as percentage of the total phosphate

tive of the levels of acidulation, was examined, a 6 hr curing time appeared best in respect of the water solubility of RP.

On the other hand, a further perusal of the data in table 3 showed that the citrate soluble phosphate as well as available phosphate content increased with increasing time of curing up to 24 hrs and remained more or less same thereafter. The effect of curing times on available phosphate content was statistically significant. Since available phosphate represent the sum total of water soluble and citrate soluble phosphate, it may be concluded that the overall efficiency of acidulation of rock phosphate with conc. HNO_3 can be favourably improved using a longer reaction period of 24 hr instead of the conventional 6 hrs of curing.

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