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INVESTIGATIONS TO USE LOW-GRADE ROCK PHOSPHATES FROM MUSSOORIE ROCK PHOSPHATE DEPOSITS,

Final Agronomic Report

for

United Nations Industrial Development Organization (UNIDO)
Vienna, Austria

by

International Fertilizer Development Center (IFDC)
Muscle Shoals, Alabama 35662, U.S.A.

June 1985

INVESTIGATIONS TO USE LOW-GRADE ROCK PHOSPHATES FROM MUSSOORIE ROCK PHOSPHATE DEPOSITS--INDIA

Final Agronomic Report

Introduction

The agronomic studies reported herein were conducted in conjunction with studies undertaken by the Fertilizer Technology Division of IFDC to determine methods of improving the chemical and physical properties of Mussoorie phosphate rock. The description of those studies is provided separately. The products selected were those that showed promise for improved physical properties (i.e., granulated phosphate rock [PR]) and/or improved chemical properties (i.e., partially acidulated PR).

The agronomic studies consisted of two components. One component involved evaluations of the products under greenhouse conditions to determine their relative supply of available phosphorus (P) to locally available soils. The second component consisted of the use of incubation studies to project the results observed in the greenhouse studies to estimate product performance when applied to soils of Indian origin. The greenhouse and the incubation studies were conducted simultaneously rather than using the incubation studies for screening prior to initiation of the greenhouse studies.

Experimental Objectives

The agronomic studies on the products derived from Mussoorie PR (MPR) had two major objectives: (1) to determine the agronomic potential of granulated Mussoorie PR as compared with that of finely ground Mussoorie PR and (2) to determine the agronomic potential of partially acidulated Mussoorie PR (PAPR) as compared with that of triple superphosphate (TSP).

The first objective relates to technology designed to improve the physical properties of Mussoorie PR for direct application to acid soils. Mussoorie PR is presently being sold in India for direct application, and positive results have been reported in Indian publications. PR is generally applied in a finely ground form to promote dissolution through increased surface contact with the acid soil. Granulation of PR to conventional fertilizer diameters has been shown to decrease the rate of dissolution by reducing the surface contact. Techniques for minigranulation to a size of 48-150 mesh have been studied by IFDC, however, and have been found to improve handling properties for transportation and application without significantly decreasing the agronomic potential.

The second objective relates to improvement of both the physical and chemical properties of Mussoorie PR. Since dissolution of directly applied PR depends on an acid soil environment, use of this material is generally restricted to those zones dominated by acid soils (pH <5.5). Acidulation of PR increases its solubility and therefore increases the agronomic effectiveness of the material when applied to soils with a wider range of soil properties.

Partial acidulation refers to use of acid in quantities less than those required to produce superphosphates. It has been shown to be an effective method for increasing agronomic effectiveness when PR properties are not amenable to production of superphosphate or when reduced acid consumption is desired because of problems of availability or cost. Partially acidulated Mussoorie PR, therefore, represents a possible technology for expanding the use of the rock into agricultural zones dominated by less-acid soils.

Phosphate Sources Studied

In accordance with the objectives stated above, the phosphate sources selected for agronomic evaluation represented two types of modifications: minigranulation and partial acidulation. The sources are identified as follows:

Modification Type	Product Number[a]	Description
Minigranulated	MSR 105-AA	Granulated with urea binder
Minigranulated	MSR 200-A	Granulated with KCl binder
Minigranulated	MSR 301	Granulated with H_2SO_4 binder
Minigranulated	MSR 400-A	Granulated with H_3PO_4 binder
Partially Acidulated	MSR 605	40% H_2SO_4 using as-received rock
Partially Acidulated	MSR 702	50% H_3PO_4 using as-received rock
Partially Acidulated	MSR 801	50% H_3PO_4 using attrition-scrubbed rock
Partially Acidulated	MSR 901	50% H_2SO_4 using attrition-scrubbed rock

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[a] Product number refers to test identification for products prepared by the Fertilizer Technology Division. A description of production methods and complete characterization is included in the final report of the technology study.

A summary of some of the characteristics of these products is shown in Table 1. From this summary, it can be seen that the total P_2O_5 content of the minigranulated products ranged from 15.9% to 24.0% depending on the type of binder. Those products using urea, KCl, and H_2SO_4 averaged 16.4% P_2O_5 as compared with 18.6% P_2O_5 in the ungranulated rock. The use of H_3PO_4 as a binder increased the total P_2O_5 content to 24.0% and also increased the water- and citrate-soluble fractions above these of the other products. For the PAPRs, the use of H_2SO_4 reduced the P_2O_5 content to 13.9%-17.6%, whereas H_3PO_4 increased the grade to 30.3%-32.6% P_2O_5 because P was supplied in the acid. Water and citrate solubilities were increased significantly by the acidulation.

Greenhouse Studies

The greenhouse studies conducted as a part of this project followed established procedures for evaluation of the relative effectiveness of phosphate carriers. The specific objectives of the greenhouse studies were as follows: (1) to determine the relative capacity of the sources in question to supply plant-available phosphorus under stressful growing conditions and (2) to determine the relationship between this capacity and soil test measurements as a means of predicting source potential in different soils.

Materials and Methods

The phosphate sources used in the greenhouse studies are identified above. The conditions under which those sources were evaluated varied depending upon the product type. Each of the minigranulated products was applied to the Mountview silt loam which had been limed to a pH of 4.77. Finely ground Mussoorie PR was used as the standard for comparison to determine whether minigranulation would influence the effectiveness of the PR when applied to an acid soil. Each of the PAPR products was applied to the Windthorst clay (pH 6.32), and TSP was used as the standard for comparison to determine whether Mussoorie PAPR would be as effective as conventional soluble P sources on soils of higher pH. Some properties of these two soils are shown in Table 2.

Also included in Table 2 are the properties of the four soils collected in India that were used in the soil incubation studies. Relevant properties of the Mountview and Windthorst soils used in the greenhouse evaluation correspond closely with some of the Indian soils. For example, the Mountview and Coorg soils are similar with respect to pH, cation status, texture, and P sorption capacity, while the Windthorst soil is similar to the Srinikctan soil with respect to pH. All soils are low in P as indicated by the Bray P-1 measurements, which range from 0.56 to 5.24 ppm P. The Mountview and Windthorst soils were used in the greenhouse portion of the project because the U.S. Department of Agriculture (USDA) plant protection authority has regulations against use of foreign soils for that purpose.

The greenhouse trial of the minigranulated products was conducted as follows: reagent grade $CaCO_3$ was applied to the Mountview soil at a rate equivalent to 0.5 mt/ha and allowed to incubate for 1 week. The soil properties reported in Table 2 are the result of analysis of the soil following incubation with the $CaCO_3$ but prior to application of the fertilizer treatments. Each pot contained 4 kg of soil. Immediately prior to planting, uniform levels of NH_4NO_3, K_2SO_4, and a micronutrient solution were applied to supply 600 mg N, 400 mg K, 19 mg Mg, 11 mg Zn, 5 mg Cu, 2 mg B, and 34 mg S per pot. Each of the sources to be tested (MPR, MSR 105-AA, MSR 200-A, MSR 301, and MSR 400-A) was then completely mixed into the 4 kg of soil in quantities to supply concentrations of 100, 200, and 400 ppm total P per pot. A treatment in which no P was added was also included to serve as a check on P response.

Following application of the fertilizers, the pots were placed in the greenhouse in a randomized block design with three replicates of each treatment.

On November 3, 1983, maize (Funk G5757) was planted; it was thinned to four plants per pot following emergence. All pots were irrigated to maintain a moisture content equal to 80% of the field moisture capacity of the soil. On January 6, 1984, the aboveground plant material was harvested, following a 64-day cropping period. A 100-g soil sample was then collected from each pot for laboratory analysis.

Following the harvest and soil sampling, N and K were reapplied at the same rates as at the initiation of the trial. On January 11, 1984 (5 days following the first harvest), a second crop of maize was planted with subsequent management identical to that of the first crop. The aboveground plant material produced during the second cropping period was harvested 37 days after planting on February 17, 1984. Soil samples were again collected for laboratory analysis.

Plant tissue collected from both harvests was dried at 60°C in a forced-air drying cabinet prior to weighing. The tissue was ground in a Wiley mill and digested in a 2:1 nitric-perchloric acid mixture in flasks that were heated in an aluminum digestion block. Phosphorus concentration in the tissue was determined on a Varian Techtron model 635 UV-Vis spectrophotometer at a wave length of 882 μm following development of the phospho-molybdate blue complex by the Murphy-Riley method. Soil samples collected from each pot were ground to 20-mesh following drying in a forced-air cabinet. Available P was measured following an extraction by the Bray P-1 method (0.03 $\underline{N}$ NH_4F + 0.025 $\underline{N}$ HCl), and pH was determined on a 1:1 soil:water suspension with a glass electrode.

The greenhouse trial of the PAPR products was conducted simultaneously with the trial of the minigranulated products and under identical conditions with the following exceptions: all products were applied to an unlimed Windthorst soil (pH 6.32) rather than to the Mountview soil (Table 2). The products evaluated included TSP, MSR 605, MSR 702, MSR 801, and MSR 901. An additional rate of application of each product was also included to result in concentrations of 50, 100, 200, and 400 ppm total P.

Greenhouse Results and Discussion

As indicated above, the agronomic efficiency of the products was tested in greenhouse studies to determine their potential effectiveness with two different types of soil. The selection of soil depended upon the type of product modification. In conjunction with these trials on the Mussoorie PR products, tests were also conducted with standard IFDC sources to verify that both soils were sufficiently responsive to applied P to allow observation of the relative P-supplying capacity of the different sources with increasing rates of application. Additionally, tests with these standard sources were conducted to verify that the acid Mountview soil was conducive to the dissolution of unacidulated phosphate rock. Both of these additional tests were positive and showed that the observations made with the Mussoorie products can be considered as valid measurements of the relative effectiveness of these phosphorus sources. Details of these tests can be provided upon request.

In each trial, product efficiency was measured by (1) plant response to P, (2) uptake of P by the maize plant, and (3) chemical extraction to estimate plant-available P in the soil following cropping. With respect to dry-matter production and P uptake by the plant, the shape of the response curves associated with different P sources can vary from source to source. Comparisons of relative effectiveness are most valid therefore when they are based on the entire response curve rather than on a given rate of application. For this reason, several statistical models were evaluated to determine which was most descriptive of the actual data obtained. From these comparisons, it was found that a quadratic function in the form of $y = \alpha + \beta P + \gamma P^2$ resulted in the highest correlation coefficient for each of the data sets.

The dry-matter production of maize from the Mussoorie PR products during the two cropping periods is given in Table 3. It can be observed from these data that production without applied P was extremely low. On the Mountview soil, only the minigranulated rock with 7.7% H_3PO_4 binder showed a systematic increase in yield with increasing rates of application. This is illustrated in the modeled data shown in Table 4 and in Figures 1, 2, and 3. These response curves clearly illustrate that the use of H_3PO_4 binder provided plant-available P that was not available from the other products in the test. Tests to determine statistical difference between the sources based on the parameters of models showed that this product (MSR 400-A) was significantly higher in effectiveness than were all other products in both cropping periods as measured by the coefficient of the P^2 term. Also, it can be seen by the shape of the response curves that a positive response was continuing even at the highest rate of application.

It can also be observed, however, that little response was obtained from the other products in either cropping period as the rate of application increased. An analysis of variance procedure showed no significant difference between the other minigranulated products and the check treatment which received no additional P (Table 3). Because of the lack of responsiveness of these particular sources, it is impossible to draw any conclusions with respect to the influence of urea, KCl, or H_2SO_4 binders on the agronomic potential of the Mussoorie PR.

The maize gave substantially greater response to the partially acidulated products than to the minigranulated products despite the fact that the PAPRs were applied to a soil with a higher pH (pH 6.32 versus pH 4.77). From these data (Table 3), it can be seen that all sources were significantly more effective than the check treatment in both cropping periods, even at the lowest rate of application. As illustrated by the modeled data (Table 5 and Figures 4, 5, and 6), all sources approached maximum production in the range of 200-400 ppm P during the first cropping, and some sources continued to show positive crop response at the highest rate during the second cropping. Table 5 summarizes statistical analysis of the modeled data. It can be observed from this statistical analysis that there was no significant difference throughout the response curve between TSP and either of the PAPR products with 50% H_3PO_4 binder during the first cropping period. Throughout the course of the two cropping periods, the product made from the attrition-scrubbed rock acidulated with 50% H_3PO_4 eventually became less effective, but still showed positive crop response. The two PAPRs prepared with H_2SO_4 were significantly less effective than TSP or MSR 702, but they also showed potential for increasing crop production with increasing rates of application.

To confirm that the effectiveness of a source was related primarily to the capacity of the source to provide plant-available P, the uptake of P by the maize plant was determined. Data obtained from this laboratory analysis are presented in Table 6. As with dry-matter production, P uptake was also best described through use of a quadratic model. The modeled data for both cropping periods and for the accumulative P uptake are shown in Tables 7-8 and in Figures 7-12. It can be seen from these figures that the same relative positions were observed with respect to P uptake as were observed with dry-matter production.

For example, in the case of the minigranulated products applied to the Mountview soil, only the product with H_3PO_4 binder resulted in increased P uptake by the maize as the rate of P applied was increased. It is suggested that this response is due to a combination of (1) a minor degree of acidulation of the Mussoorie PR and (2) a contribution of soluble P resulting from the use of H_3PO_4 as the binder.

Also, as was done with dry-matter production, the modeled response curves for P uptake were analyzed statistically to determine whether there were significant differences between the PAPR sources (Table 8). In the case of P uptake, the PAPRs approached the effectiveness of TSP in specific instances, but overall the P uptake from TSP was significantly higher. Also, 50% acidulation with H_2SO_4 was significantly more effective than 40% acidulation with H_2SO_4. The findings indicate that P uptake is a more sensitive measure of P availability from different sources than is the crop yield. They also confirm that the difference observed in yield between sources was due to the P-supplying capacity of the sources.

Another measure of the relative release of plant-available P between sources is that of P extracted from the soil following cropping. The Bray P-1 methodology has been found to be effective for this purpose. Measurements of Bray P-1 extractable P levels following each of the two cropping periods are listed in Table 9. Examination of these data supports the findings reported on dry-matter production of maize and P uptake by maize. For example, no difference was observed between any of the sources applied to the Mountview soil after either cropping period except for MS 400-A, which showed significantly higher extractable P at all rates of application. However, the Bray P-1 extractable P levels were also higher in those soils receiving unacidulated Mussoorie PR products than in the soil that did not receive an application of P. This difference is explained by the dissolution of P from apatite during extraction, which is not plant available. This phenomenon is reported in "Interpretation of Bray I-Extractable Phosphorus From Acid Soil Treated With Phosphate Rocks," by S. H. Chien (Soil Science 126:34-39, 1978).

With respect to the PAPRs, again the 50% H_3PO_4 acidulation resulted in Bray P-1 extractable P that approached the level from TSP, and in many instances there was no significant difference between them. Only the 40% H_2SO_4-acidulated rock showed consistently lower levels of Bray P-1 extractable P than did the other products.

The fact that Bray P-1 extractable P measurements are in fact effective in predicting crop response is illustrated in Figure 13, which shows the crop response to P in the second cropping period as related to Bray P-1 extractable P levels measured immediately prior to planting of the second crop.

Laboratory Soil Incubation Study

The objectives of the IFDC laboratory soil incubation study were to investigate the (1) effectiveness with which various Mussoorie products provide available P in some Indian soils and (2) soil and product properties as related to the available P provided by the Mussoorie products in the soils. In the soil incubation study, commercial TSP was also included for comparison. In addition to the Indian soils, two U.S. soils that were used for the greenhouse evaluation were included. By comparing the Indian soils with the U.S. soils in terms of the levels of available P provided by the Mussoorie products and the crop response, it may be possible to predict the relative agronomic effectiveness (RAE) of the Mussoorie products with the Indian soils.

Materials and Methods

The soils utilized were two U.S. soils (Mountview soil from Tennessee and Windthorst soil from Texas) and four unsterilized Indian soils supplied by Pyrites, Phosphates and Chemicals Ltd. (PPCL). The Indian soils were moist and unground when received. They were air-dried in the greenhouse, ground, and screened through a 2-mm sieve. Some properties of the soils are listed in Table 2.

For the soil incubation study the phosphate sources were divided into two groups: the minigranulated Mussoorie PR and the partially acidulated Mussoorie PR. In the first group the phosphate sources used were (1) MSR 105-AA, minigranulated PR with 6% urea; (2) MSR 200-A, minigranulated PR with 3.5% KCl; (3) MSR 301, minigranulated PR with 8.1% H_2SO_4; (4) MSR 400-A, minigranulated PR with 7.7% H_3PO_4; and (5) TSP. The soils used were (1) Allepey, (2) Coorg, (3) Ranchi, and (4) Mountview. In the second group phosphate sources used were (1) MSR 605, PAPR with 40% H_2SO_4; (2) MSR 702, PAPR with 50% H_3PO_4; (3) MSR 801 with 50% H_3PO_4; (4) MSR 901, PAPR with 50% H_2SO_4; and (5) TSP. The soils used were (1) Ranchi, (2) Srinikctan, and (3) Windthorst.

Each source of powdered or minigranulated phosphate material was completely mixed with 20 g of soil in a 50-ml polyethylene centrifuge tube at a rate of 200 ppm P. A check (no P) was also included. Five milliliters of distilled water was added to the soil to yield a 25% moisture content of the soil. The tube was then covered with a wax-coated paper in which five holes were punched with a pencil. This minimized the moisture loss and also maintained aeration during incubation. The soil samples were then placed in an incubator at 30°C for 1, 3, or 10 weeks. The soil moisture content was checked and maintained at 25% on a weekly basis. At the end of each incubation period, a quantity of 25 ml of Bray P-1 solution (0.025 N HCl + 0.03 N NH_4F) was added to the tube which was shaken for 30 minutes; centrifugation and filtration followed. Phosphorus concentration in the clear soil extract was determined by the Murphy-Riley colorimetric method.

All the incubations were carried out in duplicate, and the values reported are averages of the duplicates.

Results and Discussion

The amounts of Bray P-1 extractable P in the first group of soils treated with various types of minigranulated Mussoorie PR and commercial TSP after incubation are shown in Tables 10 to 13.

It can be seen that the quantity of P extracted by Bray P-1 from the soil treated with the Mussoorie PR minigranulated with urea or KCl as a binder was about the same as the check (no P added), indicating the ineffectiveness of the minigranulated PR in providing available P in the soils. When the PR was minigranulated with H_2SO_4 or H_3PO_4, a significant increase in Bray P-1 extractable P over the check was observed for the Coorg, Ranchi, and Mountview soils, but not the Allepey soil, which had the highest P-fixing capacity (Table 2). In general, the effectiveness of various phosphate materials in providing available P in the four soils follows the order of TSP > minigranulated PR with H_3PO_4 > minigranulated PR with H_2SO_4 > minigranulated PR with urea = minigranulated PR with KCl = check.

The amounts of Bray P-1 extractable P in the second group of soils treated with various Mussoorie PAPR products and commercial TSP after incubation are shown in Tables 14 to 16.

As compared with the minigranulated PR products, partial acidulation (40%-50%) with H_2SO_4 or H_3PO_4 significantly increased available P over the check in all three soils. It also should be pointed out that the effectiveness of Mussoorie PAPR products in providing available P was comparable to that of TSP as observed in this incubation study.

As stated previously, since Mussoorie products could not be agronomically evaluated on the Indian soils at IFDC Headquarters, an attempt was made to correlate Bray P-1 extractable P of the P materials tested during soil incubation to crop yield data obtained in the greenhouse study. It was felt that such a correlation might help predict the performance of Mussoorie products on Indian soils under greenhouse/field conditions.

Figure 14 shows the relationship between RAE of various Mussoorie P materials with respect to TSP at 200 ppm P applied to the U.S. soils (Mountview and Windthorst) and their relative Bray P-1 extractable P values in the soils treated with the same P materials after a 3-week incubation period at 200 ppm P. The relative Bray P-1 extractable P in the soils is similar to RAE in that the Bray P-1 extractable P is highly correlated with crop yield. It can be seen that RAE increased as relative Bray P-1 extractable P in soil increased. The relationship, however, is curvilinear rather than linear.

To predict the RAE values of the Mussoorie products on the Indian soils, the relative Bray P-1 extractable P in an Indian soil treated with a given Mussoorie product after a 3-week incubation period was first calculated. The value of RAE was then estimated from the response curve in Figure 14. Table 17 shows the predicted RAE values of various Mussoorie products on four Indian soils.

Conclusions

It can be seen that the minigranulated Mussoorie PR with urea, KCl, or H_2SO_4 binder probably would be much less effective in increasing crop yield than would TSP on the Indian soils. However, minigranulating the Mussoorie PR with a small amount of H_3PO_4 significantly increases its effectiveness on the Indian soils, particularly on the Allepey soil which has the highest P-fixing capacity of the Indian soils used in the project.

Partial acidulation of the Mussoorie PR at 40%-50% with either H_2SO_4 or H_3PO_4 seems to produce good P fertilizers for the Indian soils (Table 17). With Srinikctan soil, the predicted RAE values of Mussoorie PAPR ranged from approximately 75% to 96% as compared with TSP. For Ranchi soil, the predicted RAE values were all equal to or greater than those obtained with TSP. Thus, it may be concluded that partial acidulation should be an effective means of producing some good, promising P fertilizers from Mussoorie PR for crop production in India. This is particularly true since these studies evaluated residual effectiveness over a relatively short period of time. Since the unacidulated portion of the PAPR can be expected to behave the same as directly applied phosphate rock, the long-term residual value of the products can be expected to be significant. However, future greenhouse and/or field trials in India are needed to verify the results of the work under the specific conditions encountered in India.

Table 1. Experimental Materials for Greenhouse Trials With Mussoorie PR

Run Number	Type of Material	Binder		Acidulation		Total P_2O_5	W.S. P_2O_5	C.S. P_2O_5[e]	N	K_2O
		Type	%	Type	%[a]			(%)		
MSR 105-AA[b]	Minigranules	Urea	6	-	-	16.8	-	-	2.6	-
MSR 200-A[b]	Minigranules	KCl	3.7	-	-	16.5	-	-	-	3.1
MSR 301[b]	Minigranules	H_2SO_4	8.1	-	-	15.9	0.3	0.5	-	-
MSR 400-A[b]	Minigranules	H_3PO_4	7.7	-	-	24.0	0.9	4.0	-	-
MSR 605[b]	PAPR	-	-	H_2SO_4	40	13.9	4.5	0.2	-	-
MSR 702[b]	PAPR	-	-	H_3PO_4	50	32.6	15.5	4.1	-	-
MSR 801[c]	PAPR	-	-	H_3PO_4	50	30.3	13.1	4.3	-	-
MSR 901[c]	PAPR	-	-	H_2SO_4	50	17.6	8.5	1.9	-	-
-	Mussoorie PR[d]	-	-	-	-	18.6	-	-	-	-

a. Indicates percentage of acid required to produce SSP.
b. Prepared from as-received rock.
c. Prepared from attrition-scrubbed rock.
d. As-received phosphate rock.
e. Neutral ammonium citrate soluble P_2O_5 (AOAC procedure).

Table 2. Some Chemical Properties of the Soils Used in the Agronomic Studies

Soil	Texture[a]	pH	O.M. (%)	Bray P-1 Extractable P (ppm)	Ca	Mg	K	Na	Al	ECEC[b]	P-Fixing Capacity (%)
					- - - -	- - - -	-(meq/100 g)-		- - - -	- - -	
Allepey (India)	CL	5.20	3.88	3.56	7.60	5.41	0.42	2.49	0	16.12	52.2
Coorg (India)	SL	4.81	2.51	5.24	1.05	0.42	0.10	0.25	0.40	2.42	14.4
Ranchi (India)	SL	5.02	0.41	1.60	0.75	0.28	0.21	0.19	0.60	2.23	10.9
Srinikctan (India)	SL	6.38	0.39	1.64	1.94	0.86	0.12	2.82	0	5.84	2.3
Mountview (Tennessee)	SL	4.77	1.52	3.52	0.97	0.13	0.12	0.36	1.68	3.58	23.5
Windthorst (Texas)	C	6.32	0.66	0.36	11.50	5.04	0.75	1.88	0	19.27	26.8

a. CL--clay loam.
SL--silt loam.
C--clay.

b. Effective cation exchange capacity = sum of cations.

Table 3. Dry-Matter Production of Maize From Mussoorie PR Products During Two Cropping Periods (g/pot)

Mountview Soil (pH 4.77)

		Rate of Application (ppm P)									
		Crop 1					Crop 2				
Source	Description	0	100	200	400	Mean	0	100	200	400	Mean
Check	No P applied	1.72				1.72b	1.19				1.19b
MPR	Finely ground		2.21	2.54	2.53	2.43b		1.23	1.24	1.60	1.36b
MSR 105-AA	Urea binder		2.06	2.18	2.03	2.09b		1.74	1.55	1.57	1.62b
MSR 200-A	KCl binder		1.91	2.11	2.35	2.12b		1.36	1.56	1.62	1.51b
MSR 301	H_2SO_4 binder		2.32	2.45	2.57	2.45b		1.66	1.59	2.09	1.78b
MSR 400-A	H_3PO_4 binder		2.89	5.02	9.82	5.91a		2.07	2.98	9.52	4.86a

Windthorst Soil (pH 6.32)

		Rate of Application (ppm P)											
		Crop 1						Crop 2					
Source	Description	0	50	100	200	400	Mean	0	50	100	200	400	Mean
Check	No P applied	2.10					2.10d	1.50					1.50d
TSP	Soluble std.		10.44	12.11	13.42	12.58	12.14a		4.69	10.08	20.25	23.83	14.71a
MSR 605	40% H_2SO_4 AR		5.88	8.30	11.11	11.90	9.30c		3.94	7.42	10.60	18.82	10.20c
MSR 702	50% H_3PO_4 AR		7.97	11.65	12.39	14.41	11.61ab		7.37	12.52	15.67	21.78	14.34ab
MSR 801	50% H_3PO_4 AT		9.46	10.26	12.09	13.00	11.20abc		4.26	7.83	12.99	22.70	11.95bc
MSR 901	50% H_2SO_4 AT		7.20	10.35	11.52	12.23	10.33bc		5.39	9.07	12.65	21.14	12.06abc

AR--As-received rock.
AT--Attrition-scrubbed (concentrate) rock.

Note: Means followed by the same letter are not significantly different (P = 0.05) as determined by Duncan's multiple range test.

Table 4. Response Equations for Dry-Matter Yield (DMY) With Minigranulated Mussoorie PR Products

		Coefficients[a]	
		Linear	Quadratic
Mountview Soil (1st Crop)			
Ungranulated	$DMY = 1.64 + .0068\ P - .000012\ P^2$	a	b
Urea binder	$DMY = 1.64 + .0048\ P - .000009\ P^2$	a	b
KCl binder	$DMY = 1.64 + .0030\ P - .000003\ P^2$	a	b
H_2SO_4 binder	$DMY = 1.64 + .0067\ P - .000011\ P^2$	a	b
H_3PO_4 binder	$DMY = 1.64 + .0120\ P + .000021\ P^2$	a	a
Mountview Soil (2nd Crop)			
Ungranulated	$DMY = 1.14 + .00046\ P + .000002\ P^2$	a	b
Urea binder	$DMY = 1.14 + .00476\ P - .000009\ P^2$	a	b
KCl binder	$DMY = 1.14 + .00288\ P - .000004\ P^2$	a	b
H_2SO_4 binder	$DMY = 1.14 + .00364\ P - .000003\ P^2$	a	b
H_3PO_4 binder	$DMY = 1.14 + .00046\ P + .000051\ P^2$	a	a
Mountview Soil (Accumulative Production)			
Ungranulated	$DMY = 2.77 + .00719\ P - .000010\ P^2$	a	b
Urea binder	$DMY = 2.77 + .00952\ P - .000019\ P^2$	a	b
KCl binder	$DMY = 2.77 + .00585\ P - .000007\ P^2$	a	b
H_2SO_4 binder	$DMY = 2.77 + .01039\ P - .000014\ P^2$	a	b
H_3PO_4 binder	$DMY = 2.77 + .01250\ P + .000072\ P^2$	a	a

---

a. Linear or quadratic coefficients in each group with the same letter are not significantly different ($P = 0.05$) as determined by paired comparisons.

Table 5. Response Equations for Dry-Matter Yield (DMY) With Partially Acidulated Mussoorie PR Products

		Coefficients[a]	
		Linear	Quadratic
Windthorst Soil (1st Crop)			
TSP	$DMY = 4.63 + .0831 P - .000160 P^2$	a	a
50% H_3PO_4 conc.	$DMY = 4.63 + .0643 P - .000110 P^2$	a	a
50% H_3PO_4 as-rec.	$DMY = 4.63 + .0659 P - .000105 P^2$	a	a
50% H_2SO_4 conc.	$DMY = 4.63 + .0571 P - .000096 P^2$	b	b
40% H_2SO_4 as-rec.	$DMY = 4.63 + .0429 P + .000061 P^2$	b	b
Windthorst Soil (2nd Crop)			
TSP	$DMY = 1.41 + .11321 P - .000141 P^2$	a	a
50% H_3PO_4 conc.	$DMY = 1.41 + .06368 P - .000026 P^2$	b	b
50% H_3PO_4 as-rec.	$DMY = 1.41 + .10885 P - .000147 P^2$	a	a
50% H_2SO_4 conc.	$DMY = 1.41 + .07226 P - .000056 P^2$	b	b
40% H_2SO_4 as-rec.	$DMY = 1.41 + .05440 P - .000028 P^2$	b	b
Windthorst Soil (Accumulative Production)			
TSP	$DMY = 6.04 + .19635 P - .000301 P^2$	a	a
50% H_3PO_4 conc.	$DMY = 6.04 + .12802 P - .000136 P^2$	b	b
50% H_3PO_4 as-rec.	$DMY = 6.04 + .17471 P - .000251 P^2$	a	a
50% H_2SO_4 conc.	$DMY = 6.04 + .12931 P - .000152 P^2$	b	b
40% H_2SO_4 as-rec.	$DMY = 6.04 + .09729 P - .000089 P^2$	b	b

---

[a] Linear or quadratic parameters in each group with the same letter are not significantly different ($P = 0.05$) as determined by paired comparisons.

Table 6. P Uptake by Maize From Mussoorie PR Products During Two Cropping Periods (mg/pot)

Mountview Soil (pH 4.77)

		Rate of Application (ppm P)									
		Crop 1					Crop 2				
Source	Description	0	100	200	400	Mean	0	100	200	400	Mean
Check	No P applied	1.52				1.52b	1.03				1.03
MPR	Finely ground		1.84	2.09	2.07	2.00b		1.07	1.04	1.26	1.13
MSR 105-AA	Urea binder		1.77	1.90	1.71	1.79b		1.39	1.38	1.35	1.38
MSR 200-A	KCl binder		1.60	1.81	1.77	1.73b		1.02	1.20	1.23	1.15
MSR 301	H_2SO_4 binder		1.90	2.14	2.36	2.13b		1.32	1.96	1.71	1.41
MSR 400-A	H_3PO_4 binder		2.60	6.23	13.35	7.39a		1.69	2.84	12.84	5.79

Windthorst Soil (pH 6.32)

		Rate of Application (ppm P)											
		Crop 1						Crop 2					
Source	Description	0	50	100	200	400	Mean	0	50	100	200	400	Mean
Check	No P applied	1.66					1.66d	1.12					1.12d
TSP	Soluble std.		18.84	28.99	43.95	56.64	37.11a		4.97	15.11	39.48	76.38	33.98a
MSR 605	40% H_2SO_4 AR		7.07	11.29	21.28	35.30	18.74c		5.50	13.27	18.13	35.79	18.17c
MSR 702	50% H_3PO_4 AR		10.76	20.86	30.84	48.41	27.72b		12.25	23.86	27.92	56.54	30.14ab
MSR 801	50% H_3PO_4 AT		13.78	20.56	30.18	51.05	28.89b		8.17	13.68	20.44	57.03	24.83bc
MSR 901	50% H_2SO_4 AT		9.19	16.78	27.85	38.35	23.04c		8.14	18.22	24.51	46.06	24.23bc

AR--As-received rock.
AT--Attrition-scrubbed (concentrate) rock.

Table 7. Response Equations for P Uptake (PUP) by Maize With Minigranulated Mussoorie PR Products

		Coefficients[a]	
		Linear	Quadratic
Mountview Soil (1st Crop)			
Ungranulated	PUP = 0.63 + .0124 P - .000022 P^2	a	a
Urea binder	PUP = 0.63 + .0116 P - .000022 P^2	a	a
KCl binder	PUP = 0.63 + .0101 P - .000018 P^2	a	a
H_2SO_4 binder	PUP = 0.63 + .0125 P - .000021 P^2	a	a
H_3PO_4 binder	PUP = 0.63 + .0210 P + .000027 P^2	a	a
Mountview Soil (2nd Crop)			
Ungranulated	PUP = 0.85 + .00159 P - .000001 P^2	a	b
Urea binder	PUP = 0.85 + .00513 P - .000010 P^2	a	b
KCl binder	PUP = 0.85 + .00240 P - .000004 P^2	a	b
H_2SO_4 binder	PUP = 0.85 + .00296 P - .000002 P^2	a	b
H_3PO_4 binder	PUP = 0.85 - .00582 P + .000089 P^2	a	a
Mountview Soil (Accumulative P Uptake)			
Ungranulated	PUP = 1.48 + .0140 P - .000024 P^2	a	b
Urea binder	PUP = 1.48 + .0167 P - .000032 P^2	a	b
KCl binder	PUP = 1.48 + .0125 P - .000022 P^2	a	b
H_2SO_4 binder	PUP = 1.48 + .0155 P - .000023 P^2	a	b
H_3PO_4 binder	PUP = 1.48 + .0152 P + .000116 P^2	a	a

---

a. Linear or quadratic coefficients in each group with the same letter are not significantly different (P = 0.05) as determined by paired comparisons.

Table 8. Response Equations for P Uptake (PUP) by Maize With Partially Acidulated Mussoorie PR Products

		Coefficients[a]	
		Linear	Quadratic
Windthorst Soil (1st Crop)			
TSP	PUP = 3.09 + .2907 P - .000394 P^2	a	a
50% H_3PO_4 conc.	PUP = 3.09 + .1733 P - .000136 P^2	b	bc
50% H_3PO_4 as-rec.	PUP = 3.09 + .1750 P - .000155 P^2	b	bc
50% H_2SO_4 conc.	PUP = 3.09 + .1535 P - .000163 P^2	b	b
40% H_2SO_4 as-rec.	PUP = 3.09 + .0926 P - .000029 P^2	c	c
Windthorst Soil (2nd Crop)			
TSP	PUP = 2.25 + .14423 P + .000108 P^2	a	a
50% H_3PO_4 conc.	PUP = 2.25 + .07327 P + .000156 P^2	b	a
50% H_3PO_4 as-rec.	PUP = 2.25 + .17106 P - .000094 P^2	a	b
50% H_2SO_4 conc.	PUP = 2.25 + .13450 P - .000064 P^2	a	b
40% H_2SO_4 as-rec.	PUP = 2.25 + .08790 P - .000011 P^2	a	ab
Windthorst Soil (Accumulative P Uptake)			
TSP	PUP = 5.34 + .43489 P - .000286 P^2	a	a
50% H_3PO_4 conc.	PUP = 5.34 + .24662 P - .000020 P^2	cd	c
50% H_3PO_4 as-rec.	PUP = 5.34 + .34609 P - .000249 P^2	b	ab
50% H_2SO_4 conc.	PUP = 5.34 + .28803 P - .000227 P^2	bc	ab
40% H_2SO_4 as-rec.	PUP = 5.34 + .18048 P - .000040 P^2	d	bc

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[a] Linear or quadratic coefficients in each group with the same letter are not significantly different (P = 0.05) as determined by paired comparisons.

Table 9. Bray P-1 Extractable P From Soils Following Each of Two Cropping Periods (ppm)

Mountview Soil (pH 4.77)

		Rate of Application (ppm P)							
		Crop 1				Crop 2			
Source	Description	0	100	200	400	0	100	200	400
Check	No P applied	4.0				4.2			
MPR	Finely ground		22.4b	30.5b	34.5b		21.6b	30.5b	40.6b
MS 105-AA	Urea binder		18.1b	29.6b	34.8b		16.8b	24.7b	38.8b
MS 200-A	KCl binder		24.9b	34.0b	40.8b		21.9b	29.0b	38.9b
MS 301	H_2SO_4 binder		22.9b	30.5b	45.6b		18.6b	23.4b	37.4b
MS 400-A	H_3PO_4 binder		35.8a	73.4a	125.3a		32.8a	62.8a	108.5a

Windthorst Soil (pH 6.32)

		Rate of Application (ppm P)									
		Crop 1					Crop 2				
Source	Description	0	50	100	200	400	0	50	100	200	400
Check	No P applied	0.4					0.4				
TSP	Soluble std.		9.4a	36.4a	65.9a	139.6a		11.9a	24.1a	60.8a	167.7a
MSR 605	40% H_2SO_4 AR		6.2b	15.1c	39.5c	75.8b		4.8b	11.0bc	24.1c	71.9c
MSR 702	50% H_3PO_4 AR		8.9a	23.9b	56.5ab	138.1a		7.5ab	15.8b	44.5b	108.7b
MSR 801	50% H_3PO_4 AT		8.2ab	20.8bc	50.2bc	104.0ab		6.6b	16.4b	40.3b	91.3bc
MSR 901	50% H_2SO_4 AT		6.4b	18.0bc	43.2bc	74.3b		7.1ab	9.0c	26.8c	62.4c

Means with the same letter are not statistically different according to Duncan's multiple range test (P = 0.05). Comparisons are between sources at each different rate of application.

Table 10. Bray-1 Extractable P in Allepey Soil Treated With 200 ppm P During Incubation (ppm)

Sample Number	Treatment	Incubation Time, Weeks 0	1	3	10
MSR 105-AA	Minigranulated PR (6% urea)	0.03	0	0.02	0.03
MSR 200-A	Minigranulated PR (3.5% KCl)	0.03	0	0	0.05
MSR 301	Minigranulated PR (8.1% H_2SO_4)	0.05	0.02	0	0.05
MSR 400-A	Minigranulated PR (7.7% H_3PO_4)	0.14	0.04	0.08	0.06
TSP	Powder	0.54	0.12	0.15	0.15
Check (no P)	-	0.03	0.01	0	0.05

Table 11. Bray-1 Extractable P in Coorg Soil Treated With 200 ppm P During Incubation (ppm)

Sample Number	Treatment	Incubation Time, Weeks 0	1	3	10
MSR 105-AA	Minigranulated PR (6% urea)	0.08	0	0.09	0.14
MSR 200-A	Minigranulated PR (3.5% KCl)	0.08	0.02	0.05	0.07
MSR 301	Minigranulated PR (8.1% H_2SO_4)	0.38	0.17	0.30	0.21
MSR 400-A	Minigranulated PR (7.7% H_3PO_4)	5.58	1.53	2.25	2.14
TSP	Powder	48.5	11.3	21.3	19.3
Check (no P)	-	0.05	0.04	0.01	0.04

Table 12. Bray-1 Extractable P in Ranchi Soil Treated With 200 ppm P During Incubation (ppm)

Sample Number	Treatment	Incubation Time, Weeks 0	1	3	10
MSR 105-AA	Minigranulated PR (6% urea)	0.48	0.03	0.02	0.05
MSR 200-A	Minigranulated PR (3.5% KCl)	0.40	0.06	0.05	0.01
MSR 301	Minigranulated PR (8.1% H_2SO_4)	2.79	0.35	0.09	0.12
MSR 400-A	Minigranulated PR (7.7% H_3PO_4)	16.8	1.65	0.35	0.08
TSP	Powder	66.5	20.8	2.14	2.45
Check (no P)	-	0.08	0.06	0.09	0

Table 13. Bray-1 Extractable P in Mountview Soil Treated With 200 ppm P During Incubation (ppm)

Sample Number	Treatment	Incubation Time, Weeks 0	1	3	10
MSR 105-AA	Minigranulated PR (6% urea)	0.06	0.05	0.07	0.18
MSR 200-A	Minigranulated PR (3.5% KCl)	0.06	0.04	0.06	0.16
MSR 301	Minigranulated PR (8.1% H_2SO_4)	0.25	0.28	0.29	0.42
MSR 400-A	Minigranulated PR (7.7% H_3PO_4)	1.38	2.06	2.04	2.21
TSP	Powder	10.8	11.0	9.48	9.06
Check (no P)	-	0.07	0.05	0.06	0.05

Table 14. Bray-1 Extractable P in Windthorst Soil Treated With 200 ppm P During Incubation (ppm)

Sample Number	Treatment	Incubation Time, Weeks 0	1	3	10
MSR 605	PAPR (40% H_2SO_4), powder	1.16	1.13	1.09	1.13
MSR 702	PAPR (50% H_3PO_4), powder	2.41	2.36	2.67	2.50
MSR 801	PAPR (50% H_3PO_4), powder	1.69	1.84	1.85	2.03
MSR 901	PAPR (50% H_2SO_4), powder	1.38	1.28	1.39	1.24
TSP	Powder	2.81	2.83	3.18	3.85
Check (no P)	-	0.02	0	0	0

Table 15. Bray-1 Extractable P in Ranchi Soil Treated With 200 ppm P During Incubation (ppm)

Sample Number	Treatment	Incubation Time, Weeks 0	1	3	10
MSR 605	PAPR (40% H_2SO_4), powder	38.6	22.4	4.75	4.11
MSR 702	PAPR (50% H_3PO_4), powder	62.4	20.4	4.07	0.70
MSR 801	PAPR (50% H_3PO_4), powder	52.1	27.5	6.70	0.49
MSR 901	PAPR (50% H_2SO_4), powder	41.0	23.0	14.0	3.65
TSP	Powder	66.5	20.8	2.14	2.45
Check (no P)	-	0.08	0.06	0.09	0

Table 16. Bray-1 Extractable P in Srinikctan Soil Treated With 200 ppm P During Incubation (ppm)

Sample Number	Treatment	Incubation Time, Weeks			
		0	1	3	10
MSR 605	PAPR (40% H_2SO_4), powder	40.7	25.2	18.7	6.73
MSR 702	PAPR (50% H_3PO_4), powder	65.0	46.4	26.7	3.23
MSR 801	PAPR (50% H_3PO_4), powder	53.3	37.2	11.6	2.72
MSR 901	PAPR (50% H_2SO_4), powder	48.3	29.3	22.0	4.35
TSP	Powder	97.3	53.6	32.9	19.5
Check (no P)	-	0.08	0.02	0.02	0.01

Table 17. Predicted Relative Agronomic Effectiveness (RAE) of Various Mussoorie Products on Indian Soils

Sample Number	Treatment	Predicted RAE, %			
		Allepey	Coorg	Ranchi	Srinikctan
MSR 105-AA	Minigranulated PR (6% urea)	5	5	5	-
MSR 200-A	Minigranulated PR (3.5% KCl)	5	5	5	-
MSR 301	Minigranulated PR (8.1% H_2SO_4)	5	6	5	-
MSR 400-A	Minigranulated PR (7.7% H_3PO_4)	87	35	47	-
MSR 605	PAPR-40% H_2SO_4	-	-	≧100	90
MSR 702	PAPR-50% H_3PO_4	-	-	≧100	96
MSR 801	PAPR-50% H_3PO_4	-	-	≧100	75
MSR 901	PAPR-50% H_2SO_4	-	-	≧100	93

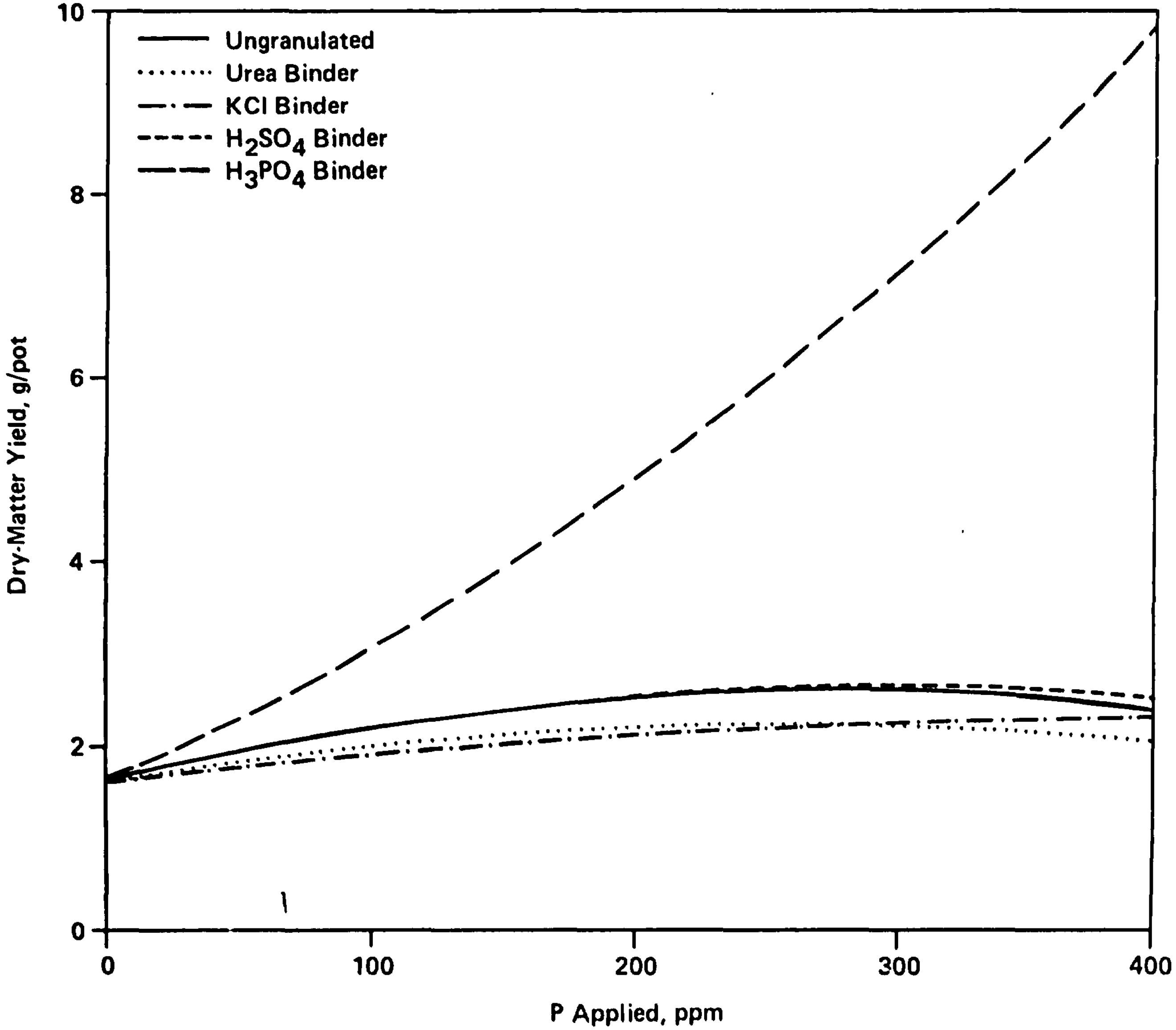


Figure 1. Maize Response to Mussoorie PR (1st Crop).

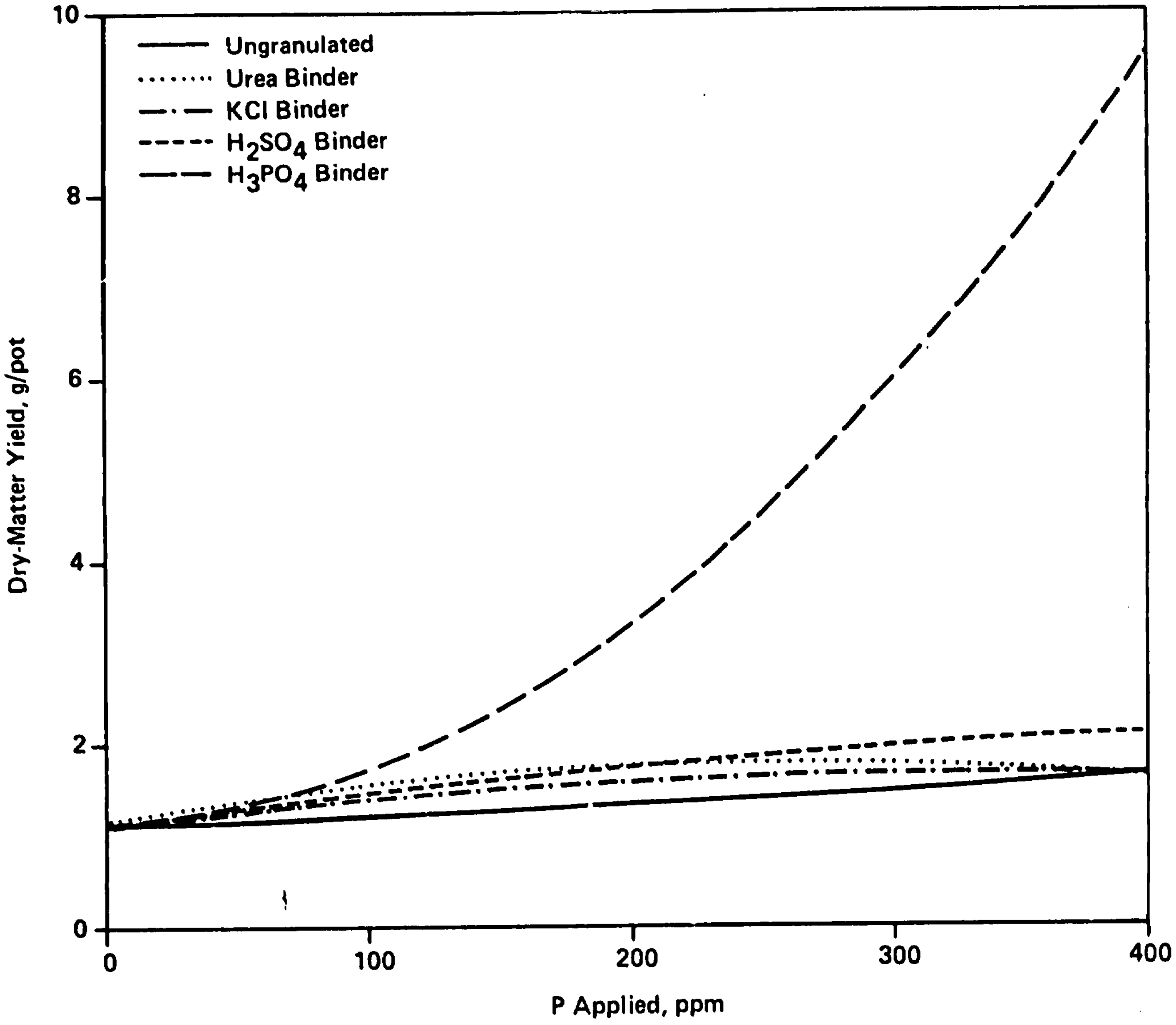


Figure 2. Maize Response to Mussoorie PR (2nd Crop).

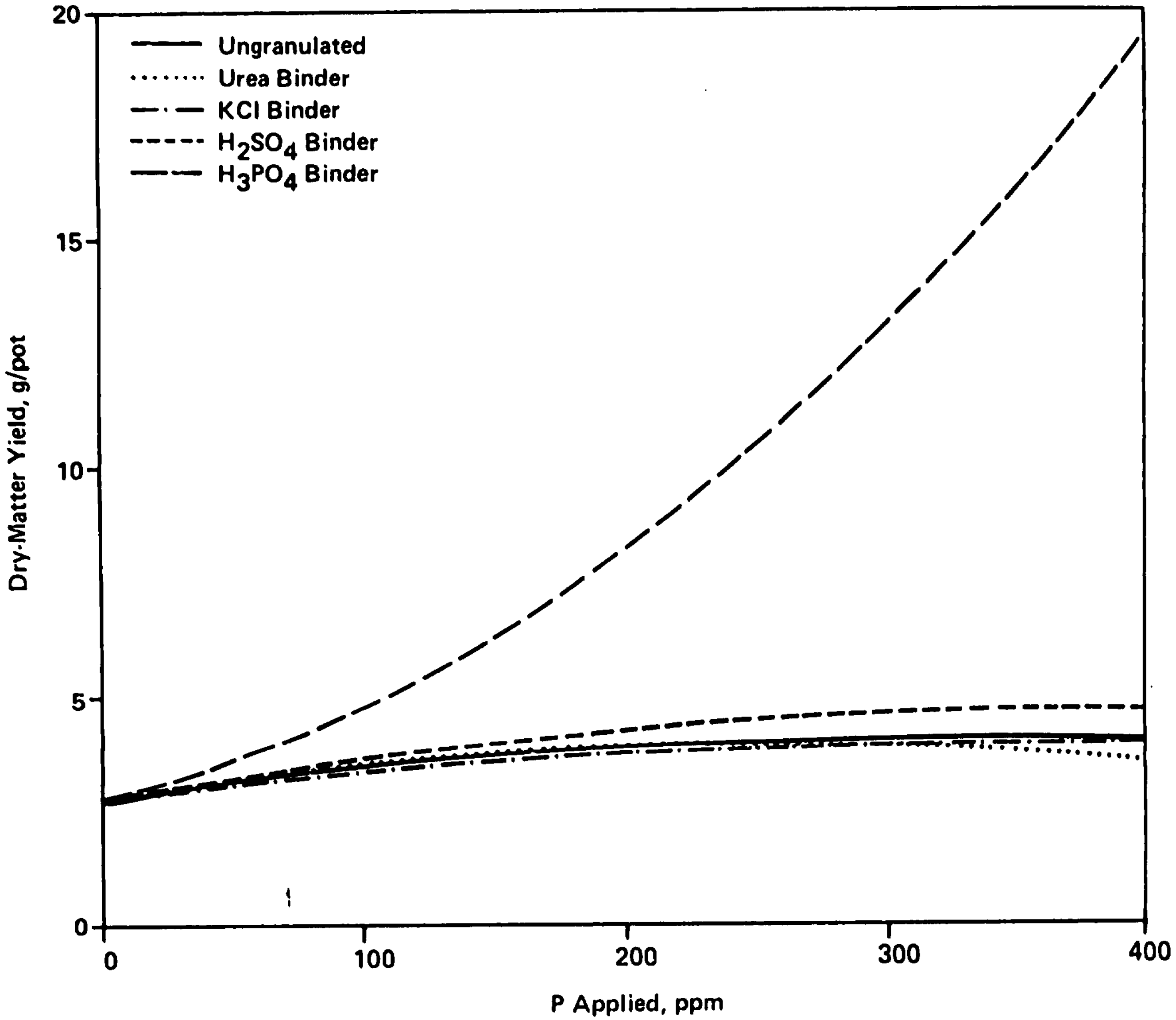


Figure 3. Maize Response to Mussoorie PR (Sum of 2 Crops).

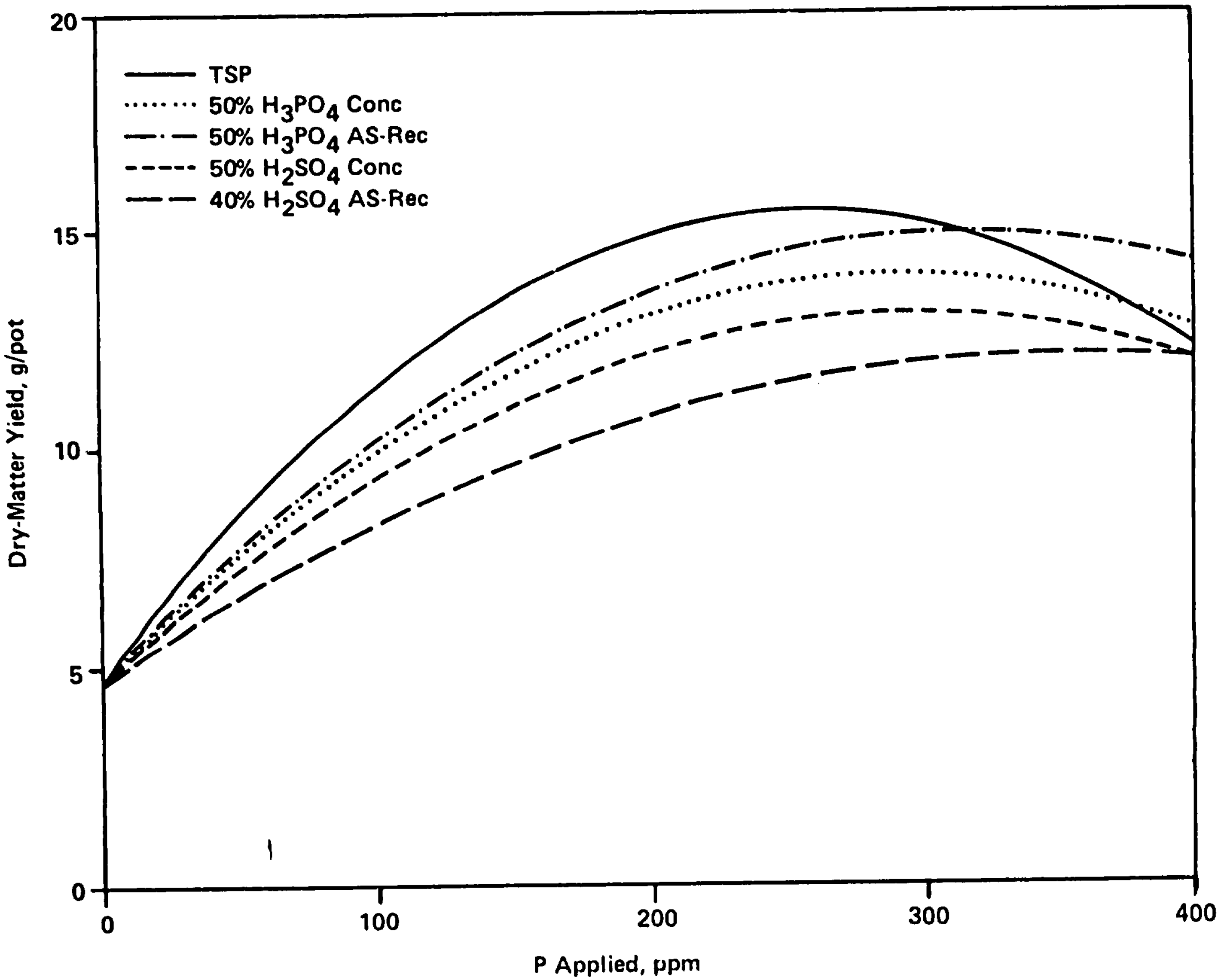


Figure 4. Maize Response to Mussoorie PAPR (1st Crop).

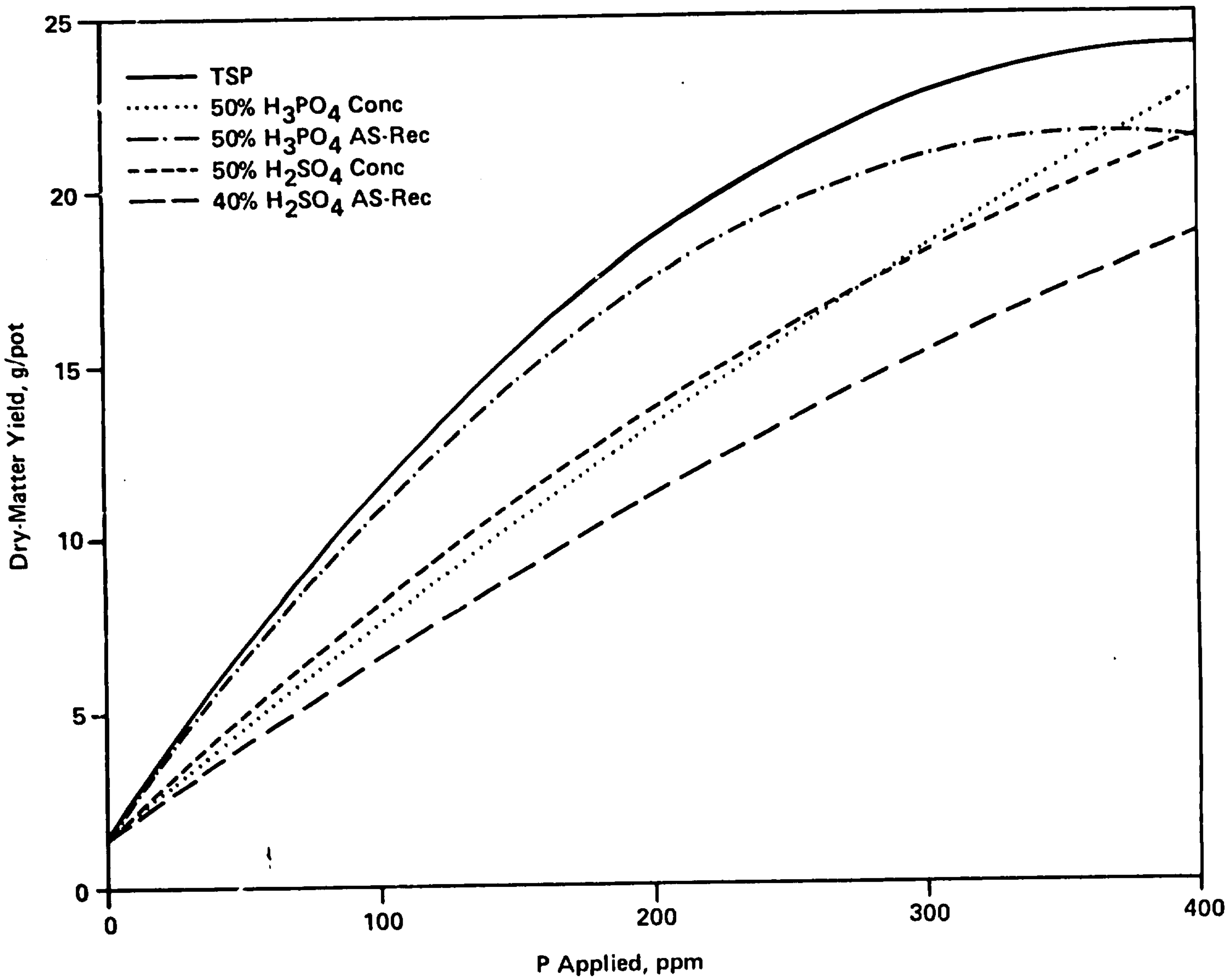


Figure 5. Maize Response to Mussoorie PAPR (2nd Crop).

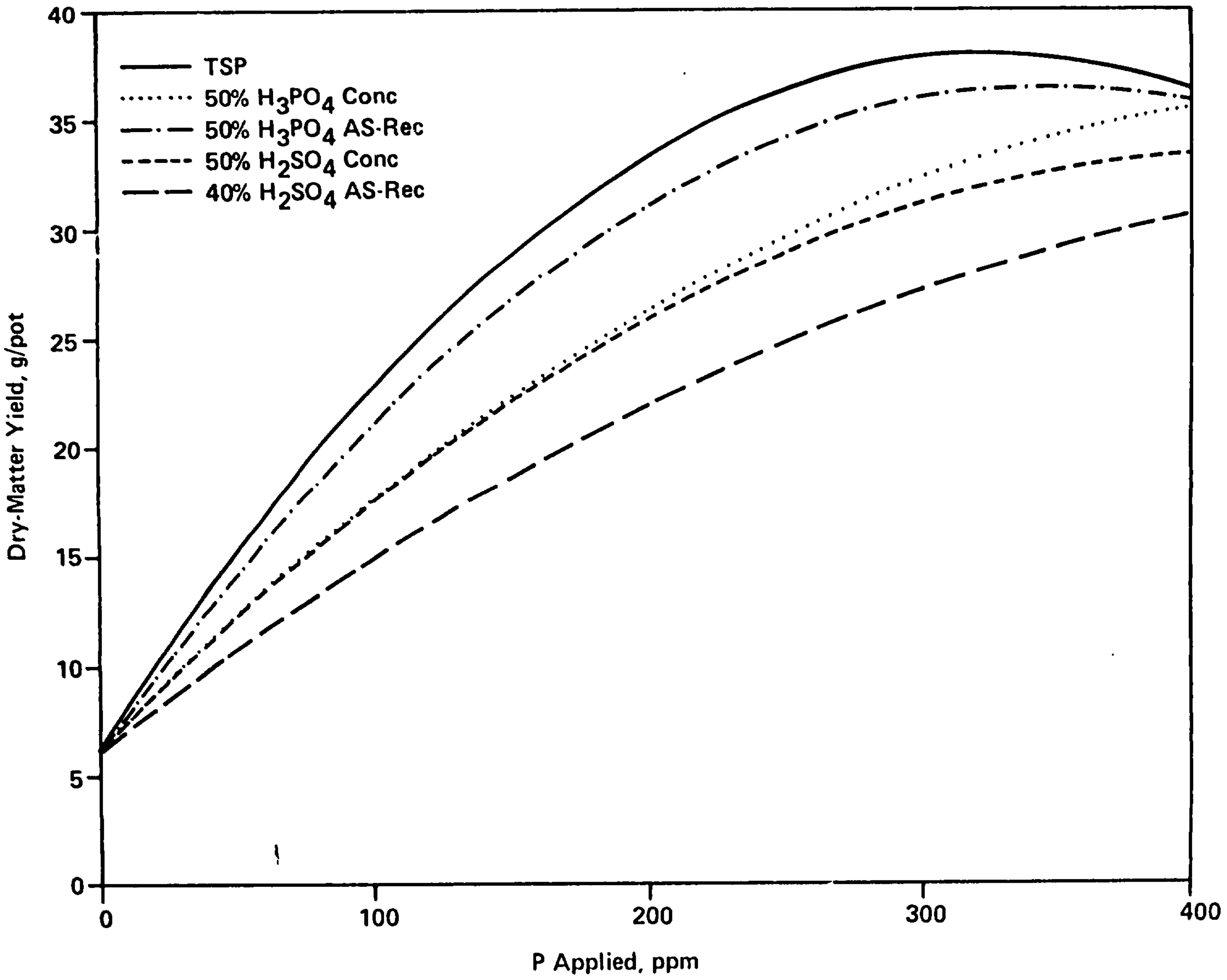


Figure 6. Maize Response to Mussoorie PAPR (Sum of 2 Crops).

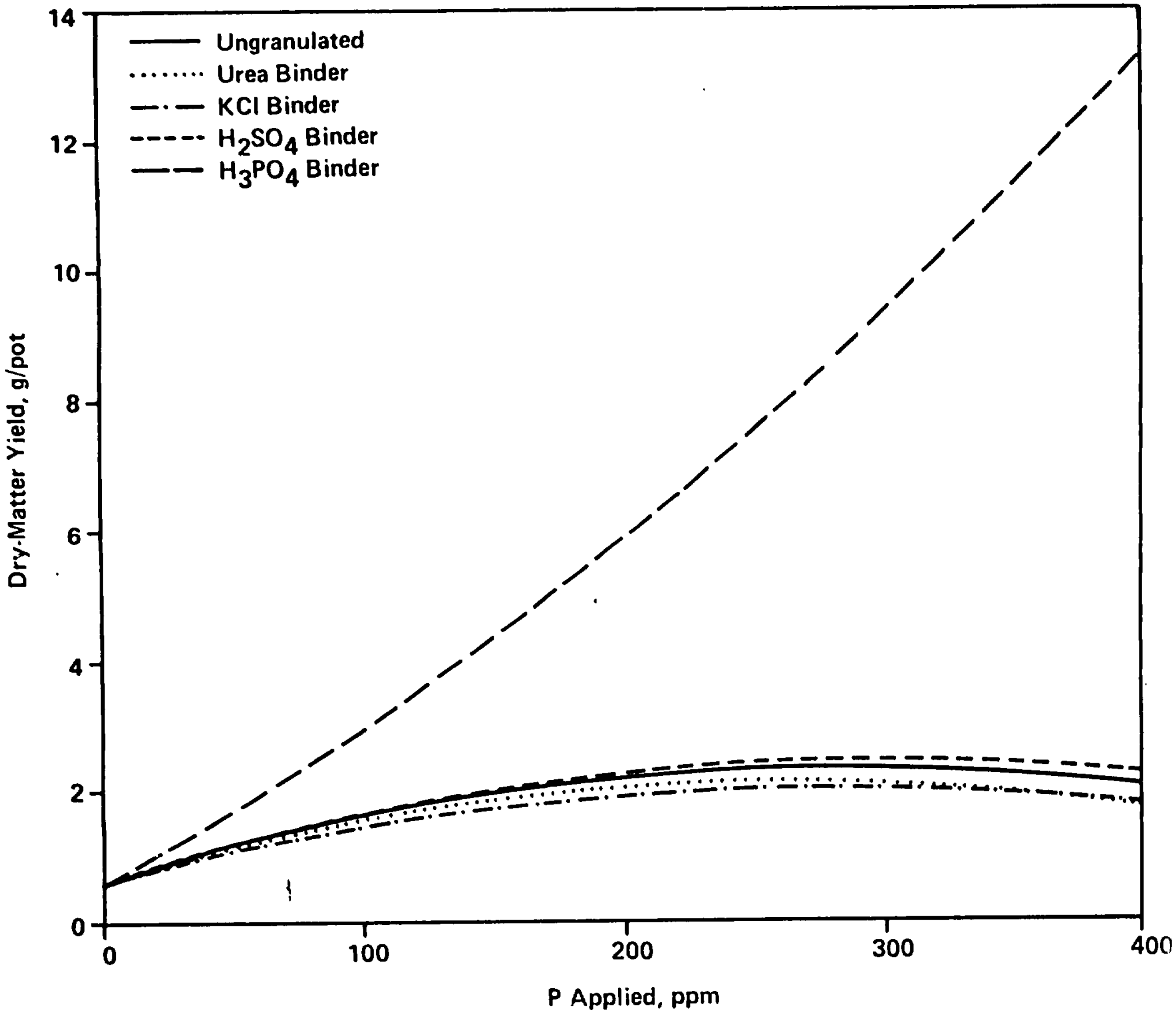


Figure 7. P Uptake by Maize From Mussoorie PR (1st Crop).

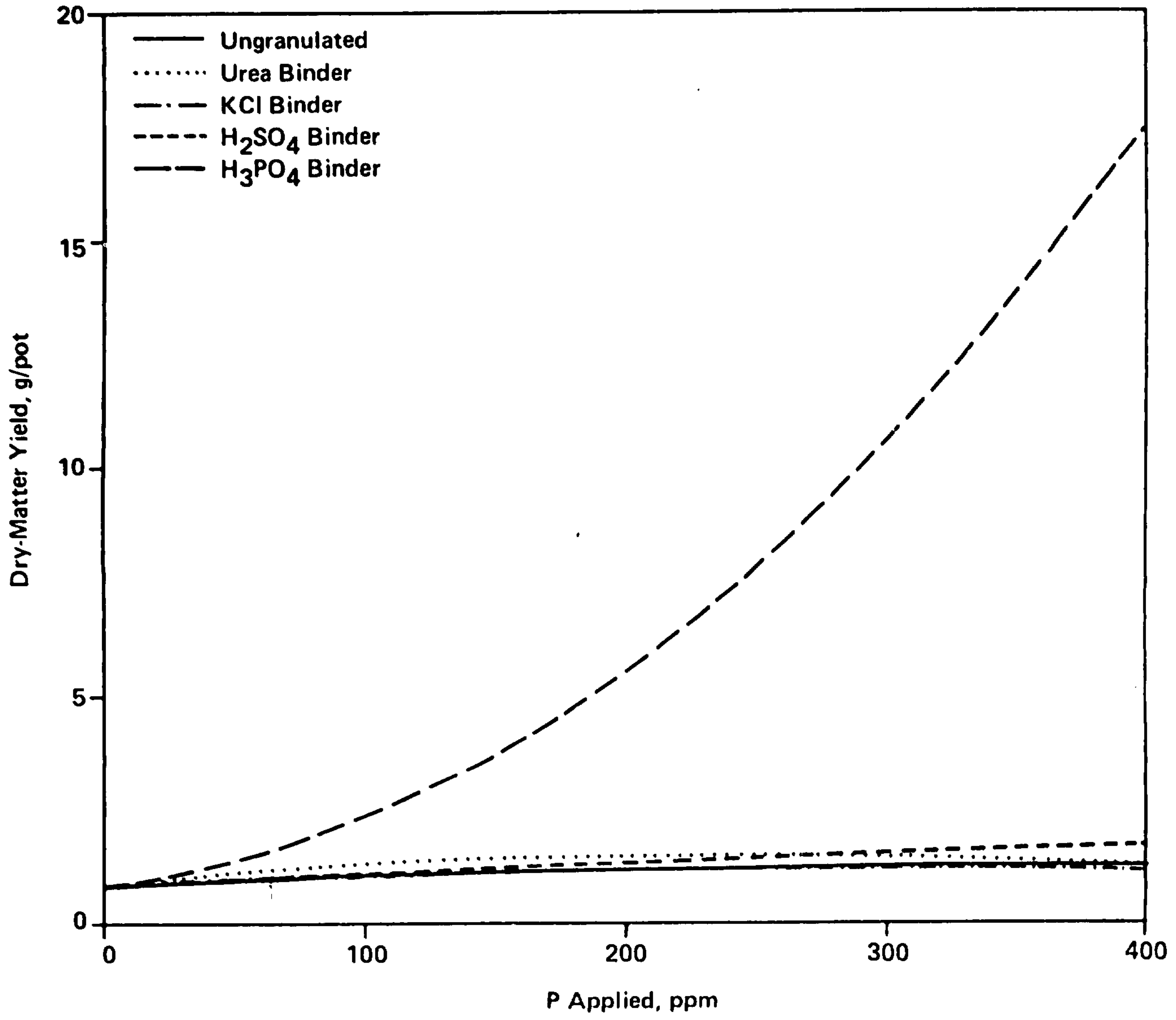


Figure 8. P Uptake by Maize From Mussoorie PR (2nd Crop).

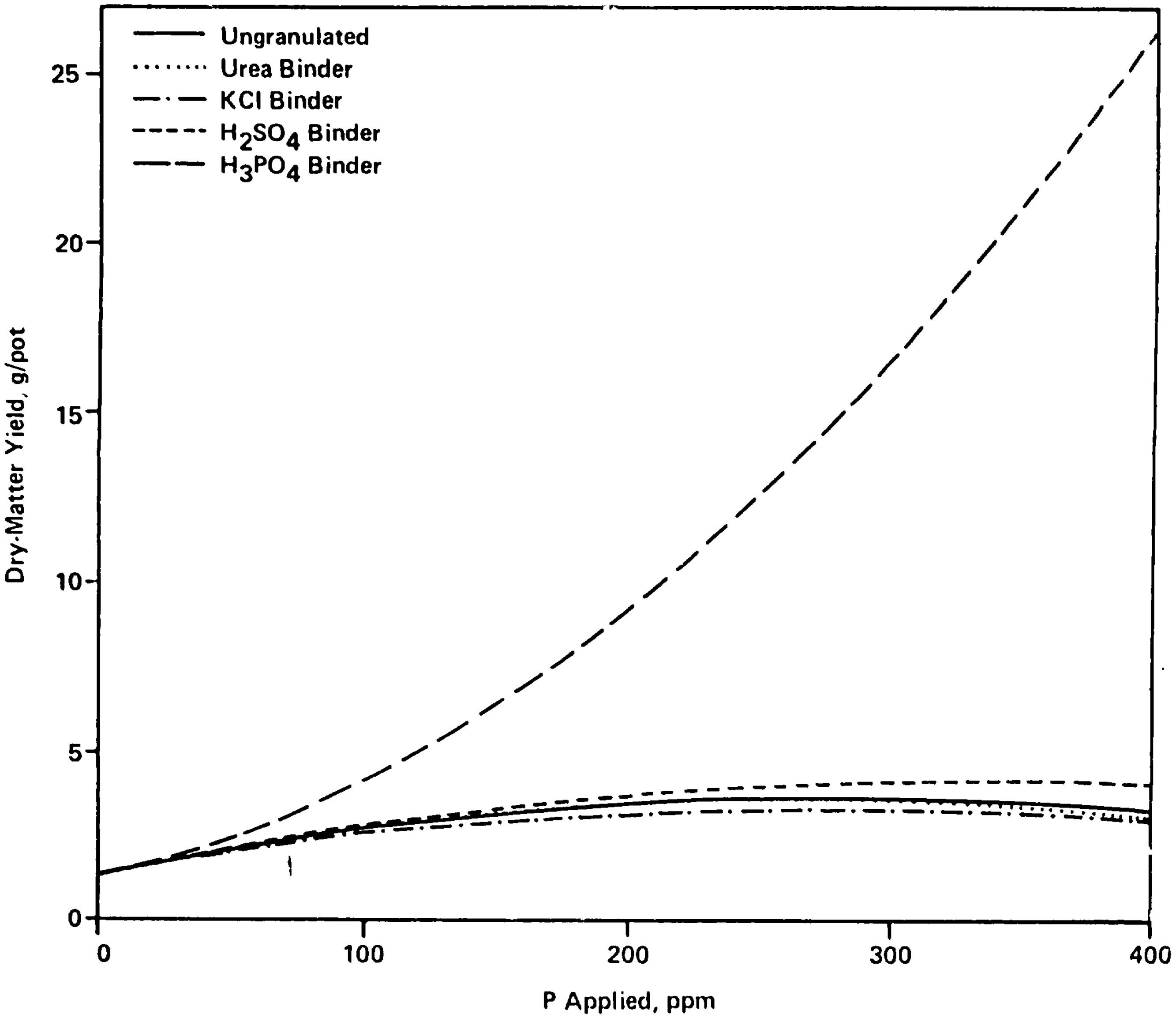


Figure 9. P Uptake by Maize From Mussoorie PR (Sum of 2 Crops).

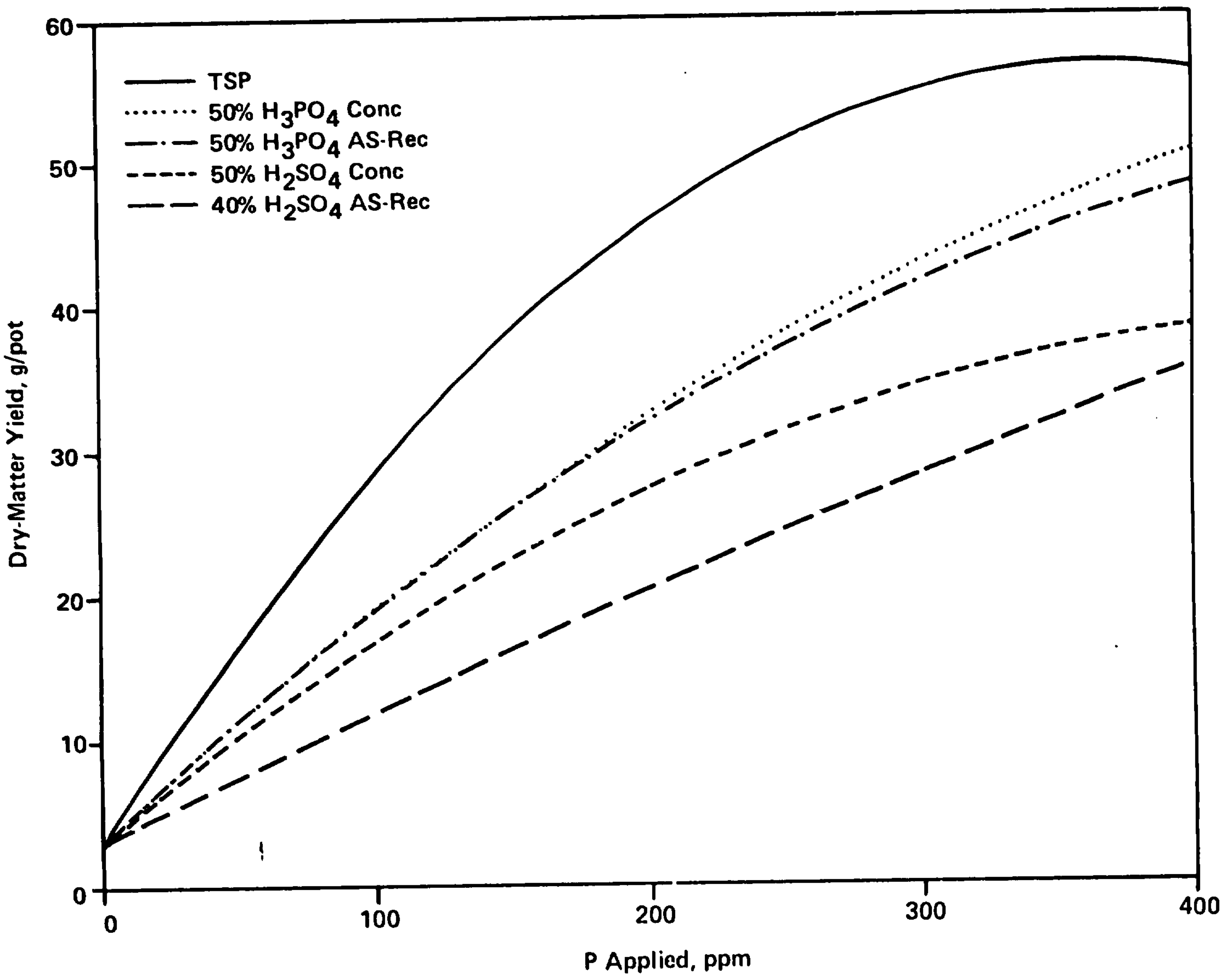


Figure 10. P Uptake by Maize From Mussoorie PAPR (1st Crop).

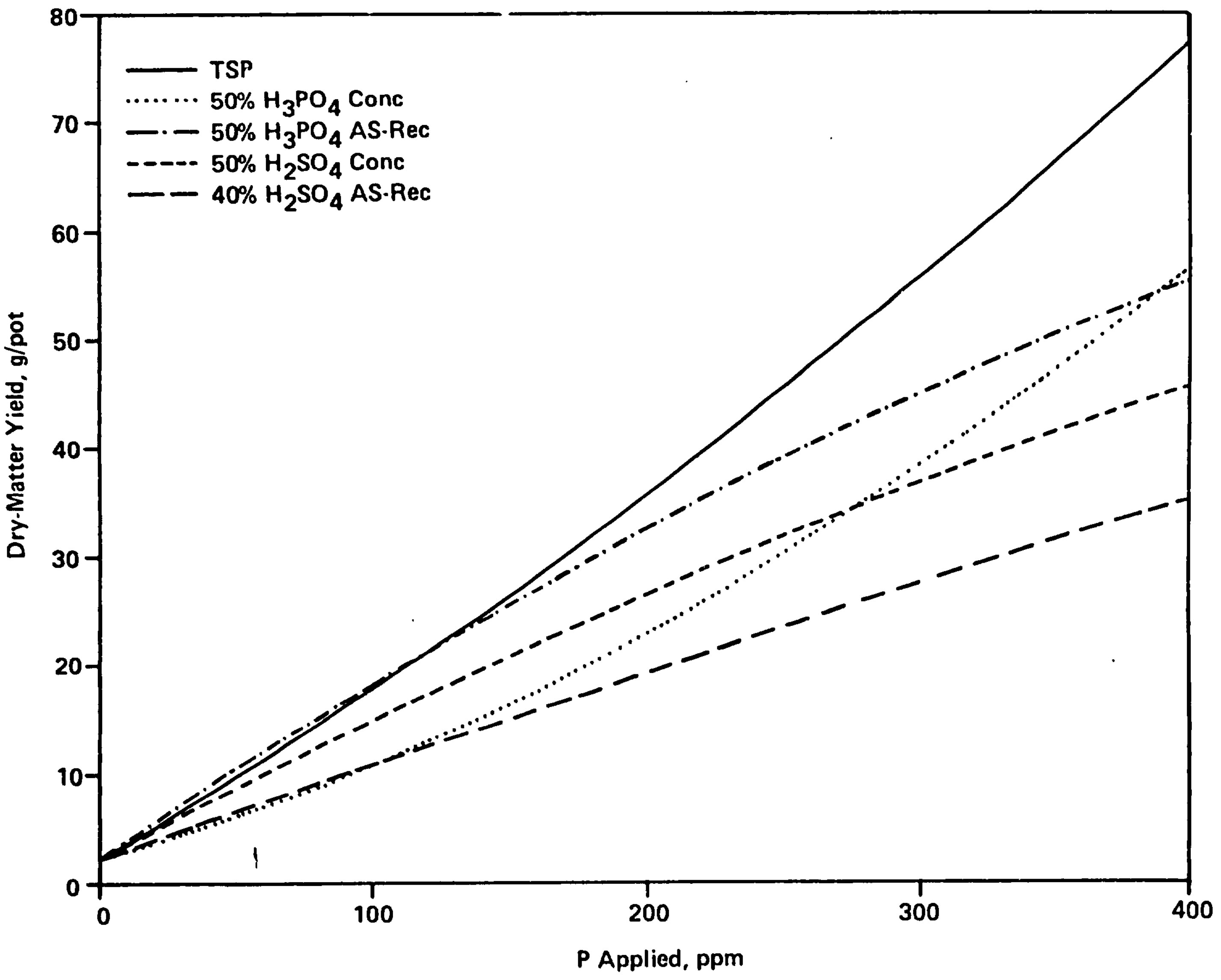


Figure 11. P Uptake by Maize From Mussoorie PAPR (2nd Crop).

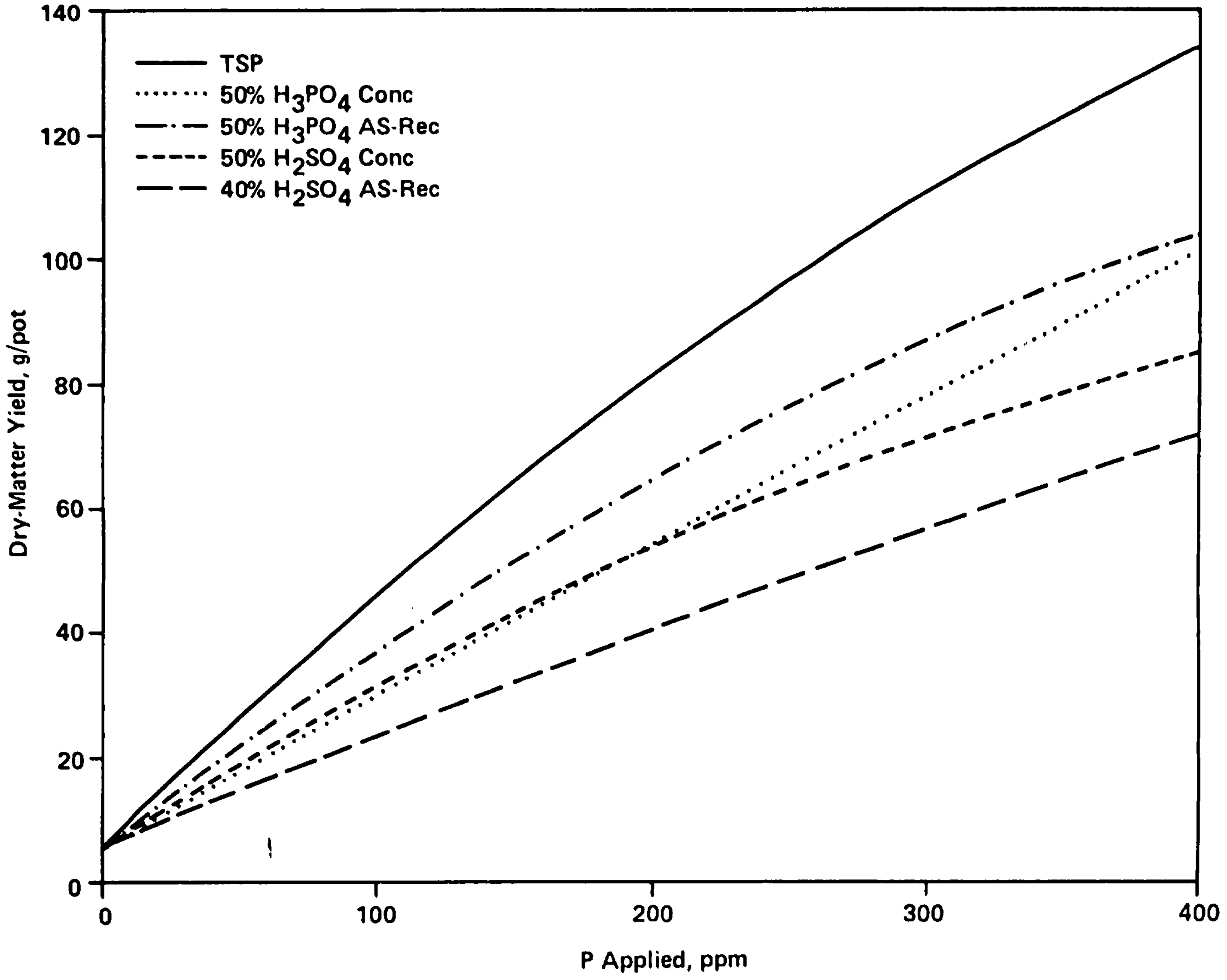
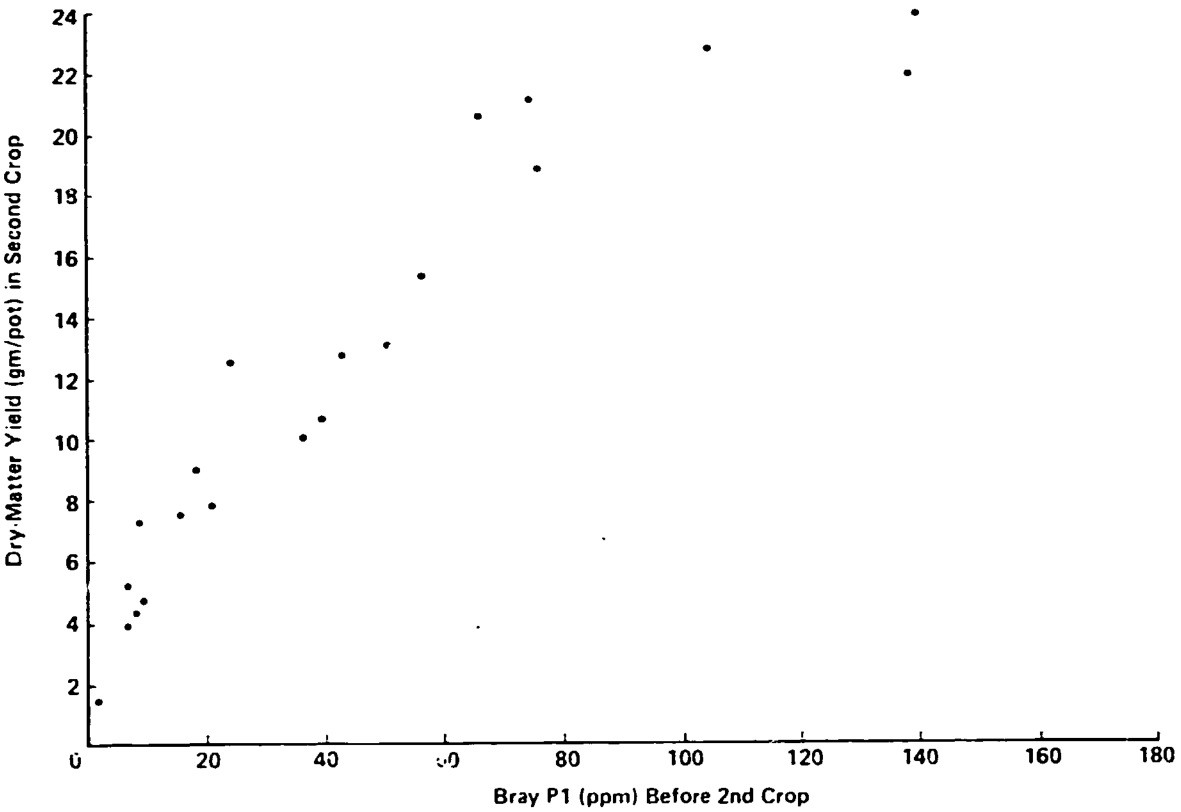


Figure 12. P Uptake by Maize From Mussoorie PAPR (Sum of 2 Crops).

Relationship Between Bray P1 and Dry-Matter Production for Mussoorie PAPRs Applied to Windthorst Soil.



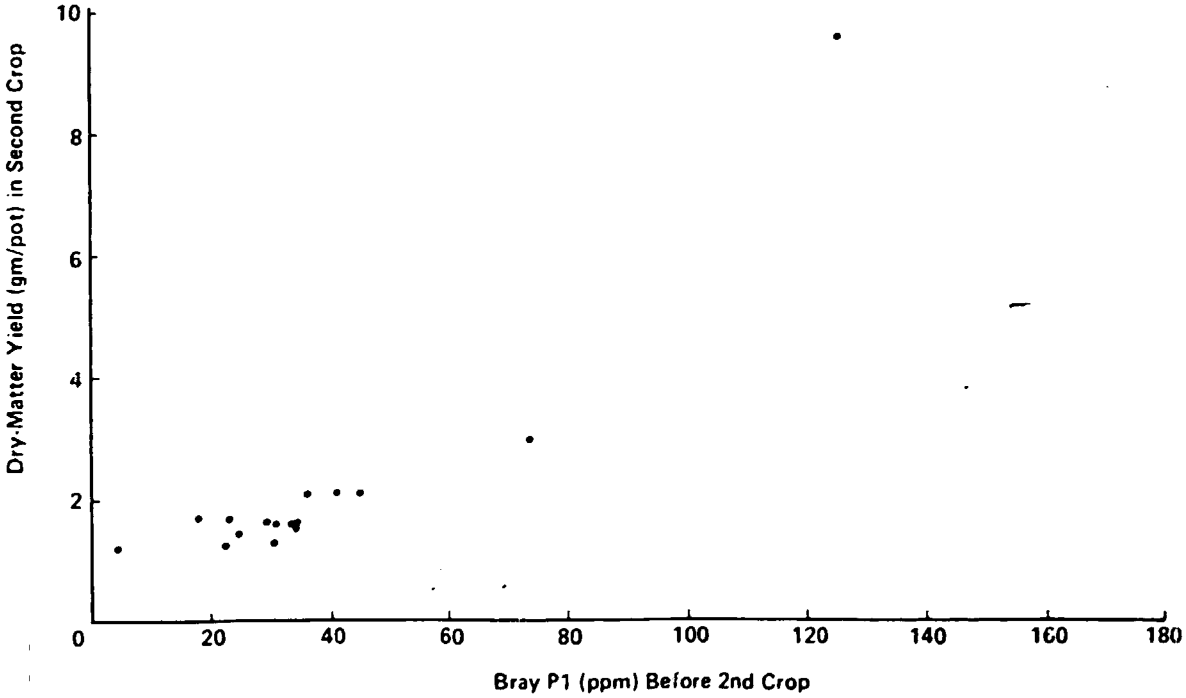


Figure 13. Relationship Between Bray P1 and Dry-Matter Production for Minigranulated Mussoorie PRs Applied to Mountview S Soil.

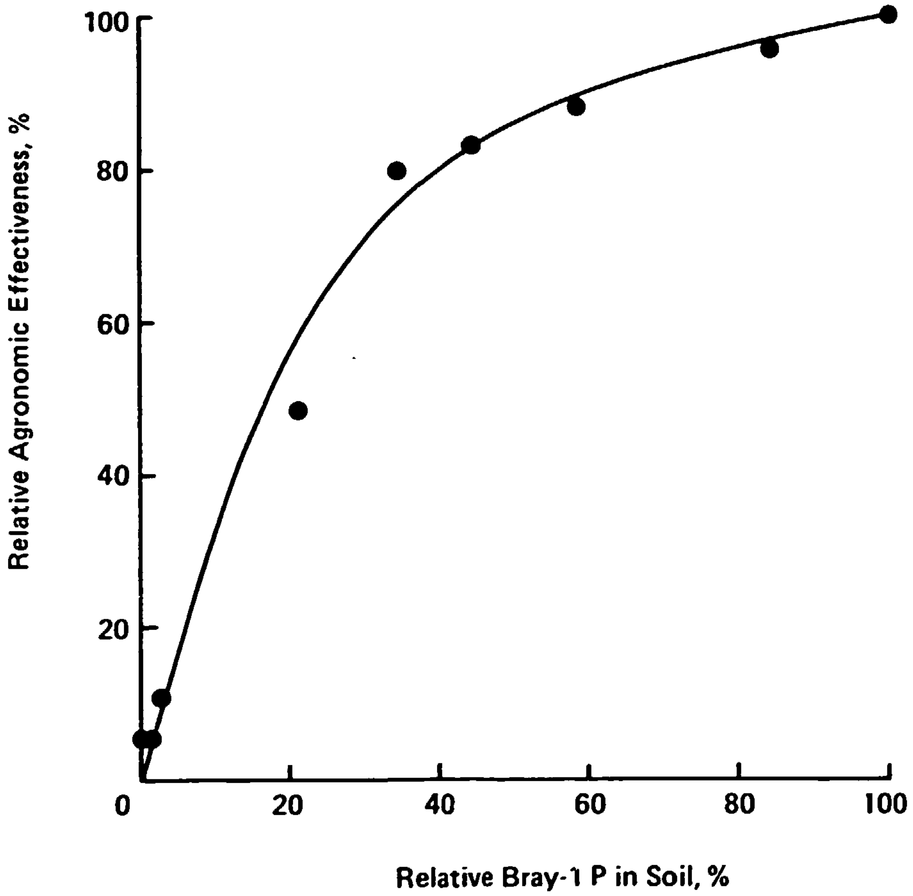


Figure 14. Relationship Between Relative Agronomic Effectiveness and Relative Bray-P1 in Two U.S. Soils (Mountview and Windthorst) Treated With Various P Materials After 3-Week Incubation.

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(2 of 2)

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INVESTIGATIONS TO USE LOW-GRADE ROCK PHOSPHATES FROM MUSSOORIE ROCK PHOSPHATE DEPOSITS--INDIA

Final Technology Report

for

United Nations Industrial Development Organization (UNIDO)
Vienna, Austria

by

International Fertilizer Development Center (IFDC)
Muscle Shoals, Alabama 35662, U.S.A.

June 1985

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INVESTIGATIONS TO USE LOW-GRADE ROCK PHOSPHATES FROM MUSSOORIE ROCK PHOSPHATE DEPOSITS--INDIA

Summary

1. The Mussoorie phosphate rock is composed of carbonate-fluorapatite and calcite, with lesser amounts of quartz, dolomite, and pyrite. The predominant petrographic texture appears to be an equigranular intergrowth of the phosphate, carbonates, and pyrite with some larger carbonate veins.
2. This ore would be classified as low-to-medium grade, containing about 15%-18% P_2O_5. Calcite is the principal diluent with a significantly lesser amount of dolomite. The quality of the ore is further diminished by the presence of pyrite (5%) and dolomite (5%).
3. The work index (Bond) is 11.7, indicating that this rock would be no harder to grind than the "average" phosphate rock.
4. Acid-medium attrition scrubbing of the run-of-mine (ROM) Mussoorie phosphate to reduce its carbonates content is feasible; however, the rock feed needs to be finely ground prior to attrition scrubbing, preferably to a size in which the carbonates are essentially liberated from phosphate. Best results were obtained when the ore was ground to 80% by weight, smaller than 0.075 mm (200-mesh, Tyler). When sulfuric acid was used, the feed had to be ground to the liberation size with the least amount of fines possible. Gypsum slimes that formed during the reaction were discarded.
5. The amount of acid required was at least 100% of the stoichiometric amount needed for the decomposition of carbonates in the ore. The acid requirement was based on the CaO contained in calcite assuming that all of the CO_2 in the ore was present as calcium carbonate. Lower acid dosages gave poor results.
6. The acids tested were found to affect the P_2O_5 grade of the scrubbed product in the following order:

$$5\%\ HCl > 5\%\ HNO_3 > 2\%\ HNO_3 > 5\%\ HNO_3 + 5\%\ H_2SO_4 > 2\%\ HNO_3 + 5\%\ H_2SO_4 > 5\%\ H_2SO_4$$

7. Because of the phosphate loss and the potential corrosion problems, hydrochloric acid is not recommended for attrition scrubbing of Mussoorie phosphate rock.
8. The suitable residence time for attrition scrubbing was found to be about 15 minutes. After that time the pH of the pulp ceased to change, which indicated that the reaction between the acid and the carbonates was essentially completed.
9. The pH value of the pulp during the scrubbing process varied with the type and concentration of acid used. Generally, the pH level was between 2.0 and 4.0.
10. The intensity of scrubbing proved to have only a minor effect on the P_2O_5 grade and the efficiency of the process.
11. The percentage of solids in the slurry during attrition scrubbing varied with the type and concentration of acid used. In 2% HNO_3 solution, the pulp density was less than 5%; therefore, attrition scrubbing in 5% HNO_3 is recommended.
12. The nitric acid consumption for attrition scrubbing of ROM Mussoorie rock was 576 kg/mt product on a 100% HNO_3 acid basis.
13. The physical and handling properties (especially dustiness) of the ROM, as-received, ground Mussoorie phosphate rock can be improved through minigranulation using such binders as urea solution, potassium chloride solution, sulfuric acid solution, phosphoric acid solution, and urea plus nitric acid solution.
14. The pinmixer granulator used for minigranulation worked satisfactorily, but the abrasive nature of the Mussoorie phosphate rock caused pin wear in the pinmixer (with all the binders) to be higher with this rock than with commercial rocks, such as Florida. The use of urea and urea plus 2% nitric acid solutions resulted in the most severe pin wear, and the phosphoric acid solution caused the least amount of pin wear.
15. The pinmixer operation had less plugging with the potassium chloride, sulfuric acid, and phosphoric acid solutions than with the urea and urea plus nitric acid solutions.
16. The small size of the minigranules (minus 0.300 plus 0.106 mm [minus 48- plus 150-mesh, Tyler]) led to blinding, which made screening difficult.
17. The single-step acidulation granulation (SSAG) process of the ROM Mussoorie phosphate rock for producing granular partially acidulated phosphate rock

(PAPR) using sulfuric acid was extremely difficult to control because of product stickiness (ex-granulator and dryer discharge). Further, the desired level of product water solubility (≅50%) could not be achieved. Even when the amount of sulfuric acid used was reduced to obtain about 30% water solubility in the product, the operation was marginal and extremely sensitive to free acid content of the granulator discharge. A slight excess of free acid (due to fluctuation in the acid/rock ratio) caused buildups in the chutes, dryer, screens, and crusher. Further the dried product tended to be sticky and soft.

18. The operation and the product strength can be improved by pretreatment of the ROM Mussoorie rock with phosphoric acid followed by acidulation with sulfuric acid.

19. In contrast to the sulfuric acid acidulation, the phosphoric acid acidulation of the as-received rock in the SSAG process was quite simple and the operation was trouble free. The P_2O_5 water solubility in the product was about 50%.

20. In comparison with the as-received rock, the attrition-scrubbed material (prepared using 5% HNO_3 solution) was well suited for the SSAG process. With either sulfuric or phosphoric acid, the products had the desired chemical property of about 50% water-soluble P_2O_5.

21. The Mussoorie phosphate concentrate (prepared by Sala International, Sweden) also was suitable for producing granular PAPR using the SSAG process. Further, this concentrate also was amenable to the production of a semi-granular, relatively nondusty PAPR product using the run-of-pile (ROP) process. In both processes 83% sulfuric acid was found to be suitable. When 93% sulfuric acid was used, the operation was difficult to control, and the product was quite sticky at 50% product water solubility.

Introduction

India has very meager resources of high-grade phosphate rock. Therefore, substantial quantities of the required grades of commercial phosphate concentrates are being imported for use as feedstock for the manufacture of fertilizers. This importation of raw materials causes a severe drain on the country's foreign exchange resources. The country possesses about 115 million mt of low-grade phosphorites of which about 45 million mt (with an average P_2O_5 content of 18%) occurs in the Mussoorie area in the State of Uttar Pradesh.

Major deposits in this area contain carbonates, silica, and other gangue materials, which render it difficult to beneficiate. Pyrites, Phosphates & Chemicals Ltd. (PPCL), a Government of India undertaking, is presently mining, crushing, and grinding this low-grade material. This finely ground phosphate rock is sold to farmers for direct application on acidic soils of southern and eastern India, about 2,500 km from the deposits.

The finely powdered form of this direct-application material, which is dusty, causes difficulties in transportation and results in large losses and farmers' unfavorable response to the product. Hence, there is a need to improve the physical properties of the product without impairing its agronomic performance. The International Fertilizer Development Center (IFDC) has been experimenting with a granulation process using a pinmixer granulator for producing minigranules (small granules) of phosphate rock. These small granules (minus 0.300 plus 0.106 mm [minus 48- plus 150-mesh, Tyler]) are relatively nondusty and free flowing compared with the original finely ground rock. Granule strength, in most cases, is sufficiently high for handling and application. By use of the proper binder to promote granulation, the particles disintegrate upon exposure to soil moisture and thus revert back to the powder form.

In addition to direct application, PPCL is interested in furthering the use of this locally available material through partial acidulation and granulation of run-of-mine (ROM) and beneficiated rocks using sulfuric and phosphoric acids. Partial acidulation implies the use of only a portion of the acid normally required to produce single or triple superphosphate (SSP) (TSP). Beneficiation of the rock may involve attrition scrubbing with a dilute acid (sulfuric/hydrochloric) to reduce the carbonate content and consequently increase the P_2O_5 grade. IFDC has developed a single-step acidulation granulation (SSAG) process in continuous bench-scale equipment for production of granular partially acidulated phosphate rock (PAPR). The partially acidulated material contains a varying amount of water- and citrate-soluble P_2O_5 (neutral ammonium citrate [NAC]) and citrate-insoluble P_2O_5, depending on the quantity of acid used and the reaction conditions. Such materials are being evaluated on acid soils in Latin America and Africa. These materials have been found to be agronomically effective in comparison with superphosphates.

On December 30, 1982 (telex), the United Nations Industrial Development Organization (UNIDO), on behalf of PPCL, contracted with IFDC for both a laboratory-scale evaluation of minigranulation and partial acidulation processes with phosphate rock from the Mussoorie District in northern Uttar Pradesh, India, and laboratory and agronomic tests in the greenhouse with experimental products made from this rock. These and other tests specified in the "Terms of Reference" of the agreement form the basis of the contract between UNIDO (Contract No. 82/99; Project No. DP/IND/81/019) and IFDC (IFDC-00519/83).

This project was initiated in January 1983 after receipt of a 10-kg sample of Mussoorie phosphate rock which was used for mineralogical and chemical characterization studies. Subsequently, in May 1983 IFDC received 12 mt of ground ROM Mussoorie rock and 8 mt of crushed ROM Mussoorie rock for laboratory-scale minigranulation and partial acidulation studies. In January 1984 IFDC also received about 1 mt of Mussoorie concentrate prepared by Sala International, Sweden. This concentrate was used for demonstration of the SSAG process.

During this project PPCL representatives and PPCL and UNIDO representatives visited IFDC in June and November 1983, respectively, to review the progress and discuss the results. In December 1983 a PPCL engineer visited IFDC to discuss the production economics of minigranulation and partial acidulation processes, and in March 1984 three PPCL representatives visited IFDC to observe the minigranulation and partial acidulation process-demonstration trials and to discuss the results of the greenhouse and laboratory soil incubation studies.

IFDC was responsible for coordinating all of the activities and reporting the results. This is the Final Report on the technology phase of the project and incorporates the comments formulated by the PPCL staff, on the Draft Final Report, during the review meeting held at IFDC on March 4, 1985. The Final Report containing the soil incubation and greenhouse studies is being reported separately in accordance with the contract.

Scope of Work and Objectives

The objectives of the project were to (1) identify a substitute for imported high-grade phosphate rocks (being used at present as feedstock for domestic production of phosphate fertilizers in India) and (2) establish alternatives other than direct application of locally available low-grade Mussoorie phosphate rock in order to further commercial exploitation of this indigenous resource. During bench-scale tests attempts were made to improve the physical and handling properties of the rock by minigranulation using such binders as sulfuric acid, phosphoric acid, potassium chloride solution, and urea solution, without impairing the agronomic effectiveness of finely ground rock presently being used as a direct-application fertilizer. Additionally, the project attempted to determine the technical feasibility of producing a solid phosphate fertilizer containing about 50% of its total P_2O_5 in a water-soluble form by partial acidulation/granulation of ROM and beneficiated (attrition-scrubbed) rocks using sulfuric and phosphoric acids in the SSAG process. Furthermore, the project included a study to agronomically evaluate the experimental products (minigranulated and partially acidulated) under greenhouse conditions.

Specific activities of the project to meet the above objectives were as follows:

1. Complete chemical and mineralogical characterization of Mussoorie phosphate rock.
2. Beneficiation of the ROM Mussoorie phosphate rock through attrition scrubbing with a dilute acid (sulfuric/hydrochloric/nitric and some combinations).
3. Evaluation of ROM, as-received, ground Mussoorie phosphate rock through continuous laboratory-scale tests for production of minigranules using sulfuric acid, phosphoric acid, potassium chloride solution, and urea solution as binders to promote granulation.
4. Evaluation of ROM and beneficiated Mussoorie phosphate rocks through continuous laboratory-scale tests using sulfuric and phosphoric acids in the SSAG process for production of granular PAPR.
5. Evaluation of the physical properties of minigranulated and partially acidulated products.
6. Soil incubation studies with the experimental products using up to five soil samples from India.
7. Greenhouse evaluation at IFDC of the experimental products.

8. Demonstration of the attrition scrubbing, minigranulation, and SSAG processes to the PPCL engineers for transfer of technical know-how.
9. Reporting of results in a clear, concise manner to PPCL and UNIDO.

Raw Materials

IFDC received a 10-kg sample of crushed (13 mm [1/2 inch]) Mussoorie phosphate rock on January 20, 1983. This sample was used for mineralogical and chemical characterization studies. Subsequently, on May 12, 1983, IFDC received 12 mt of ground (80% minus 0.075 mm [200-mesh, Tyler]) and 8 mt of crushed (minus 13 mm [1/2 inch]) ROM Mussoorie phosphate rock in seventy-seven (77) 55-gal metal drums. Each drum was inspected, labeled (ground or crushed), and numbered. Four drums each of ground and crushed samples were selected at random and sampled for chemical analyses. Although the variation in chemical composition among the drums of ground material was quite small, the variation was significant for the crushed sample. This variation was reduced by jaw crushing the as-received crushed rock to 100% minus 9.5 mm (3/8 inch). The chemical analyses of the ground and jaw-crushed samples are shown in Table 1.

On January 11, 1984, IFDC received about 1 mt of crushed (100% minus 25 mm) Mussoorie phosphate concentrate prepared by using a heavy-media separation technique by Sala International, Sweden. This concentrate was used for the SSAG process demonstration runs. The chemical analysis of this sample is shown in Table 2.

Physical, Chemical, and Mineralogical Characterization of Mussoorie Phosphate Rock

Preliminary studies by IFDC on the characterization of Mussoorie phosphate rock showed carbonates of calcium and magnesium and sulfides of iron to be the main impurities, with carbonates being intimately mixed with the apatite (1). As part of this project, a fres. representative sample was characterized, including detailed chemical, mineralogical, and textural studies as well as reactivity and particle-size analysis. This type of work identifies the kinds and amounts of impurities present and the relationship of the components in the rock fabric. The 10-kg sample received at IFDC on January 20, 1983, was assigned IFDC inventory No. R231.50 and used for this study.

Mineralogical Characterization

An approximate mineralogical composition derived from petrographic and x-ray diffraction (XRD) examinations (Appendix A) is tabulated as follows:

Compound	Composition	Approximate Weight %
Apatite	See text	35
Calcite	$CaCO_3$	45
Dolomite	$(Ca,Mg)(CO_3)_2$	5
Pyrite	FeS_2	5
Quartz	SiO_2	10
Organic matter	C	1
Clay	Variable	2

The sample contains about 30%-40% apatite and should be classified as a low- to medium-grade ore. Calcite and dolomite are the principal diluents. Pyrite (FeS_2) is also present in the ore. Silica in the ore occurs primarily in the form of quartz with minor amounts of clay (muscovite and/or illite). This estimated mineralogical composition corresponds well with the chemical analysis, indicating that no important mineral components have been omitted.

Textural Description

Rock fragments of the Mussoorie ore examined are of two textural types. One type is predominately coarse-grained sparry carbonate and phosphatic clasts; the other is a fine-grained intergrowth of apatite, quartz, and carbonate gangue. Macroscopically, the rock is a dark gray to very dark gray (2.5Y4/0-2.5Y3/0 Munsell color chart) compact laminated siltstone. Coarse veinlets of calcite can be seen between and crosscutting the laminae (Figure 1).

Under the polarized-light microscope, the coarse-grained areas of the rock consist of angular to subrounded clasts of isotropic apatite (Figure 2). These clasts appear dark gray and contain small inclusions of both quartz and calcite (Figure 3). No internal structure, such as oolitic laminations, is seen in the clasts, but some of the clasts have a thin (10-20 μm) outer layer of secondary apatite. The clasts shown in Figure 4 range in size from 50 μm to several millimeters. Inclusions in the clasts average about 30-50 μm.

Pyrite occurs as crystalline particles in the apatite and the carbonate (Figure 5). Average grain size of the pyrite ranges from 10 to 50 µm. In some areas of the rock, pyrite fills the cracks and surrounds the apatitic clasts. The XRD analysis of 10% HCl-insoluble material revealed that no other sulfide or silicate minerals are present in significant quantities.

Phosphatized fossil fragments are also present in the ore but are less abundant than the clasts. Because of their shape and fibrous texture, these fragments appear to be particles of shells (Figure 6).

The second ore texture observed in the Mussoorie ore is fine grained and characterized by an intergrowth of apatite, carbonate, and quartz with minor amounts of pyrite (Figure 7). The mineral species are nearly equal in grain size, ranging from 30 to 100 µm. The fine-grained texture can be seen grading into the coarser, sparry material.

The XRD patterns for the Mussoorie ore confirm the presence of apatite, calcite, and quartz with minor amounts of dolomite. A sample of HCl-insoluble material consisted of pyrite and quartz. One clay mineral--illite--was also identified, and this accounted for the trace amounts of K and Al in the ore.

Apatite Composition

Carbonate-fluorapatite (francolite) was the only phosphate mineral identified. XRD methods were used to determine the unit-cell parameters, which were measured as follows:

$$a = 9.352 \pm 0.001\ \text{Å}$$

$$c = 6.888 \pm 0.001\ \text{Å}$$

The mean refractive index of the apatite was 1.630 ± 0.002.

The unit-cell dimensions correspond to a francolite with the following empirical formula:

$$Ca_{9.80}\ Na_{0.14}\ Mg_{0.06}\ (PO_4)_{5.42}\ (CO_3)_{0.58}\ F_{2.23}$$

The theoretical P_2O_5 content for this francolite composition is 38.81%.

Chemical Composition

The sample was analyzed for its principal constituents using x-ray fluorescence and wet-chemical methods (Table 3). The ratio of CaO/P_2O_5 is very high because the ore contains more than 30% calcite. The ratio of R_2O_3/P_2O_5 or $(MgO + Al_2O_3 + Fe_2O_3)/P_2O_5$ is 0.38. This is significantly higher than the 0.12 ratio that is considered acceptable for commercial ores. The MgO content of the ground ore is 1.4%, which is slightly higher than the 1% desirable level for production of wet-process phosphoric acid. The chloride content is within the acceptable limits for chemical processing.

Evaluation of Rock Reactivity

Neutral ammonium citrate was used to determine the P_2O_5 solubility of the Mussoorie rock sample. The plot of this value and that predicted from XRD analysis is shown in the reactivity scale (Figure 8). The NAC solubility values are lower than the 2.0%-2.5% NAC-soluble P_2O_5 reported for other samples from the Mussoorie deposit. This variation seems to indicate that the reactivity of the ore may vary from one part of the deposit to another. These values indicate rather low reactivity compared with that of other sedimentary apatites.

Suggestions for Beneficiation

In order for the Mussoorie rock to be of commercial value, the calcite and dolomite contents must be lowered significantly. Beneficiation problems that would be encountered in the processing of the Mussoorie rock are primarily related to the intimate intergrowth of apatite, carbonate, and pyrite. Fine grinding of the ore will be necessary to liberate the gangue minerals.

A liberation study was made on the ore to determine the amount of grinding necessary to produce an acceptable percentage of liberated apatite particles. Liberation of an ore is required for the successful application of any of the various beneficiation processes.

To determine the liberation size of Mussoorie rock, samples of four screen fractions were point-counted (Table 4). A ground ore is considered sufficiently liberated when 80% or more of the ore particles are free. In the Mussoorie ore, this percentage is reached when grinding reduces the particle size to minus 100-mesh. The minus 100- plus 200-mesh fraction contained only 18% locked grains. This is somewhat smaller than the particle size used for conventional flotation (minus 0.425 plus 0.106 mm [minus 35- plus 150-mesh, Tyler]).

The grindability of a rock (i.e., its work index) is a measure of the energy required to reduce a rock from an infinite particle size to a finite particle size. One method for measuring grindability uses the procedure and equipment described by Bond (2). The work index (Bond) for Mussoorie rock (expressed as kWh/short ton) was measured at 11.7, which is in the normal range of values for phosphate rocks. This indicates that grinding of the Mussoorie rock would not require excessive energy.

Beneficiation (Attrition Scrubbing) of Mussoorie Phosphate Rock

The mineralogical characterization of the ROM Mussoorie phosphate rock showed it to contain large amounts of carbonate minerals, mainly calcite and dolomite, which may adversely affect its performance during chemical processing. A number of processes have been developed to decrease the amount of carbonates in a phosphate ore and thus yield concentrates that can be utilized in the preparation of phosphate fertilizers. These include attrition scrubbing in acid solutions, flotation, heavy-media separation, and calcination. Calcination is expensive because of the high energy consumption and the lack of locally available fuels in India. Thus, attrition scrubbing of the ore in an acid medium to remove carbonates seems to be an alternative that might be effective.

This section describes attrition scrubbing tests using various acid solutions in laboratory-scale tests to evaluate process parameters. These conditions provide a basis for pilot-plant preparation of a large sample of concentrate for partial acidulation/granulation studies.

Description of the Sample

As stated earlier, the Mussoorie phosphate rock was supplied to IFDC in two samples: 12 mt finely ground (80% minus 0.075 mm [200-mesh, Tyler]) and 8 mt crushed (minus 13 mm [1/2 inch]). The crushed sample was further reduced in size at IFDC by passing through a jaw crusher. One drum each of the ground and jaw-crushed material was used for the laboratory-scale attrition scrubbing tests. Chemical analysis and size distribution of the as-received ground and the jaw-crushed ROM samples are shown in Tables 5 and 6, respectively. The chemical analysis indicates that the jaw-crushed ore contains 13.8% CO_2 and has a $CaO:P_2O_5$ weight ratio of 2.42. The ground ore contains 15.4% CO_2 and has a $CaO:P_2O_5$ weight ratio of 2.52. The normal $CaO:P_2O_5$ weight ratio of carbonate fluorapatite minerals ranges from 1.32 to 1.60; thus, the chemical data indicate a high percentage of carbonate minerals, mainly calcite, that need to be removed before chemical processing.

Analyses of the various size fractions of the jaw-crushed phosphate sample (Table 7) show that the carbonate minerals are essentially distributed over all the size ranges studied. As expected, the clay minerals are enriched in the fine-size fraction (less than 0.075 mm [200-mesh, Tyler]) that contains a relatively high percentage of alumina, silica, and iron oxides. In order to prepare material to study the effect of particle size on attrition scrubbing, subsamples of the jaw-crushed ore were ground in a ball mill for various periods of time. The ball mill grinding reduced the particle size of the jaw-crushed ore to nearly 80% minus 0.075 mm [200-mesh, Tyler] in only 12 minutes (Table 8).

A series of laboratory-scale attrition scrubbing tests in various acid media were made to determine the effects of a number of variables on the process as well as to identify the conditions to be used in preparation of a sample in the pilot plant.

The variables investigated in attrition scrubbing tests included the following independent variables:

1. Acid type.
2. Acid concentration.
3. pH value of the pulp.
4. Particle size of rock.
5. Scrubbing time.
6. Scrubbing intensity.
7. Percentage of solid in pulp.

The dependent variables measured were P_2O_5 content in the scrubbed product and P_2O_5 recovery.

In the scope of work of this contract, only dilute sulfuric and hydrochloric acids were required to be used for the attrition scrubbing tests. However, during the visit in June 1983, PPCL representatives requested that IFDC also include (1) dilute nitric acid and (2) a mixture of dilute nitric and sulfuric acids. Dilute nitric acid is expected to be produced at the plant site using the "arc process" developed by the Kettering Research Institute, Ohio, U.S.A.

Equipment and Procedure

Attrition scrubbing tests were conducted in a Denver laboratory-scale conditioner. The pH of the pulp was monitored through the use of a pH meter and combination electrode. In this process the ore is tested in acid solutions at various residence times, pH values, solid:liquid ratios, and particle sizes. For best results, the particle-size range should be that in which the carbonate particles are liberated from phosphate particles. The principle of attrition scrubbing is that the dilute acid will readily dissolve the carbonate minerals with a minimum loss of phosphate. The acid-scrubbed material then is filtered, and the phosphate concentrate is recovered as the filter cake. For each test 500 g of rock was used; acid quantity varied as required for the particular test.

The acids tested included nitric, sulfuric, hydrochloric, and mixtures of nitric-sulfuric at a 1:1 ratio. The amount of acid used for an attrition scrubbing test was at least 100% of the stoichiometric amount needed for the decomposition of carbonates. The acid requirement was based on the CaO contained in calcite, with the assumption that all CO_2 in the sample was present as calcium carbonate according to the following equations:

$$\underset{\text{(nitric acid)}}{2HNO_3} + \underset{\text{(calcium carbonate)}}{CaCO_3} \rightarrow \underset{\text{(calcium nitrate)}}{Ca(NO_3)_2} + \underset{\text{(carbon dioxide)}}{CO_2\uparrow} + \underset{\text{(water)}}{H_2O} \tag{1}$$

$$\underset{\text{(sulfuric acid)}}{H_2SO_4} + \underset{\text{(calcium carbonate)}}{CaCO_3} \rightarrow \underset{\text{(calcium sulfate)}}{CaSO_4} + \underset{\text{(carbon dioxide)}}{CO_2\uparrow} + \underset{\text{(water)}}{H_2O} \tag{2}$$

$$\underset{\text{(hydrochloric acid)}}{2HCl} + \underset{\text{(calcium carbonate)}}{CaCO_3} \rightarrow \underset{\text{(calcium chloride)}}{CaCl_2} + \underset{\text{(carbon dioxide)}}{CO_2\uparrow} + \underset{\text{(water)}}{H_2O} \tag{3}$$

The acid concentration for scrubbing was varied from 2% to 5%. With 2% HNO_3, the percentage of solids in the pulp was 4.8% by weight for the jaw-crushed ore and 4.0% for the as-received ground sample at 100% of the stoichiometric amount required for carbonate decomposition. Such low pulp densities markedly reduced the process capacity; therefore, 5% HNO_3 may be more economical.

The pH value of the pulp varied with acid type and concentration. Generally, the pH value was between 2.0 and 4.0 in the slurries at the end of the attrition scrubbing tests.

The effect of particle size was studied by using various screen fractions from minus 1.70 mm (10-mesh, Tyler) to minus 0.075 mm (200-mesh, Tyler). The test material was prepared by grinding the jaw-crushed ore in a batch-type ball mill for periods of 3, 6, and 12 minutes. This ground ore (Table 8) was sized into fractions prior to the individual scrubbing tests.

The residence times for attrition scrubbing in acid solutions were varied; they were 5, 15, 30, 45, and 60 minutes. In general, scrubbing times of 15 to 30 minutes were considered sufficient because the slurry pH became essentially constant, indicating that the reaction of the acid with the carbonate had ceased.

Scrubbing intensity was indicated by the impeller speed of the agitator and was varied between 100 and 700 rpm, corresponding to tip speeds of 37 and 256 cm/second, respectively. Because agitation seemed to have almost no effect on the process, the minimum tip speed (37 cm/second) was used in all tests.

The percentage of solids in the slurry varied with the type and concentration of acid used. In general, the weight percentage of solids varied from 4.8% in 2% HNO_3 to 17.9% in 5% HCl.

These variables were studied in order to optimize the process parameters to obtain a phosphate concentrate with the highest P_2O_5 grade and P_2O_5 recovery.

Results and Discussion

Attrition Scrubbing in Nitric Acid--The prepared ground phosphate samples (from the jaw-crushed material) and the as-received ground phosphate samples were attrition scrubbed for 30 minutes at 37 cm/second tip speed in 2% and 5% nitric acid solutions at 100% of stoichiometry. The scrubbed product (from the prepared ground sample) was wet screened, and the various size fractions were chemically analyzed (Table 9 and Figure 9). The size distribution and frequency curves of the main components of the prepared ground (from jaw-crushed material) sample scrubbed in 2% HNO_3 showed that the P_2O_5 grade increased and the CO_2 decreased with reduced particle size. This might have been expected in that the dilute acid reacts more efficiently with the fine carbonate particles than with the coarse particles, which may not be liberated from phosphate. Because the efficiency of attrition scrubbing increased with reduced particle size, the prepared ground (from jaw-crushed material) ore was further ground in a ball mill for 12 minutes to reduce the particle size to 80% by weight less than 0.075 mm (200-mesh, Tyler). Results given in Table 10 show that a phosphate concentrate assaying 19.5% P_2O_5 and 3.86% CO_2 could be obtained at 97.8% phosphate recovery from a feed containing 17.7% P_2O_5 and 13.8% CO_2. Because of the low pulp densities (less than 5% by weight solids) when the ore was attrition scrubbed in 2% HNO_3 solution, the acid concentration was increased to 5%. The solids percentages then were 11.23% and 10.20% for the prepared ground sample and the as-received ground sample, respectively. It can be noticed from the chemical analysis of the filtered solutions (Tables 10 and 11) that the effect of 5% HNO_3 on phosphate decomposition was quite minimal (less than 1% P_2O_5). The concentrate prepared from the as-received ground phosphate contained 21.9% total P_2O_5 and 3.77% CO_2 with a phosphate recovery of 95.9%. These values for concentrate prepared from jaw-crushed material were 22.1%, 3.68%, and 96.1%.

Attrition Scrubbing in Sulfuric Acid--The prepared ground (from jaw-crushed material) and the as-received ground phosphate samples were attrition scrubbed in 5% H_2SO_4 under the same equipment conditions described above. The results are summarized in Tables 10, 11, and 12 and illustrated in Figure 10. The final pH of the pulp was 2.2-2.6, and the solids percentages were 14.1% and 12.7% for the prepared ground and the as-received ground samples, respectively. From the results obtained it is clear that, although the CO_2 content of the various sizes was decreased, the phosphate grade was markedly diminished because the acid reacted with calcite to form gypsum, which diluted the final concentrate. The minus 0.075-mm (200-mesh, Tyler) size fraction contained 0.32% P_2O_5 and 12.6% S, indicating that it was enriched in gypsum. By discarding the 0.150-mm (100-mesh, Tyler) size fraction, a phosphate product assaying 16.58% P_2O_5, 5.7% CO_2, and 2.4% S could be obtained at a phosphate recovery of 94.90%.

To study the effect of sulfuric acid on attrition scrubbing of the finely ground phosphate sample, the crushed ore was ground in a ball mill for 12 minutes to 80% minus 0.075 mm (200-mesh, Tyler) to compare it with the as-received finely ground sample. Results shown in Tables 10 and 11 indicate that the phosphate grade of the scrubbed products decreased to 13.1% and 12.7% P_2O_5, whereas the sulfur content increased to 8.9% and 9.9% for both finely ground samples (laboratory prepared and bulk), respectively. From these results it can be concluded that attrition scrubbing of the ore in sulfuric acid can be achieved if the ore is liberated to allow the carbonate particles to react and if the fine gypsum precipitate is discarded to minimize sample dilution.

Attrition Scrubbing in Nitric-Sulfuric Mixture--Because sulfuric acid adversely affects the P_2O_5 grade of the acid-scrubbed product by forming gypsum, mixtures of 2% and 5% HNO_3 plus 5% H_2SO_4 were tested at a 1:1 ratio (based on 50% CO_2 removal by each acid). To increase the pulp solids percentage, the concentrated sulfuric acid (98%) was diluted by the prepared 2% and 5% HNO_3. Figure 11 and Table 13 show the chemical analysis and distribution of the main components of the prepared ground (jaw-crushed material) sample attrition scrubbed in 2% HNO_3 + 5% H_2SO_4. From the illustrated data it is evident that the acid mixture gave better results than those obtained when only 5% H_2SO_4 was used. The P_2O_5 grade and recovery of the various sizes are higher than those obtained with 5% H_2SO_4 (compare Figures 10 and 11). By discarding the minus 0.075-mm (200-mesh, Tyler) size (mainly gypsum), a phosphate concentrate assaying 21.04% P_2O_5, 4.85% CO_2, and 2.05% S could be obtained at a phosphate recovery of 96.80%. The results of attrition scrubbing tests of prepared and as-received finely ground phosphate samples (80% minus 0.075 mm [200-mesh, Tyler]) in mixtures of 2% HNO_3 + 5% H_2SO_4 and 5% HNO_3 + 5% H_2SO_4 are shown in Tables 10 and 11. From the data it is clear that the P_2O_5 grade was markedly diminished by the formation of gypsum, which could not be separated from the finely ground phosphate particles.

Attrition Scrubbing in Hydrochloric Acid--As required by the contract, HCl was used in an attrition scrubbing test of the finely ground phosphate rock to determine its efficiency on carbonate decomposition. A 5% HCl solution was used at the same mechanical conditions described before. The pH of the pulp was 2.5, and the solids percentage was 17.9%. The results are shown in Tables 10 and 11 for the laboratory-prepared sample and the finely ground bulk ore sample, respectively. From the results it is evident that hydrochloric acid is superior to the other acids used. The P_2O_5 grade of the scrubbed product increased to 23% P_2O_5, and its CaO content decreased to 31%. The MgO content did not markedly decrease, which indicated that the diluted acid reacted more efficiently with calcite than with dolomite at the test conditions studied. However, the phosphate loss in the filtered solution was more than that encountered when other acids were tested at the same concentration. The phosphate recovery of the acid-scrubbed product was 84.24% compared with 96.7% and 94.9% in 5% HNO_3 and 5% H_2SO_4, respectively.

Because of this relatively high phosphate loss and the expected corrosion problems with HCl, its use in attrition scrubbing of Mussoorie phosphate rock does not seem to be attractive.

On the basis of the acid efficiency on the P_2O_5 grade of the scrubbed product, the pulp density, and the P_2O_5 recovery in the laboratory-scale tests, 5% HNO_3 was selected for batch pilot-plant runs. The purpose of these runs was to prepare a sufficient amount of this phosphate concentrate for partial acidulation/granulation studies. The chemical analysis of the attrition-scrubbed product is given in Table 14.

Minigranulation Studies of Mussoorie Phosphate Rock

The minigranulation process being studied by IFDC is based on an intensive mixer of the pin-mill type--a commercially available machine (3, 4). This intensive mixer (pinmixer) is used to distribute the binder solution onto the surface of the phosphate rock. Pinmixers have been used for the purpose of dust granulation and compaction in the carbon black industry for many decades (5, 6). Its use in the fertilizer industry has been suggested (7) for granulation of NP and NPK products.

The pinmixer is based on a design that uses a high-speed horizontal shaft containing a helicoidal arrangement of radial rods or pins. This shaft rotates inside a stationary shell having a length-to-diameter ratio of about 3:1. The machine has the capability of producing a wide range of granule sizes from powdered phosphate rock. During the initial development of the minigranulation process, the pinmixer required high maintenance, mainly because of pin breakage and bearing problems that were direct results of the cake formation. The design was improved to minimize maintenance, by making modifications such as bearing location and rubber lining of the shell. This rubber lining has essentially eliminated the pin breakage.

In the scope of work of this contract, the binders evaluated for the minigranulation studies were sulfuric acid, phosphoric acid, potassium chloride solution, and urea solution. However, during the visit in June 1983, PPCL representatives requested that IFDC also evaluate urea plus 2% nitric acid solution as a binder. This concentration of nitric acid is expected to be available at the plant site.

Experimental

The IFDC laboratory-scale continuous granulation unit was configured to simulate the minigranulation process using a pinmixer that was designed and fabricated by IFDC. The laboratory unit has a capacity of about 20 kg/hour of production (about 60 kg/hour throughput). The equipment was operated with each binder for about 2 days (8 hours/day) to determine the operating conditions and the binder solution concentration that allowed a desirable granulation characteristic (control of fines and/or oversize in the dryer discharge). The system was then operated continuously for about 10 hours, 4 hours of which was usually required to reach steady-state operations. The criteria for steady-state operations were similar values of recycle ratio (defined later), product and recycle size distribution, and temperatures of granulator and dryer discharge of two samples taken at half-hour intervals. The major operating data and samples for physical/chemical analyses and greenhouse evaluations were collected after steady-state operations were reached.

The raw materials and the equipment setup used for the minigranulation studies are as follows.

Raw Materials--Four drums of finely ground Mussoorie phosphate rock (≅1 mt) were selected at random from the 12-mt sample and used for the minigranulation studies. The chemical analysis (Table 15) of this sample shows that it contained about 18.6% P_2O_5 with the main impurities being SiO_2 (15.4%), Fe_2O_3 (4.0%), and CO_2 (13.6%). The size distribution analysis (Table 15) shows that about 12% of the sample is plus 0.106 mm (150-mesh, Tyler). Since the specified size range of the minigranulated product is minus 0.300 plus 0.106 mm (minus 48- plus 150-mesh, Tyler), it was initially decided to remove the plus 0.106-mm fraction (150-mesh, Tyler) prior to minigranulation studies. However, during the meeting in June 1983, PPCL representatives requested that the plus 0.106-mm (150-mesh, Tyler) fraction not be removed since the discharge from their grinding mill has a similar size distribution, and in a commercial operation this fraction would be relatively difficult to separate.

The potassium chloride (KCl) binder used was in the form of a saturated (≅13.5 wt %) solution at 27°C prepared from commercial grade (60% K_2O) KCl. The amount of KCl solution used varied with the recycle ratio (defined later), but, in general, about 3% K_2O in the product was sufficient to achieve good granulation. This level is usually considered adequate to achieve products having good physical properties (resistant to degradation during handling). A concentration of the KCl solution that is higher than 13.5% can be used for minigranulation of phosphate rock, but this requires raising the temperature of the solution and insulating (and in some cases heat tracing) the delivery (solution) line to the pinmixer in order to prevent precipitation of KCl. Even with these precautions, nozzle and line pluggings are quite common and sometimes severe.

The urea binder used was a 50% (by weight) solution at 105°C, and the amount in the product was between 5% and 6%. A lower urea content (in the product) caused excessive degradation of the material during drying and screening. The 50% concentration of urea solution seemed best for the laboratory-scale tests and equipment. A lower concentration of urea solution usually resulted in an inadequate control of granulation, and a higher concentration resulted in line and nozzle pluggings.

The sulfuric acid (H_2SO_4) binder was a 50% H_2SO_4 solution. A binder level of around 8% tested best. A decrease in the binder content caused the product to degrade during drying and screening; an increase in the concentration of H_2SO_4 solution caused localized acidulation and, consequently, poor granulation.

The phosphoric acid (H_3PO_4) binder was a 40% P_2O_5 solution. Again, as with the H_2SO_4 binder, an 8% binder level was required to achieve adequate handling characteristics of the product. An effort to use an increased H_3PO_4 (solution) concentration was unsuccessful because it resulted in a poor dispersion of solution in the pinmixer. This resulted in localized acidulation and lump formation.

The urea plus 2% nitric acid binder was in the form of a mixture containing 48% urea solution at 105°C and nitric acid (about 2% by weight). The binder level was such that the amount of nitrogen in the product was about 2.5%. This level of nitrogen content in the product was the best tested; a lower content caused degradation of the product during handling, while a higher content resulted in excessive caking in the pinmixer.

Process Description--A flow diagram of the IFDC continuous laboratory-scale process for minigranulating phosphate rock (Figure 12) shows a configuration which is quite similar to that of any normal granulation plant, except that no cooler is used. The dryer discharge is screened hot, and each size fraction cools in its respective collection bin.

Ground phosphate rock was continuously fed to the pinmixer using a variable-speed, screw-type feeder. Simultaneously, the desired binder solution (urea [50%], or KCl [13.5%], or H_2SO_4 [50%], or H_3PO_4 [40% P_2O_5], or urea [48%] plus nitric acid [2%]) was metered through a magnetic flowmeter to the pinmixer by use of a peristaltic pump. The amount of binder, determined through the exploratory tests, was such that the pinmixer operation was trouble free and the "green" (undried) minigranules had both structural integrity and strength to withstand mechanical handling (transportation to the dryer). The binder solution, in all cases, was injected inside the pinmixer using an air-atomized, internal-mix nozzle. The atomizing pressure was about 0.35 atm (5 psig). Along with the ground rock feed, the recycle material (described later) was fed by use of a variable-speed, screw-type feeder. In all cases, except for the urea plus 2% nitric acid binder, water was used to control granulation. Water was metered through a rotameter and injected inside the pinmixer using an air-atomized, internal-mix nozzle at an atomizing pressure of 0.35 atm (5 psig). When urea plus 2% nitric acid was used as a binder, 2% nitric acid solution instead of water seemed to work better in terms of reduced plugging of the pinmixer discharge.

The pinmixer (Figure 13) used for the tests had a horizontal housing 46 cm in length and 14 cm in diameter and was equipped with a 2-hp motor having a variable-speed belt drive. A shaft fitted with 36 case-hardened carbon steel pins (0.8 cm in diameter) rotated inside the housing to produce an intensive mixing action and push the material from the entrance to the exit port. The feed port for the rock was located on the top of the housing, and the binder and the water (or 2% nitric acid solution) inlet points were 7 cm and 13 cm, respectively, from the feed port toward the discharge end. The inside housing of the pinmixer was lined with 1-cm thick, soft Neoprene rubber to reduce pin breakage.

The moist, granular material from the pinmixer discharged by gravity into a rotary dryer 25.4 cm in diameter by 152.4 cm in length. The rotating bed of material in the dryer was heated with a cocurrent airflow that passed through a propane-fired combustion chamber located at the inlet (material feed end) of the dryer. An air exhaust system, consisting of a cyclone-type dust collector and a wet scrubber, was used to remove dust and fluorine compounds (when H_2SO_4 and H_3PO_4 were used as binders) emitted from the pinmixer and the dryer. The scrubber liquor was then routed to the effluent pond. The dust collected from the cyclone separator was mixed with the recycle material (discussed later) prior to feeding the pinmixer. The dryer was operated at a rotational speed of 6 rpm and had a slope of 2.5° from the feed to the discharge end.

The granular discharge from the dryer was screened using a 46-cm diameter double-deck, self-cleaning, mechanically vibrated screen. The screen was fitted with a 0.300-mm opening (48-mesh, Tyler) oversize screen and a 0.106-mm opening (150-mesh, Tyler) undersize screen to yield a product in the 0.106-0.300 mm size range. Oversize material from the screen was routed to a single-shaft chain mill. The material discharged from the chain mill was returned to the screen. Normally, the quantity of oversize material was small (varying between 7% and 15% of the total dryer discharge), and the amount of crushed oversize in the product was usually less than 15%.

The undersize material, dust from the dryer cyclone separator, and a fraction of the product were returned to the pinmixer as recycle. Under normal operating conditions the quantity of recycle fed to the pinmixer was maintained at a relatively constant rate by regulating the fraction of product diverted to recycle.

The temperature of the recycle material when fed to the pinmixer was usually close to the ambient. This was due largely to the relatively high proportion of heat losses during physical handling of the recycle material. In larger scale operations the recycle material would be transferred continuously with only a small loss of sensible heat. In the present series of tests no attempt was made to raise the temperature of the recycle material prior to feeding it into the pinmixer. However, during the process demonstration trials (see section on Process Demonstration Trials), the recycle was heated to raise its temperature.

The process data with Mussoorie phosphate rock and the binders tested in the continuous minigranulation process are shown in Table 16. These data were usually collected every half hour after reaching steady-state operation, and the average of these data sets is presented in the above-mentioned table. In most cases the variations among the sets were minimal and well within the experimental error.

Grab samples of product collected every half hour, after reaching steady-state operation, were composited for chemical analysis and physical properties determinations. Occasionally, the dryer discharge material was collected and batch screened into five or six size fractions that were analyzed to detect any possible variation in the binder concentration with particle size. No such variations were noted.

Physical Properties Evaluation--As required by the contract, the physical properties of the minigranulated products were evaluated. The physical properties tests included measurements of bulk density, angle of repose, porosity, abrasion resistance, disintegration in water, and hygroscopicity. Except for tests of porosity and disintegration in water, all tests were performed according to the procedures outlined in the Tennessee Valley Authority (TVA) Special Report No. S-444 (8). Porosity and disintegration in water were determined according to the procedure developed by IFDC. A brief description of each procedure follows.

The bulk density value is required for bag sizing and to determine the capacity of the storage bins and transport vehicles if fertilizer is moved in bulk. The bulk density is measured by simply pouring the fertilizer into a container with a known volume, leveling the top with a straightedge, and weighing on appropriate scales. The value obtained in this manner is known as the "loose pour density." For the present test, the loose pour density was determined by pouring the fertilizer into a 746-ml cylinder.

The angle of repose of a fertilizer is the angle with the horizontal at which the fertilizer will stand when poured or dropped into a pile from a fixed overhead point. The angle of repose affects the capacity of bulk storage areas and bins; it is also of interest in designing the roof slope of bulk storage buildings and in designing hoppers, chutes, and conveyors. This measurement is usually made with 10 kg or more of sample, but because only a limited quantity of product was available for testing, an alternate method was used. This method involved simply pouring a quarter section of a conical pile in the corner of a small box and measuring the slope of the surface.

The porosity of a granular fertilizer is an indication of the internal pores enclosed by the surface of the granule. This value is often used in the development of granulation processes. Porosity was determined according to the procedure developed by IFDC and involved determination of percentage change in volume in 20 minutes of a 15-g portion of granular material immersed in 30 ml of orthoxylene.

Abrasion resistance is a measure of degradation and dust formation under simulated handling. This test employs a stainless steel, totally enclosed drum 17.8 cm in diameter and equipped with six lifting flights. For minigranulated products, the material first was screened to remove any material smaller than 0.106 mm (150-mesh, Tyler). A 100-ml weighed sample was placed in the drum together with 50 steel balls, each 7.9 mm in diameter. The drum then was closed and rotated for 5 minutes at 30 rpm. The contents were removed, and particles smaller than 0.106 mm were removed by screening to determine the percentage degradation to fines.

Disintegration in water is a measure of how effectively (quickly) the minigranules revert back to the original fineness when exposed to mildly agitated water. Disintegration of minigranules in water was measured as percentage losses in weight of a 30-g sample held on a screen with an opening of 0.106 mm (150-mesh, Tyler) and exposed for 5 and 15 minutes to mildly agitated water at 25°C.

Hygroscopicity evaluation gives information as to how rapidly moisture will be absorbed and how rapidly and to what depth wetting and physical deterioration will progress once a fertilizer is exposed to a humid atmosphere. Hygroscopicity is evaluated through the absorption-penetration test, which involves exposing a bulk fertilizer surface of known surface area to moving air at a controlled temperature and humidity and measuring the rate of moisture absorption per unit of fertilizer surface and the rate of moisture penetration into the bulk of the fertilizer. An open-top cylindrical glass jar (37.3 cm^2 exposed surface and 20 cm in depth) was filled to the top with minigranules. The material then was placed in a controlled humidity cabinet at 30°C and 80% relative humidity. After 3, 7, 24, 48, and 72 hours the jar was removed and weighed, and the moisture absorption per unit surface area was calculated. Additionally, measurements made on the interior surface of the glass wall of the jar permitted the depth of moisture penetration to be determined.

The physical properties of the minigranulated products are listed in Tables 17 and 18.

Results and Discussion

The continuous tests in laboratory-scale equipment using a pinmixer granulator suggest that minigranulation of ROM finely ground Mussoorie phosphate rock is feasible with the binders (urea solution, potassium chloride solution, sulfuric acid, phosphoric acid, and urea plus nitric acid solution) tested. However, the operating conditions (Table 16) and product physical properties (Tables 17 and 18) varied with the binder type.

In order to maintain steady operation of the system, the following indicators were closely observed: (1) pinmixer speed (rpm); (2) product characteristics and handling problems during granulation, drying, screening, and crushing; and (3) recycle ratio required to obtain good granulation.

Except with urea solution the pinmixer speed for all binders was around 850 rpm, which corresponded to a tip speed of the pins of 5.4 m/second. When the urea solution was used, the pinmixer speed was slightly higher and averaged around 1,000 rpm (tip speed 6.4 m/second). In general, the pinmixer speed was quite constant for sulfuric and phosphoric acid binders. However, with urea, potassium chloride, and urea plus nitric acid solutions, the speed tended to fluctuate, especially toward the end of the test runs. This fluctuation was mainly due to the cake formation in the pinmixer. A higher cake buildup usually impedes the free movement of the pins with a resultant decrease in the speed. In addition to affecting the pinmixer speed, the cake buildup accelerated the pin wear. For example, when urea, potassium chloride, and urea plus nitric acid solutions were used, the average pin wear expressed as millimeter per kilogram of product ranged between 0.21 and 0.26. This value for sulfuric and phosphoric acids was 0.066 and 0.034, respectively. A typical pin-wear profile (Figure 14), after 10 hours of continuous operation, indicates that pin wear is most severe around the injection points of the liquid phase. Similar pin-wear patterns also have been observed with central Florida and North Carolina phosphate rocks (9), although the amount of pin wear with these rocks is much less than that of Mussoorie phosphate rock under similar operating conditions. This relatively high pin wear while using Mussoorie phosphate rock is probably due to its high silica content, which is quite abrasive.

During the pinmixer tests, the recycle ratio varied between 0.5 and 1.5 depending on the binder used. Illustrative data are as follows:

	Urea	Potassium Chloride	Sulfuric Acid	Phosphoric Acid	Urea Plus Nitric Acid
Recycle ratio[a]	1.0	1.5	0.5	1.4	1.0

a. Rounded figure. Refer to Table 16.

These recycle ratios were required to obtain near-optimum granulation and to minimize production of an excessive amount of oversize that is difficult to dry and crush. The recycle ratio for the present study was defined as the weight ratio of total recycle to phosphate rock plus binder fed to the pinmixer on a dry basis. Under ideal operating conditions this ratio would correspond to the recycle fed to the granulator and the amount of product produced.

The temperature of the granulated material fed to the dryer was higher for urea and potassium chloride solutions than for sulfuric and phosphoric acids. For example, with urea and potassium chloride solutions the material temperature averaged around 75°C, whereas with phosphoric acid this value was 44°C. This higher temperature with urea and potassium chloride solutions was mostly due to the friction caused by constant contact of the pins with the well-compacted cake in the pinmixer.

The wet granular material from the pinmixer was relatively nonsticky and could be easily transported to the dryer, except when urea and urea plus nitric acid solutions were used. With these binders the material tended to be extremely sticky. This stickiness resulted in frequent plugging of the pinmixer outlet and the dryer inlet.

Depending on the type of binder used, the product temperature at the dryer discharge was 5°-10°C lower than the temperature of the air at the dryer outlet, which ranged between 65° and 85°C. At this temperature the moisture in the product was less than 1%.

Problems were encountered during screening of the dryer discharge material to remove the product size fraction (minus 0.300 plus 0.106 mm [minus 48- plus 150-mesh, Tyler]). The extremely small size of the minigranules tended to plug the screens, thus necessitating rescreening of the oversize fraction. The screening efficiency on a once-through basis ranged between 50% and 70%, depending on the binder used. For urea and urea plus nitric acid binders, the dryer discharge material, although relatively cool and dry (between 60° and 75°C and 1% moisture), was quite soft and sticky. This caused frequent blinding of the oversize and undersize screens and buildup in the crusher chain mill. However, when a batch of the dryer discharge was air cooled, the material became crisp and easy to screen and crush. For this reason, cold screening (i.e., use of a cooler) of the minigranulated Mussoorie rock containing urea in excess of about 5% would be required in a larger scale operation.

For all the test runs, about 10% of the total solids fed could not be accounted for and were presumed lost during in-process handling through occurrences such as spillage from the chute connecting the pinmixer and dryer and leaks at the crusher outlet and screens. It is expected that such losses would be much smaller in large-scale operation.

The approximate pinmixer power consumption, based on the relative ampere reading of loaded and empty pinmixer operation, ranged between 35 (Run MSR 301) and 54 kWh/mt of product (Run MSR 200-A). These values are probably on the high side when compared with those for larger equipment because the pinmixer used was disproportionately small and the material characteristics, including granule size, lumps, and buildups, were more typical of a larger scale operation.

The grade of the minigranulated products containing urea, urea plus nitric acid, and potassium chloride was 2.6-16.8-0, 2.6-16.4-0, and 0-16.5-2.8, respectively, with virtually no change in available P_2O_5 with respect to the original rock. However, as expected, the use of sulfuric and phosphoric acids increased the available P_2O_5 in the product, with phosphoric acid being more effective. For example, with urea, urea plus nitric acid, and potassium chloride binders, about 2% of the total P_2O_5 was in an available form, whereas with sulfuric and phosphoric acids, the availabilities were 5% and 20%, respectively. The grade of the minigranulated products with sulfuric and phosphoric acids was 0-15.9-0 and 0-24-0, respectively.

The minigranulated products in all cases were free flowing and relatively nondusty; however, their physical properties, such as bulk density, angle of repose, porosity, abrasion resistance, disintegration in water, and hygroscopicity, were binder specific (Tables 17 and 18).

The bulk density of the minigranulated materials ranged between 1,065 kg/m^3 (66.5 lb/ft^3) and 1,132 kg/m^3 (70.7 lb/ft^3). These values are lower than those for the ROM, as-received, ground rock (1,290 kg/m^3 [80.6 lb/ft^3]) that is being sold as a direct-application fertilizer. These decreased bulk densities will necessitate a corresponding increase in bag sizes for a given weight of product when compared with the finely ground rock.

The angle of repose of the as-received, finely ground Mussoorie rock was 42°; this is considerably higher than that of other commercial phosphate rocks (central Florida, Morocco, etc.), the values for which range between 30° and 35°. This high angle of repose of the Mussoorie rock caused clinging and bridging in the hoppers and chutes during the minigranulation tests and resulted in an inconsistent flow (<u>10</u>, <u>11</u>, <u>12</u>, and <u>13</u>). This problem was greatly alleviated by installing vibrators at the material discharge points. The angle of repose of the minigranulated products, in contrast, ranged between 28.5° and 32.0°. This decreased value is expected to improve the flow through hoppers and chutes.

The porosity of the minigranulated products varied between 2.5% (phosphoric acid binder) and 5.9% (sulfuric acid binder). These values are very similar to those of other minigranulated products prepared from central Florida and North Carolina phosphate rocks. Previous studies at IFDC (9) have shown that porosity in excess of 10% caused granules to disintegrate under simulated handling.

Under the conditions tested, the percentage degradation of the minigranulated products (under simulated handling) was relatively high (about 12%) for potassium chloride and phosphoric acid binders. With urea, sulfuric acid, and urea plus nitric acid binders, these values were 8.0%, 6.5%, and 6.8%, respectively. The percentage degradation in excess of 10% is considered undesirable because of dustiness problems. However, evaluation under actual handling conditions is needed to assess the extent of degradation and associated handling problems.

The percentage of disintegration in water of minigranulated products containing urea and potassium chloride binders was higher than for those products containing either phosphoric or sulfuric acid (Table 17). The phosphoric acid binder resulted in granules that were the slowest to disintegrate in water; this could be due to the formation of dicalcium phosphate (through reaction of calcite in the rock with phosphoric acid) that coated the granule surface and thus made the disintegration time longer. Similarly, for sulfuric acid the coating of granule surface with calcium sulfate may have retarded its disintegration rate in water.

The data obtained in an absorption-penetration test series at 80% relative humidity, 30°C, and 72 hours' exposure time for minigranulated products are given in Table 18. Moisture-holding capacities of products that showed some evidence of moisture penetration were calculated as milligrams of moisture per cubic centimeter of product by dividing the moisture absorption per square centimeter by the depth of penetration in centimeters. These values also were converted to percentage of moisture-holding capacity, by weight, by use of the weight-per-unit volume (bulk density) of the materials in the cup. The holding capacity thus calculated represents the maximum amount of moisture that a granule will absorb before transferring it to adjacent granules. High moisture-holding capacity is a desirable characteristic that can offset the effects of the high rate of moisture absorption. For example, the products prepared using a urea plus nitric acid binder (Sample MSR 501-A) had a relatively high moisture absorption rate (123.3 mg/cm^2 in 72 hours). This value coupled with a low moisture-holding capacity resulted in wetting of a part of the sample and medium caking. The products containing only urea (Sample MSR 105-AA), on the other hand, had a reduced moisture-absorption rate and moderate moisture-holding capacity that resulted in a light-to-medium set that could be easily broken by finger pressure to make the material relatively free flowing. In contrast to the above samples, the other products (Samples MSR 200-A, MSR 301, and MSR 400-A) were made up of free-flowing individual particles at the end of the entire test period.

Results of this absorption-penetration test are indicative of the expected behavior of products under steady, high-humidity conditions, but it should be realized that under cycling conditions, such as occur in actual bulk storage, the results may be altered by crusting (self-sealing) of pile surfaces of some materials during dry cycle periods. The effect of such cycling was not evaluated in this study.

Partial Acidulation/Granulation Studies of Mussoorie Phosphate Rock

The PAPR products are commercially produced in West Germany (14) and Brazil (15), and the process involves rock acidulation, denning for a few minutes to several hours, and curing for several days to produce ROP PAPR. If granular material is desired, the ROP PAPR is recovered from the pile, granulated with steam and water, dried, and sized. The disadvantage of this process is that the product is not ready for use for several weeks; thus, it requires more storage space in the plant, as well as several additional handling steps to produce a finished product. All this adds to the cost of the final product. Furthermore, this process is only suitable for commercial phosphate rocks that are relatively reactive and low in iron, aluminum, and like impurities. Rocks with low reactivity may contain a high amount of unreacted acid that reacts with the iron and aluminum impurities to form phosphate compounds that may be unavailable to the plants. These impurity reaction products also may cause the product to be quite sticky.

The SSAG process for production of granular PAPR using sulfuric and/or phosphoric acid(s) developed by IFDC is suitable not only for commercial phosphate rocks but also for relatively unreactive rocks high in iron and aluminum impurities. Through proper control of acidulation conditions during the SSAG process, selective attack on the calcium phosphate by the acid(s) minimizes the dissolution of the undesirable iron and aluminum components in the phosphate rock and results in a product with a desired level of available phosphate, low free acid, and good physical properties (i.e., nonsticky and free flowing). Furthermore, the selectivity of acidulation in forming available phosphate during the SSAG process is improved, especially at relatively high acidulation levels, through substitution of a part of the sulfuric and/or phosphoric acid(s) by nitric acid and through the addition of such additives as potassium chloride to the phosphate rock prior to, and/or during, acidulation with the above acid(s). Also, the SSAG process eliminates the denning and curing stages and reduces the material handling equipment required, thereby saving capital investment and reducing cost of production.

This contract required that both sulfuric and phosphoric acids be evaluated for partial acidulation/granulation of the ROM and attrition-scrubbed Mussoorie phosphate rocks to produce a product containing about 50% of its total P_2O_5 in a water-soluble form.

At the initiation of this project, it was recognized that the ROM Mussoorie phosphate rock would require a pretreatment step prior to acidulation with sulfuric acid because of its relatively high (≅13.6%) CO_2 content. The pretreatment step involved a process step in which the ROM rock was reacted with sulfuric acid to reduce its CO_2 content. Previous studies at IFDC of the SSAG process with sulfuric acid indicated that the rocks containing CO_2 in excess of 8%-10% caused operational problems in terms of nonuniform acidulation, excess free acid, and weak granules that completely degraded in the rotary dryer. With phosphoric acid these problems were not encountered in the SSAG process.

Experimental

The IFDC laboratory-scale continuous granulation unit was designed to simulate the SSAG process using a pan granulator. The pan granulator was selected for the present studies mainly because the effect of changes in the process variables on the granulation conditions could be visually observed and evaluated. The laboratory unit has a nominal capacity of about 20 kg/hour of production (about 45 kg/hour throughput).

During the initial tests with the ROM rock and sulfuric acid (including H_2SO_4 pretreatment to reduce CO_2, followed by SSAG), several operational problems were encountered, including high free acid in the granulator discharge and less-than-desired product water solubility (percentage of total P_2O_5 in a water-soluble form) in the product. At 10% and 20% water-solubility levels, these problems were not very acute; however, at higher water-solubility levels the problems were quite severe, including plugging of the dryer inlet and blinding of the screens. From an operational standpoint, the maximum product water solubility that could be achieved in the laboratory-scale unit using sulfuric acid was about 32%. This water solubility could, however, be increased to about 40% through the addition of potassium chloride (≅5% of the weight of the rock) to the rock without any detrimental effect on the operations and product quality. An attempt was made to use 2% nitric acid solution instead of potassium chloride, but the results were not too promising because of an unfavorable water balance associated with the nitric acid solution.

With the attrition-scrubbed material, on the other hand, the operational problems were minor, and the desired water solubility of about 50% could be achieved.

With phosphoric acid both ROM and attrition-scrubbed rocks worked well, and the products were free flowing and nonsticky.

With ROM rock and at each water-solubility level, for both sulfuric and phosphoric acids about 4 days (8 hours/day) of exploratory test runs was required to determine the operating conditions, including the acid concentration (discussed later) that allowed desirable granulation characteristics (recycle ratio, bed temperature, etc.) and acceptable handling properties of the "green" (ex-granulator) products. With the attrition-scrubbed materials, and for each acid (sulfuric and phosphoric), about 2 days (8 hours/day) of exploratory runs was required to establish the operating conditions. Following these exploratory runs, the system was operated for about 10 hours. Steady-state conditions were attained within 4 hours after the start of the run. These conditions were based on similar (±5%) values of free acid and monocalcium phosphate (the water-soluble compound in PAPR) of the granulator/dryer discharge of two half-hour samples. The major operating data and samples for physical/chemical analyses and greenhouse evaluations were collected after these steady-state conditions had been reached.

A description of the raw materials and the equipment setup used for the partial acidulation/granulation studies follows.

Raw Materials--The ROM finely ground (80% minus 0.075-mm [200-mesh, Tyler]) Mussoorie phosphate rock and the attrition-scrubbed material prepared from it (see Beneficiation section) were used for the partial acidulation/granulation studies. The chemical analysis (Table 19) of these samples shows that attrition scrubbing of the ROM rock with 5% nitric acid reduced the CO_2 (mainly calcite) content from 13.6% to 3.5% and increased its grade (P_2O_5 content) from 18.6% to 21.6%. This reduction in CO_2 content is quite significant in that, with the scrubbed material, less acid (sulfuric and phosphoric) would be required to achieve the desired water solubility in the product. Further, the lower CO_2 content would eliminate the need for pretreating the rock prior to the SSAG process. The size distribution analysis indicates that the scrubbed material is slightly coarser than the ROM rock (71% versus 77% minus 0.075 mm [200-mesh, Tyler]), but this grind is well within the range required for the SSAG process.

The sulfuric acid used was of technical grade (93% H_2SO_4), which was diluted to the desired concentration and cooled to the ambient temperature prior to use. The desired acid concentration was determined through the exploratory tests. The use of 93% sulfuric acid in the pretreatment step (to reduce the CO_2 content) worked well, and the material was relatively dry and free flowing. However, acid of the same concentration in the granulator caused the (granulator) bed temperature to be relatively high (>60°C), especially with the ROM rock. This high bed temperature (which indicates a faster reaction rate and, consequently, a rapid precipitation of reaction products on the surface of the phosphate rock particles and an incomplete reaction) resulted in a "green" (ex-granulator) product that was relatively high (>8%) in free acid and extremely sticky. This problem was alleviated by using acid of a lower (≅73%) concentration, which reduced the bed temperature to between 40°-50°C.

The phosphoric acid (≅54% P_2O_5) used in the SSAG process was obtained from TVA and prepared by the wet-process method. This acid did not require any adjustment in its concentration since the "green" (ex-granulator) product was quite low in free acid and was free flowing.

Process Description--A flow diagram of the IFDC continuous laboratory-scale SSAG process (Figure 15) shows a configuration which is quite similar to that of the minigranulation process, except that a pan granulator is used instead of a pinmixer.

Ground phosphate rock was fed continuously to the pan granulator using a variable-speed, screw-type feeder. Simultaneously, sulfuric or phosphoric acid having a concentration of about 73% H_2SO_4 or 54% P_2O_5, respectively, was metered through a magnetic flowmeter to the pan granulator to acidulate the rock and thus obtain the desired water-soluble P_2O_5. The acid was sprayed on the rolling bed of material using an air-atomized, internal-mix nozzle having a spray pattern of a 70° cone. The atomizing pressure was about 0.2 atm (3 psig). Water also was metered and sprayed on the rolling bed of material through a hydraulic spray nozzle operated from a pressure pot ($\cong$1.7 atm [25 psig]) equipped with a level controller. Along with the ground rock feed, recycle material consisting of the undersize from the screens and cyclone-separator fines (discussed later) was fed using a variable-speed, screw-type feeder. The locations of solid feeds and sprays were such that the rock was wetted with water before it was in contact with acid (Figure 16).

The pan granulator was 45 cm in diameter, 7.5 cm in depth, and equipped with a variable-speed motor. The inclination of the pan was adjustable between 40° and 60° from the horizontal. A single-blade (7.5 cm in width), pneumatic reciprocating scraper traveling from the center of the pan to the 4 o'clock position continuously cleaned the bottom of the pan while a fixed scraper located at the 11 o'clock position cleaned the side of the pan.

The moist, plastic granular material from the pan granulator discharged by gravity into a rotary dryer 25.4 cm in diameter by 152.4 cm in length. The rotating bed of material in the dryer was heated with a cocurrent airflow that passed through a propane-fired combustion chamber located at the inlet (material feed end) of the dryer. An air exhaust system consisting of a cyclone-type dust collector and a wet scrubber was used to remove dust and fluorine compounds emitted from the granulator and the dryer. The scrubber liquor was then routed to the effluent pond. The dust collected from the cyclone separator was mixed with the recycle material prior to being fed into the granulator. The dryer was operated at a rotational speed of 6 rpm and had a slope of 2.5° from the feed to the discharge end.

Material from the dryer discharge was screened on a 46-cm diameter, double-deck, self-cleaning, mechanically vibrated screen. The screen was fitted with a 3.35-mm (6-mesh, Tyler) oversize screen and a 1.18-mm (14-mesh, Tyler) undersize screen to yield a product in the 1.18- to 3.35-mm size range. Oversize material from the screen was routed to a single-shaft chain mill. The chain mill discharge was returned to the screen. Normally, the quantity of oversize material varied between 10% and 15% of the total dryer discharge.

Undersize material and the cyclone dust from the dryer cyclone separator were returned to the granulator as recycle.

Because of its relatively high heat loss during physical handling, the recycle material was usually near the ambient temperature when fed to the granulator. In these tests no attempt was made to raise the temperature of the recycle material before it was fed to the granulator. However, during the process demonstration trials (discussed later), the recycle was heated to raise its temperature by about 15°C above ambient.

As stated earlier, the ROM rock required pretreatment with 93% sulfuric acid to reduce the carbonate content prior to carrying out the SSAG process. The pretreatment involved intensive mixing of acid and rock in the pinmixer used for minigranulation studies. The pinmixer was selected because it was readily available and its capacity was compatible with the pan granulator used. Other intensive mixers may be suitable, but they were not evaluated. The pinmixer discharge in the form of slightly moist, powdered material was transferred by a belt conveyor to the granulator for subsequent acidulation/granulation.

Process data for the ROM and the attrition-scrubbed Mussoorie phosphate rocks treated in the continuous SSAG process are shown in Tables 20 and 21, respectively. These data were usually collected every half hour after steady-state was reached; the average of these data sets is presented in the above-mentioned tables. In most cases the variations among the sets were quite small and well within the experimental error.

Grab samples of product, collected every half hour after steady-state was reached, were composited for chemical analysis and physical properties determinations. Occasionally the dryer discharge material was collected and batch screened into five or six size fractions, which were analyzed to detect any possible variation in water solubility with particle size. No significant variations were noted.

Physical Properties Evaluation--In accordance with the terms of the contract, the physical properties of the PAPR products were evaluated. The physical properties measurements were the same as those made for minigranulated products; in addition, the average crushing strength of granules was also determined. Except for abrasion resistance, disintegration in water, and granule hardness, the test procedures were identical to those outlined earlier (see

Minigranulation Studies section). For abrasion resistance and disintegration in water measurements, a 1.18-mm (14-mesh, Tyler) screen was used instead of a 0.106-mm (150-mesh, Tyler) screen. The granule hardness was determined by measuring the crushing strength of individual granules of equal size. The test was performed according to the procedures outlined in the TVA Special Report No. S-444 (8) and involved screening of granular samples to the narrow size range of minus 2.36 plus 2.80 mm (minus 7- plus 8-mesh, Tyler). An individual granule was then placed on a flat metal plate on the platform of a small spring scale of about 7-kg capacity, and downward pressure was applied until the granule fractured. The crushing strength of 10 granules was determined to obtain an average evaluation.

The physical properties test results are given in Tables 22 and 23.

Results and Discussion

The primary objective of partial acidulation of rock is to convert the phosphate contained in apatitic minerals to a more soluble form which is available to plants. The chemistry of PAPR using sulfuric and phosphoric acids is similar to that of SSP and TSP production, respectively. The water-soluble compound in PAPR, as in SSP and TSP, is monocalcium phosphate monohydrate. Other compounds, present in varying amounts, include dicalcium phosphate dihydrate, calcium sulfate, calcium/iron phosphate, calcium/aluminum phosphate, and such inert materials as silica, fluosilicate salts, unreacted rock, organic matter, and phosphates of other metals present in the rock. The principal chemical reactions (4 and 5) and some of the major side reactions (6, 7, 8, 9, and 10) are shown below:

$$\underset{\text{(fluorapatite)}}{Ca_{10}F_2(PO_4)_6} + \underset{\text{(sulfuric acid)}}{7H_2SO_4} + \underset{\text{(water)}}{3H_2O} \rightarrow$$

$$\underset{\substack{\text{(monocalcium phosphate}\\ \text{monohydrate)}}}{3Ca(H_2PO_4)_2 \cdot H_2O} + \underset{\text{(calcium sulfate)}}{7CaSO_4} + \underset{\text{(hydrofluoric acid)}}{2HF} \qquad (4)$$

$$\underset{\text{(fluorapatite)}}{Ca_{10}F_2(PO_4)_6} + \underset{\text{(phosphoric acid)}}{14H_3PO_4} + \underset{\text{(water)}}{10H_2O} \rightarrow$$

$$\underset{\text{(monocalcium phosphate monohydrate)}}{10Ca(H_2PO_4)_2 \cdot H_2O} + \underset{\text{(hydrofluoric acid)}}{2HF} \qquad (5)$$

$$\underset{\text{(fluorapatite)}}{Ca_{10}F_2(PO_4)_6} + \underset{\text{(phosphoric acid)}}{4H_3PO_4} + \underset{\text{(water)}}{20H_2O} \rightarrow$$

$$\underset{\text{(dicalcium phosphate dihydrate)}}{10CaHPO_4 \cdot 2H_2O} + \underset{\text{(hydrofluoric acid)}}{2HF} \qquad (6)$$

$$\underset{\text{(calcite)}}{CaCO_3} + \underset{\text{(sulfuric acid)}}{H_2SO_4} \rightarrow$$

$$\underset{\text{(calcium sulfate)}}{CaSO_4} + \underset{\text{(carbon dioxide)}}{CO_2} + \underset{\text{(water)}}{H_2O} \qquad (7)$$

$$\underset{\text{(calcite)}}{CaCO_3} + \underset{\text{(phosphoric acid)}}{H_3PO_4} + \underset{\text{(water)}}{H_2O} \rightarrow$$

$$\underset{\text{(dicalcium phosphate dihydrate)}}{CaHPO_4 \cdot 2H_2O} + \underset{\text{(carbon dioxide)}}{CO_2} \qquad (8)$$

$$\underset{\text{(calcite)}}{CaCO_3} + \underset{\text{(phosphoric acid)}}{2H_3PO_4} \rightarrow$$

$$\underset{\text{(monocalcium phosphate monohydrate)}}{Ca(H_2PO_4)_2 \cdot H_2O} + \underset{\text{(carbon dioxide)}}{CO_2} \qquad (9)$$

$$\underset{\text{(aluminum oxide)}}{Al_2O_3} \quad \underset{\text{(or iron oxide)}}{(\text{or } Fe_2O_3)} + \underset{\text{(phosphoric acid)}}{2H_3PO_4} \rightarrow$$

$$\underset{\text{(aluminum phosphate)}}{2AlPO_4 \cdot H_2O} \quad \underset{\text{(or iron phosphate)}}{(\text{or } FePO_4 \cdot H_2O)} + \underset{\text{(water)}}{2H_2O} \qquad (10)$$

The production data with the ROM Mussoorie phosphate using sulfuric acid in the SSAG process indicate that the desired level (50%) of P_2O_5 water solubility in the product could not be attained even when potassium chloride was added to the rock prior to acidulation. Under the conditions tested, the maximum water solubility that could be achieved through the addition of potassium chloride without significant operational problems was 40%. This less-than-desired P_2O_5 water solubility was probably due to the relatively high (≅28%) calcite content of the ROM rock. This calcite preferentially reacted with the sulfuric acid (used for acidulation) to form $CaSO_4$ (reaction 4), which may have precipitated on the surface of the phosphate rock particles and blocked further reaction of acid and apatite (reaction 1). The unreacted acid probably caused the product to be extremely sticky.

In contrast with use of the sulfuric acid, the phosphoric acid acidulation of the ROM rock in the SSAG process was quite simple and the operation was trouble free. The calcite, in this case, reacted with phosphoric acid to form a mixture of monocalcium and dicalcium phosphates.

In comparison with the ROM rock, the attrition-scrubbed material, because of its relatively low (≅8%) calcite content, was well suited for the SSAG process. With both sulfuric and phosphoric acids the products had desirable chemical and physical properties.

In order to maintain steady operation of the system, the following indicators were closely observed: (1) pinmixer operation, when pretreatment was required; (2) product characteristics and handling properties during granulation, drying, screening, and crushing; and (3) recycle ratio required to obtain good granulation.

The pinmixer operation with the ROM rock and sulfuric acid to reduce the CO_2 content was quite steady. The average pinmixer speed was about 750 rpm (tip speed 4.8 m/second), and fluctuations were minimal. The pinmixer caking and the average pin wear were similar to those observed for the minigranulation test using a sulfuric acid binder. The CO_2 content of the pinmixer discharge averaged around 9.5%, compared with 13.6% for the ROM rock. An attempt to decrease this CO_2 content further was unsuccessful because the material became too wet to transport to the granulator.

The operation of the pan granulator was routine for most tests. On a few occasions a buildup of material accumulated on the walls and the bottom of the pan, which caused the scrapers to float and the pan to lose its rotational speed. This occurred only during acidulation/granulation of ROM rock with sulfuric acid when the level of free acid in the granulator discharge was more than 7%-8% (Runs MSR 605 and MSR 608). The pan angle in all cases was 57° (from the horizontal), and the rpm was 19 which corresponded to about 36% of critical speed. (The critical speed is that speed at which the centrifugal force balances the gravitational force and the granules cease to roll.) In general, the granulation was easy to control by adjusting the amount of water sprayed onto the rolling bed of material. This was the major method used to control granulation because the flow rates for rock and acid were held constant to obtain the desired level of water solubility.

The granulator bed temperature, which is an indicator of the rate of reaction, varied between 34° and 51°C depending on the rock (ROM or attrition scrubbed) and the acid type (sulfuric or phosphoric), although the effect of the acid was slightly more pronounced. For example, with ROM and attrition-scrubbed materials, the bed temperatures when phosphoric acid was used were 38°C (Run MSR 702) and 34°C (Run MSR 801), respectively, whereas these temperatures using sulfuric acid were 51°C (Run MSR 605) and 43°C (Run MSR 901), respectively.

The recycle ratio, which ranged between 0.3 and 2.10, was similarly affected by the rock and acid type. Illustrative data follow:

Run number	MSR 605	MSR 702	MSR 901	MSR 801
Acid type	Sulfuric	Phosphoric	Sulfuric	Phosphoric
Rock type	ROM		Attrition-Scrubbed	
Recycle ratio, kg/kg	2.10	0.30	1.1	0.38

It should be noted that the above granulator bed temperatures and recycle ratios were obtained in small-scale equipment where the heat losses are relatively high. In a larger scale operation, a lower heat loss and consequently a higher recycle temperature would probably cause these values to change. Hence, the laboratory-scale data should be viewed in relative terms.

During the acidulation/granulation of the ROM rock with sulfuric acid (Runs MSR 605 and MSR 608), the products were relatively sticky, which caused a buildup of material on the walls and lifting flights near the inlet and midsection of the dryer. Furthermore, this stickiness caused the product to contain a large amount of oversize. This material was difficult to screen and crush. In addition to being sticky because of excessive free acid, the crushed oversize was also very moist. This material, after passing through the chain mill-type crusher, was recirculated to the screens and caused them to blind. Buildup of material in the chutes leading to the crusher also occurred during this period, and the chain mill had to be cleaned frequently. For all other tests no buildup in the dryer was encountered, and the material fed to the screen and crusher was dry and crisp.

The air at the dryer outlet was controlled in such a way as not to exceed the product temperature at the dryer discharge of about 105°C. Previous studies at IFDC (9) indicated that an increase in the material temperature above 120°C caused a decrease in water solubility with an accompanying increase in citrate-soluble P_2O_5.

Fluorine is a common constituent in phosphate rock, and the acidulation of rock results in the release of some gaseous fluorine compounds. Fluorine gases, even in small quantities, are very toxic to plant and animal life. Removal of fluorine from process gas steams before they are exhausted into the atmosphere is essential and, therefore, is closely monitored by the pollution control authorities. In the present series of tests, because of the relatively small flow rates, the actual fluorine concentrations in the granulator and dryer off-gases could not be measured. However, analyses of the products indicated that the amount of fluorine evolved, for products with about 50% water solubility, was around 25%-30% of the fluorine contained in the rock.

The chemical analyses of products depended on the rock compositions and the type (sulfuric or phosphoric) and amount of acid used. With sulfuric acid and ROM rock, an increase in the acid:rock ratio was accompanied by an increase in water-soluble and available P_2O_5 with a decrease in total P_2O_5. For example, at acid:rock ratios of 0.325 (Run MSR 604) and 0.356 (Run MSR 605), the total P_2O_5 of the products was 14.5% (3.9% water-soluble P_2O_5 and 0.2% P_2O_5 soluble in NAC solution) and 13.9% (4.5% water-soluble P_2O_5 and 0.2% P_2O_5 soluble in NAC solution), respectively. The use of attrition-scrubbed material, besides consuming less sulfuric acid, resulted in an increased total P_2O_5 content in the product due to a lesser dilution effect by $CaSO_4$ formed by the reaction of calcite and sulfuric acid. The following tabulation illustrates the point:

Run number	MSR 605	MSR 901
Type of rock	ROM	Attrition-Scrubbed
Acid:rock ratio	0.356	0.264
Total P_2O_5, %	13.9	17.6

The grades of the products produced from ROM and attrition-scrubbed materials using phosphoric acid were 0-32.6-0 (Run MSR 702) and 0-30.3-0 (Run MSR 801), respectively. These grades are substantially higher than those of the rocks themselves, thereby suggesting that a significant portion of the P_2O_5 in the product was derived from the acid, especially with the ROM rock. An analysis of the data (see the following tabulation) shows that for the ROM and attrition-scrubbed materials about 56% and 43%, respectively, of the P_2O_5 in the product was derived from phosphoric acid.

Run number	MSR 702	MSR 801
Type of rock	ROM	Attrition-Scrubbed
Acid:rock ratio	0.436	0.300
Ratio of P_2O_5 from acid to P_2O_5 from rock	1.26	0.75
P_2O_5 derived from acid, %	56	43

Thus, attrition scrubbing results in a saving in phosphoric acid consumption during the acidulation step. However, it should be pointed out that the attrition scrubbing process is an acid-consuming step. Hence, the cost of attrition scrubbing should be considered in making a true assessment of the significance of the phosphoric acid savings.

The free acid (measured as % P_2O_5) of the products was within the acceptable limits (less than 4%), except when the product contained potassium chloride (Run MSR 608). In that case the free acid was 6.3%.

All the PAPR products had good physical properties, especially those prepared with phosphoric acid. The materials appeared to be relatively free flowing, and the bulk densities ranged between 910 and 1,090 kg/m^3. The porosities of the granules were well within the acceptable limits for such fertilizers; however, the porosities were rock specific. For example, with both acids the porosity of products was higher for ROM rock (Runs MSR 608 and MSR 702) than for attrition-scrubbed feed (Runs MSR 801 and MSR 901). This is probably due to a higher carbonate content of the ROM rock.

The crushing strength of the granules varied with the acid type and was essentially independent of the rock source. With sulfuric acid the average crushing strength was below 1 kg/granule, while with phosphoric acid these values ranged between 1.5 and 1.8 kg/granule. These values are lower than the 2-3 kg/granule normally required for satisfactory handling and transportation characteristics. PAPR products produced in a commercial plant can be expected to have a higher crushing strength than those produced in this laboratory-scale equipment.

The percentage of degradation due to simulated handling showed a similar trend as the crushing strength. For example, with sulfuric acid and both rock types, the degradation was in excess of 20%, whereas with phosphoric acid this value varied between about 3% and 9%. This excessive degradation with sulfuric acid is probably due to the weak granular material. It is expected that the products prepared in a commercial plant will have an increased abrasion resistance.

With respect to hygroscopicity, none of the products showed any tendency to cake, and the moisture absorption properties of the products were favorable. The moisture penetration of all products, except those prepared from the ROM rock and sulfuric acid (Run MSR 605), was well within the limits normally set for commercial granular TSP. For Run MSR 605 the moisture penetration was slightly higher; however, long-term storage tests are needed to more closely identify the effect of cycling conditions that occur in actual bulk storage.

Process Demonstration Trials

As part of this contract, four experts from PPCL were scheduled to visit IFDC to study the processes for attrition scrubbing, partial acidulation/granulation, and minigranulation in order to obtain as much design data as possible for the purpose of sizing various equipment for larger scale plants. However, during the meeting between IFDC, PPCL, and UNIDO representatives in November 1983, PPCL requested that the attrition scrubbing process for beneficiation of Mussoorie phosphate rock not be considered for the demonstration trial because of: (1) a relatively high acid consumption and (2) the promising results obtained by Sala International, Sweden, for beneficiating Mussoorie phosphate rock using the heavy-media separation technique. Further, PPCL also requested that the SSAG process demonstration run be made using the concentrate prepared by Sala International.

During the course of this meeting, PPCL suggested that prior to any demonstration run, a preliminary estimate of the production economics of minigranulation and SSAG processes be made to determine the relative effect of binder and acid type on the minigranulated and PAPR products, respectively. As a result, in December 1983 a PPCL engineer visited IFDC; following discussions with IFDC engineers, potassium chloride was selected as the binder for the minigranulation process and sulfuric acid as the acidulant for the SSAG process.

In March 1984 three PPCL engineers visited IFDC for 2 weeks, and during this time the laboratory-scale equipment was operated continuously to demonstrate the process and collect as much engineering data as possible. Subsequently, in March 1985, four representatives from PPCL visited IFDC as part of the project review meeting. During this meeting it was suggested that partial acidulation/granulation of ROM Mussoorie rock using sulfuric acid and sulfuric/phosphoric acids also be demonstrated. These process demonstration trial runs are discussed below.

Minigranulation Process

During visits in December 1983 and March 1984, the PPCL engineers expressed reservation regarding the minigranulation process, especially as it pertained to the pinmixer granulator. Their concern mainly stemmed from the limited commercial experience with the pinmixer-type granulator in the fertilizer industry and the anticipated high maintenance requirement due to excessive pin wear while using the Mussoorie phosphate rock. Hence, it was suggested that a more conventional granulator, such as a pug mill, also be considered in place of a pinmixer (the pug mill is a horizontal or inclined U-shaped trough equipped with rotating blades or pins on one or two shafts to agglomerate the material and move it through the trough). Additionally, PPCL requested that phosphoric acid also be evaluated as a binder while using the pug mill. This was based on preliminary agronomic results obtained in the greenhouse trials with the phosphoric acid-minigranulated Mussoorie phosphate rock (see Final Report on agronomic studies under this contract). Thus the options evaluated were as follows:

1. Pinmixer granulation using a potassium chloride binder.
2. Pug mill granulation using a potassium chloride binder.
3. Pug mill granulation using a phosphoric acid binder.

Pinmixer Granulation Using Potassium Chloride Binder--The equipment configuration for the pinmixer run was the same as that described earlier (see Minigranulation Studies section), except that the recycle to the pinmixer was heated to offset the relatively high heat loss encountered in the laboratory-scale unit. The recycle was heated to raise its temperature about 16°C above ambient (to 30°C) before it was fed to the granulator. The equipment used for heating the recycle was a rotary drum, 31.8 cm in diameter, 67.3 cm in length, and equipped with a variable-speed drive. A 5-cm-high retaining dam was located 6.5 cm from the discharge end of the drum. The recycle material, fed continuously to this rotary drum by the recycle feeder, was heated to the desired temperature by a countercurrent flow of hot gases from a laboratory Bunsen burner. The startup recycle material was obtained from the previous minigranulation test run using the same binder (Table 16, Run MSR 200-A). The results of this test are shown in Table 24.

The production data essentially confirm the previous test results with the same binder, except for the recycle ratio which was slightly less in this case (see following tabulation).

Run number	MSR 200-A[a]	MSR 205[b]
Recycle ratio[c]	1.5	1.0

a. Refer to Table 16.
b. Refer to Table 24.
c. Rounded figure.

The screening of the dryer discharge again caused some problems in that the minigranules tended to plug the screens; thus, rescreening of the oversize fraction was required. The screening efficiency, on a once-through basis, was about 75%.

The granulated product was free flowing, and its physical/chemical properties (Tables 25 and 26) were similar to those of the previous product prepared with the same binder.

Pug Mill Granulation Using Potassium Chloride Binder--The equipment configuration for pug mill granulation was identical to that for pinmixer granulation except that a pug mill was used instead of a pinmixer. The pug mill was a horizontal U-shaped trough equipped with rotating blades on two shafts driven by a variable-speed 1/2-hp motor. The housing was 40 cm long, 14 cm wide, and 15 cm deep (at the deepest part of the trough) and constructed of 316 stainless steel. The shafts were about 1.5 cm^2, and each was fitted with 16 blades (2.54 cm x 2.86 cm) that were slightly pitched to cause the material to agglomerate and move through the trough. The feed port for the rock was located on top of the housing, and the binder and water inlet points were 8 cm and 15 cm, respectively, from the feed port toward the discharge end.

Initially, tests were conducted at shaft speeds of 100, 200, 300, and 400 rpm (corresponding to tip speeds of 0.4, 0.8, 1.2, and 1.6 m/second, respectively) to determine the effect of speed on the yield of minigranules (minus 0.300 plus 0.106 mm [minus 48- plus 150-mesh, Tyler]) in the dryer discharge. The yield increased with an increase in the shaft speed and ranged between 2% (at 100 rpm) and 8% (at 400 rpm). The percentage of oversize fraction (plus 0.300 mm [plus 48-mesh, Tyler]), however, was inversely related to the shaft speed; at a lower speed more oversize was created. For example, at 100 and 400 rpm about 80% and 70%, respectively, of the dryer discharge was larger than

0.300 mm. Such a voluminous amount of oversize tended to choke the chain mill and reduce its grinding efficiency. Hence, it was decided, through discussions with the PPCL engineers, to redefine the product size fraction as 100% minus 3.35 plus 0.212 mm (minus 6- plus 65-mesh, Tyler). Such a product is being sold in Brazil under the trade name "Microgranulado" (16).

Further tests were conducted to evaluate the effect of shaft speed on the product yield. The following tabulation shows that the product yield increased with an increase in speed up to about 300 rpm and then leveled off.

Shaft speed, rpm	100	150	200	300	400
Produce size, %[a]	41.1	48.6	52.4	57.7	57.6

a. Between 3.35 and 0.212 mm.

An extended test run lasting for about 6 hours was then made at a pug mill shaft speed of 300 rpm; the operating data and product for physical/chemical analyses were collected, and the results are given in Tables 24, 25, and 26.

The pug mill operation during the entire test run was simple to control, and the shaft speed was relatively constant. The materials from the pug mill and dryer discharges were relatively easy to handle, and the screens remained relatively clean during the entire operation. The oversize fraction (larger than 3.35 mm [plus 6-mesh, Tyler]) routed to the chain mill usually was less than 15% of the dryer output. Grinding of the oversize contributed between 7% and 8% to the product size fraction. The recycle ratio was about 1.0--very similar to that obtained using a pinmixer.

The major difference between the pinmixer and pug mill operations was the cake formation. After 6 hours of operation, the inside of the pug mill did not have any cake buildup.

The pug mill granulated product consisted of free-flowing particles that had physical properties, including disintegration in water, that were similar to those of the minigranules (with potassium chloride binder) produced using a pinmixer.

Pug Mill Granulation Using Phosphoric Acid Binder--As stated earlier, because of a good preliminary agronomic performance (under greenhouse conditions) of minigranulated Mussoorie phosphate rock made in a pinmixer using a phosphoric acid binder, a test was conducted to evaluate the production of a similar product in a pug mill. At the beginning of the test, it was recognized that the heat of reaction of phosphoric acid and phosphate rock might be high enough, if contained, to reduce the moisture content of the product to an acceptable limit and thereby eliminate the need for a drying step.

The equipment setup for this test was similar to that for the pug mill granulation test using potassium chloride, except that the recycle, drying, screening, and crushing systems were not required. This was a once-through process, and the acidulated product from the pug mill was directly transferred to a box-type, insulated den 56 cm long, 36 cm wide, and 30 cm deep (volume ≅0.06 m^3). The top of the box had vent holes that allowed (1) moisture to escape from inside the den and (2) measurement of temperature of the product inside the den. After denning (≅60 minutes), the product was recovered and stored in a pile at room temperature (24°C) for 24 hours. The material was then recovered from the pile and sampled for physical/chemical analyses. The physical properties were evaluated on a minus 3.35- plus 0.212-mm size fraction so that the results could be compared with a similar sample (MSR 206; pug mill granulation using potassium chloride binder).

The limited production data (Table 24) indicate that, under the conditions tested, a relatively nondusty, semigranular material can be produced by reacting Mussoorie phosphate rock with wet-process phosphoric acid followed by denning for 1 hour and pile curing for 24 hours. The pug mill operation was fairly steady, and the discharge material was reasonably free flowing, although slightly sticky. This stickiness, however, did not cause any plugging problem.

The temperatures of the pug mill discharge and den were about 40° and 43°C, respectively. This den temperature was high enough to reduce the moisture content from 8.0% (pug mill discharge) to 4.8% in 1 hour. The ex-den material was free flowing, although its larger granules (plus 1.18 mm [14-mesh, Tyler]) were somewhat plastic and soft. Pile curing for 24 hours, however, made the larger granules relatively hard, and they could not be easily broken under finger pressure.

The size distribution of the ex-den material (Table 24, footnote m) showed that the product contained about 65% between 3.35 and 0.212 mm (minus 6- plus 65-mesh, Tyler). About 13% of the material was larger than 3.35 mm (plus 6-mesh, Tyler); the fines fraction (minus 0.212 mm [65-mesh, Tyler]) was about 22%. In a larger scale operation, depending on the desired size distribution of the product, the oversize would be crushed and rescreened and the undersize would be returned to the pug mill as recycle.

The chemical analysis of the product showed it to contain about 26% P_2O_5, of which approximately 42% was in an available form. The variation in total P_2O_5 and availability between the various size fractions of the product was small. The free acid in the product, expressed as % P_2O_5, was well within the acceptable limits of such fertilizers.

Except for moisture absorption, the physical properties of the product size (minus 3.35- plus 0.212-mm [minus 6- plus 65-mesh, Tyler]) fraction were similar to those of Sample MSR 206. The moisture absorption for the phosphoric acid-granulated sample after 72 hours of exposure at 80% relative humidity and 30°C was less than that of the material prepared using potassium chloride (MSR 206).

Partial Acidulation Process

As stated earlier, the ROM Mussoorie rock and the Mussoorie concentrate prepared by Sala International, Sweden, were used for the SSAG process demonstration trials. Chemical analyses (Table 2) of this concentrate showed that it contained 25% P_2O_5 and 10% CO_2. This CO_2 content, although slightly lower than the ROM rock (Table 19), is still relatively high and would consume sulfuric acid during acidulation. The Sala concentrate received at IFDC was wet and relatively coarse (between 1 and 25 mm) when compared with the ROM rock (Table 19). This material was air dried, crushed in a jaw crusher, and ground in a ball mill to prepare a feed (≅81% smaller than 0.075 mm [200-mesh, Tyler]) for partial acidulation with sulfuric acid (Table 27).

Initially, plans were made to use this ground concentrate in the SSAG process; however, during the visit of the PPCL engineers in March 1984, IFDC suggested that the production of PAPR in an ROP semigranular form also be considered because of the simplicity of such a process and a potential for reducing the cost of production. The process demonstration trials included the following:

1. Single-step partial acidulation/granulation of the concentrate.
2. Partial acidulation in an ROP form of the concentrate.
3. Single-step partial acidulation/granulation of the ROM rock.

Single-Step Partial Acidulation/Granulation of the Concentrate--The equipment configuration for the process demonstration trial was essentially the same as that described earlier (see section on Partial Acidulation/Granulation Studies of Mussoorie Phosphate Rock) except that a drum granulator was used instead of a pan granulator and the recycle feed was heated to simulate conditions in larger scale equipment (with less heat loss). A drum was used because it is a more common type of granulator in the fertilizer industry. The laboratory drum granulator was 31.8 cm in diameter, 67.3 cm in length, and equipped with a variable-speed drive. A 5.1-cm-high retaining dam was located 6.4 cm from the discharge end of the granulator. The recycle heating system was the same as that used for the minigranulation process demonstration run.

Before the actual demonstration run was begun, exploratory tests were required to determine the acid concentration that allowed desirable granulation characteristics (recycle ratio, bed temperature, etc.) and acceptable physical properties (nonsticky, free flowing) of the "green" (ex-granulator) material and chemical analysis (about 50% water solubility) of the dried products. The acid concentrations tested were 73%, 83%, and 93% H_2SO_4. The granulation was difficult to control at both 73% and 93% concentrations.

With the 73% acid and a recycle ratio of 2:1, the bed was too wet; this caused the material to overgranulate into larger than desired lumps, even when water was not added to the granulator. The granulation could be improved (easily controlled) by increasing the recycle ratio to about 7:1, but this significantly reduced the production rate.

The problem was somewhat different while using 93% acid. The bed temperature was relatively high (≅60°-65°C), which resulted in a "green" (ex-granulator) product that was high (>8%) in free acid and extremely sticky. This stickiness caused buildups in the granulator, dryer, screens, and crusher.

From an operational standpoint, the 83% acid appeared to be better than either the 73% or the 93% acid. The granulation was easy to control, and the "green" product was nonsticky and free flowing. It should be pointed out that this acid concentration is not necessarily the optimum, and in a larger scale operation the acid concentration may be different, although the trend should be similar.

Once the acid concentration was established, the equipment was operated for about 6 hours to stabilize the operating conditions and to study the drum granulator operation, especially as it related to the buildup of material within the drum and the effect of moisture on the size distribution of the granulator discharge. Further, this period also allowed the PPCL engineers to study the drying, screening, crushing (of oversize material), and material handling systems. After this run period, an 8-hour data collection run was made. The data were collected usually every half hour, and the average of these data sets is presented in Table 28.

The production data indicate that it is technically feasible to produce a granular product with about 50% of its total P_2O_5 in a water-soluble form from

Mussoorie phosphate concentrate (prepared by Sala International, Sweden) through the SSAG process using sulfuric acid. The drum granulator operation was routine, and the buildup was quite small throughout the test run. The drum was rotated at 27 rpm, which corresponded to about 36% of the critical speed. This value is very similar to that obtained with other phosphate rocks tested at IFDC.

Under the conditions tested, the recycle ratio was about 3, which is higher than that required when other phosphate rocks (viz, central Florida, North Carolina, etc.) have been used. This is probably due to the relatively high CO_2 content of the concentrate and unfavorable heat balance resulting from the small size of the equipment. In a larger scale operation and under optimum conditions (acid concentration, bed temperature, etc.), this recycle ratio will likely be lower.

The grade of the product was 0-18.2-0 with about 50% water solubility and 55% availability. The free acid (measured as % P_2O_5) in the product was less than 4%, which is considered acceptable for such products.

The granular material had good physical properties (Tables 29 and 30). The average crushing strength of about 2 kg/granule is well within expected values for similar products (SSP, TSP, etc.) and corresponds to a fairly resistant fertilizer material (2.1% degradation under simulated handling). The moisture absorption properties of the product were favorable, and no measurable penetration of atmospheric moisture into an exposed sample (after 72 hours at 80% relative humidity and 30°C) was detected.

In spite of the relative difficulty in controlling granulation while using 93% concentration sulfuric acid, IFDC conducted acidulation/granulation tests using this concentration during March 1985 at the request of PPCL. The potential advantage of using the 93% acid is the elimination of the acid dilution step. The equipment configuration was similar to that used for the previous test except a pan granulator was substituted for the drum. The test was begun by using recycle material from the previous run (MSR 810-C-S). As before the granulation was difficult to control with 93% acid and the bed temperature varied between 62° and 68°C. This caused the "green" (ex-granulator) product to be extremely sticky (due to high free acid), which resulted in buildups in the granulator, dryer, screens, and crusher. Consequently, through discussions with the PPCL representatives, it was decided to reduce the acidulation level whereby the granulator discharge was less sticky and had an acceptable physical property. This condition could be achieved when the product water solubility was about 33%.

The equipment was operated in this mode for about 4 hours to observe the granulation characteristics and obtain samples for chemical analyses. However, 4 hours of run time was not long enough to obtain any meaningful engineering data. The chemical analysis of the product is shown in Table 28.

After 4 hours of operation in the above mode, the combustion chamber was turned off and the dryer was used as a conveyor for the granulator discharge to the screens. The purpose of this test was to evaluate the technical feasibility of screening the "green" (ex-granulator) material followed by pile curing of the product-size fraction (minus 3.35- plus 1.18-mm [minus 6- plus 14-mesh, Tyler]) and bagging. Such a mode of operation has the advantage of a reduced product cost (due to the elimination of a dryer) and is being practiced in a plant in Brazil using an indigenous phosphate rock (17). For the present test, the operation was started using the recycle material from the previous test (when a dryer was used); an attempt was made to screen the "green" material, but was not possible due to a weak granule strength. Pile curing for 1 week improved the granule strength to the point where the material could be screened. The acidulation/granulation circuit was operated for about 3 hours to observe the granulation characteristics and obtain samples for chemical analyses, but no engineering data were collected. The chemical analysis of the product is shown in Table 28.

From an operational standpoint, it is technically feasible to produce a granular product with about 33% of its total P_2O_5 in a water-soluble form from Mussoorie phosphate concentrate (prepared by Sala International, Sweden) through the SSAG process using 93% sulfuric acid. The pan granulator operation was routine, and granulation was easy to control by using water.

When a dryer was used to dry the "green" (ex-granulator) material, the buildup in the dryer, screens, and crusher was quite minimal. Under the conditions tested, the entire operation was quite routine and the granulated material was free-flowing individual particles.

In contrast, when the "green" (ex-granulator) material was not dried, it was difficult to screen due to a weak granule strength. The screens, crusher, and chutes tended to blind very quickly. However, when the "green" material was pile cured, screening and crushing operations were relatively simple without any noticeable buildup.

The grade of the products, whether dried or pile cured, was about 0-20-0. The water solubility and availability of freshly prepared (@ 24 hours) products were 33% and 34%, respectively. The free acids (measured as % P_2O_5) of dried and undried products (@ 24 hours) were 4% and 5%, respectively; after 1 week these values were 2.4% and 0.4%, respectively.

The physical properties of products were dependent on their mode of preparation (Table 29 and 30). For example, the average crushing strengths of the dried and 1-week cured and undried products were 1.8 and 0.4 kg/granule. respectively. Due to this low crushing strength of the latter, the percentage degradation under simulated handling was extremely high (14.4%), which would probably cause serious handling problems due to degradation, breakage, etc. The moisture absorption properties of both products were favorable, and no measurable penetration of atmospheric moisture into an exposed sample (after 72 hours at 80% relative humidity and 30°C) was detected.

Partial Acidulation in a Run-of-Pile Form of the Concentrate--As mentioned earlier, continuous laboratory-scale ROP PAPR studies were made using Mussoorie phosphate concentrate (prepared by Sala International, Sweden) and sulfuric acid to determine the technical feasibility of producing an ROP semi-granular product that would be less costly than the granular products previously studied in the SSAG process. The tests were aimed toward determining the effect of curing on the product quality (physical/chemical properties). In the known commercial plants in Europe and Brazil, the acid-rock reaction product usually requires between 7 and 14 days of curing before it is ready for further handling.

The equipment configuration for the present test was similar to that of the pug mill granulation test of ROM rock using phosphoric acid (see Mini-granulation Process Demonstration Trial). This was a once-through process with no drying. The unit consisted of phosphate rock and sulfuric acid feed systems, a double-shaft pug mill mixer, and a simple insulated box den. The dimensions of the pug mill and box den were given earlier. The laboratory-scale unit was operated continuously at a phosphate rock feed rate between 10 and 15 kg/hour. Sulfuric acid of selected concentration was fed to the pug mill to obtain a product with about 50% water solubility. The fluorine-laden gases from the pug mill and box den were treated in a wet scrubber to remove dust and fluorine compounds. The scrubber liquor was then routed to the effluent pond. The pug mill discharge was denned for 1 hour followed by pile curing at room temperature for 24 hours.

A series of preliminary tests were made to determine the acid concentration that would produce a handleable acid-rock reaction product. The acid concentrations evaluated were 73%, 83%, and 93% H_2SO_4.

When 73% H_2SO_4 acid was used, the viscosity of the acid-rock slurry was unsatisfactorily low, which caused the material to be extremely "soupy" and difficult to transport to the den. Further, the ex-den material (after 1 hour) was sticky and uncuttable.

With 93% H_2SO_4 acid, the liquid phase was not sufficient to completely wet the material, and the result was a pug mill discharge mixture of large sticky lumps and unacidulated phosphate rock dust. The 1-hour denned product had a similar appearance. Additionally, the chemical analyses (total and water-soluble P_2O_5) of the denned product varied with the particle size, thereby suggesting a nonuniform acidulation. When water was added to the pug mill during acidulation with the 93% sulfuric acid, the material tended to be much more uniform in appearance. However, the pug mill discharge temperature tended to be extremely high (150°-160°C), causing the product to be very dry. The net result was a relatively high (>9%) free acid content in the 1-hour denned product.

The 83% H_2SO_4 acid produced the most acceptable product in terms of physical and chemical properties. The pug mill discharge had a uniform consistency and could be easily transported to the den, and the ex-den product was cuttable and friable.

After the operating conditions were established, the unit was operated for a total of 8 hours to produce four batches of product, and each batch was denned for 1 hour followed by pile curing for 24 hours. The pile-cured material was subsequently screened on a 46-cm diameter, double-deck, self-cleaning, mechanically vibrated screen. The screen was fitted with a 3.35-mm (6-mesh, Tyler) oversize screen and a 1.18-mm (14-mesh, Tyler) undersize screen to yield a product in the 3.35-1.18 mm size range. Oversize material from the screen was routed to a jaw crusher. The jaw crusher discharge was returned to the screen. The quantity of oversize material varied among batches and averaged around 15%. The production data for this ROP PAPR are given in Table 31, and the selected physical properties results are shown in Tables 32 and 33.

After completion of the above ROP PAPR demonstration run, an exploratory test run was made to determine the feasibility of granulating the undersize ROP fraction (smaller than 1.18 mm [14-mesh, Tyler]) into a conventional size (3.35- to 1.18-mm [6- to 14-mesh, Tyler]) product. The equipment setup was similar to that used for the partial acidulation/granulation studies and consisted of a dry feed system, pan granulator, dryer, screening system including a crusher, and a recycle heating system. Water heated to about 70°C was used to promote and control granulation. The amount of material available for this test was not sufficient to obtain any meaningful engineering data; however, some rather general observations regarding granulation were made. No attempt was made to evaluate the chemical/physical properties of the granulated product.

The production data (Table 31) indicate that it is feasible to partially acidulate ROP Mussoorie phosphate concentrate (prepared by Sala International, Sweden) using 83% H_2SO_4 sulfuric acid to produce a product with about 50% water solubility. The pug mill discharge was relatively viscous but flowable and could be easily transported to the den. The discharge temperature of 108°C was high when compared with that encountered with commercial phosphate rock (e.g., central Florida) acidulated to the same level of water solubility. This relatively high reaction temperature was probably due to the exothermic heat of reaction between carbonate and sulfuric acid. This level of reaction temperature, however, was beneficial in that it caused the ex-den material to be dry, cuttable, and friable. The free acid (measured as % P_2O_5) and moisture content of the denned material were 4.1% and 4.5%, respectively. By industry standards these values are slightly higher than is acceptable in a finished product. However, this material would be suitable for granulation if that is desired.

Pile curing of the denned material at ambient temperature (30°C) reduced its free acid and moisture contents to 0.8% and 2.6%, respectively. The cured product had an appearance similar to that of ROP SSP and was a mixture of lumps (≅20 mm) and fine particles. About 30% of the ROP product was in the size range of 3.35-1.18 mm (6- to 14-mesh, Tyler); however, another 10% in the above size range could be realized by crushing the oversize fraction (larger than 3.35 mm [14-mesh, Tyler]). Thus, the total yield was about 40%. The screened product (3.35-1.18 mm) was relatively granular and compared favorably with the material produced in the SSAG process. It should be noted that the above yield and the granule structure were obtained in the laboratory-scale equipment and under conditions that were not optimal. In larger scale equipment and under optimum conditions, these results may be improved.

The grade of the ROP PAPR was 0-18.4-0 with about 52% and 59% of the total P_2O_5 in water-soluble and available forms, respectively. The free acid and moisture in the product were well within acceptable limits.

The physical properties of the product-size fraction of ROP PAPR (Tables 32 and 33) were very similar to Sample MSR 810-C-S (Tables 29 and 30), except for porosity, crushing strength, and abrasion resistance. The ROP samples were more porous, less resistant to abrasion (simulated handling), and had a lower granule strength.

On the basis of the limited test run, the pan granulation of ROP PAPR fines (smaller than 1.18 mm [14-mesh, Tyler]) is feasible and relatively simple. The granulation was easy to control by using water, and the granulation characteristics were similar to those of ROP SSP granulation. The dryer, screens, and crusher operations were routine, and the granulated material was free-flowing granules that could not be broken under normal finger pressure.

Single-Step Partial Acidulation/Granulation of the ROM Rock--The ROM Mussoorie phosphate rock was used in the process demonstration trial for producing PAPR using the SSAG process and a combination of sulfuric and phosphoric acids. The equipment configuration was similar to that used for the previous test except a pan granulator was used instead of a drum. Initial tests involved pretreatment of ROM rock using 40% P_2O_5 phosphoric acid in a pinmixer. The purpose of this pretreatment was to partially convert the calcite in the rock to a mixture of monocalcium and dicalcium phosphates, thereby reducing its CO_2 content. After pretreatment, the pinmixer discharge was transferred by a belt conveyor to the pan granulator where it was partially acidulated/granulated using 93% H_2SO_4 sulfuric acid. The pan discharge was dried and screened to remove the product-size fraction. The oversize was crushed and rescreened while the undersize was recycled to the pan granulator. The objective of this test was to obtain a 50% water solubility level in the product. The equipment was operated in this mode for about 4 hours to observe the granulation characteristics and obtain samples for chemical analyses; however, no engineering data were collected. The chemical analyses and the raw materials consumption data are given in Table 34.

After 4 hours of operation in the above mode, the ROM rock was directly fed to the pan granulator, without pretreatment, and partially acidulated/granulated using 93% H_2SO_4 sulfuric acid. As expected, at a 50% water solubility level in the product, the granulation was difficult to control and the bed temperature was relatively high (about 66°C). This caused the "green" (ex-granulator) product to be very sticky (due to high free acid), which resulted in buildups in the granulator, dryer, screens, and crusher. Hence, through discussions with the PPCL representatives, less sulfuric acid was used in the acidulation/granulation step with the result that the product water solubility was around 30%. The equipment was operated for about 3 hours in this configuration to observe the granulation characteristics and obtain samples for chemical analyses. The relevant data are in Table 34.

As an extension of the above acidulation/granulation with 93% sulfuric acid, the combustion chamber was turned off and the dryer was used as a conveyor for the granulator discharge to the screens. As with the Sala concentrate, the "green" (ex-granulator) product could not be screened due to a weak granule strength. Hence, the material was pile cured for 1 week prior to screening. The acidulation/granulation circuit was operated for about 3 hours to observe the operation and obtain samples for chemical analyses. The results are shown in Table 34.

From an operational standpoint, it is technically feasible to produce a granular product containing about 50% of its total P_2O_5 in a water-soluble form from ROM Mussoorie phosphate rock through pretreatment with phosphoric acid followed by partial acidulation/granulation using 93% sulfuric acid in the SSAG process. The pretreatment and acidulation/granulation steps were relatively simple, and the entire operation was easy to control.

Under the conditions tested the material discharging from the dryer was crisp and dry, resulting in a minimum buildup in the screens and crusher. The granulator dryer and the transfer chutes remained relatively clean.

In contrast, when the ROM rock was directly acidulated and granulated with 93% sulfuric acid without pretreatment with phosphoric acid, the operation was extremely difficult to control due to a relatively high free acid content in the granulator discharge. Even when the amount of sulfuric acid used was reduced to obtain about 30% water solubility in the product, the operation was marginal and extremely sensitive to the free acid content of the granulator discharge. A slight excess of free acid (due to fluctuations in the acid/rock ratio) caused buildups in the chutes, dryer, screens, and crusher. Further, the dried product tended to be sticky and relatively soft.

In comparison, when the "green" (ex-granulator) material was not dried, it was difficult to screen due to stickiness and a weak granule strength. The screens, crusher, and chutes tended to plug very quickly. However, when the "green" material was pile cured, screening and crushing operations were relatively simple without any appreciable buildup.

The grade of the product while using phosphoric and sulfuric acids (Sample MSR 1000) was 0-19.5-0, with about 41% and 46% water solubility and availability, respectively. After 1 week there was a slight improvement in water solubility and availability values. The free acid (measured as % P_2O_5) of the fresh product was 3%, which is considered acceptable by industry standards.

The grade of the sulfuric acid acidulated products (Runs MSR 1002 and MSR 1002-A), whether dried or pile cured, was about 0-15-0. The pile-cured product (Run MSR 1002-A) was slightly higher in water solubility and availability than the dried product (Run MSR 1002). For example, the water solubility and availability of 1-week dried and pile cured products were 29.0% and 34.8% (Run MSR 1002) and 30.7% and 35.3% (Run MSR 1002-A), respectively. The free acids (measured as % P_2O_5) of dried and undried products (@ 24 hours) were 4.6% and 4.9%, respectively; after 1 week these values were 1.6% and 0.6%, respectively.

The average crushing strength of products prepared using phosphoric and sulfuric acids (Run MSR 1000) was 1.8 kg/granule (Table 35). This value is well within that required for satisfactory handling and is much higher than granules prepared using only sulfuric acid (0.5 kg/granule [Run 1002] and 0.4 kg/granule [Run 1002-A]). Due to the low crushing strength of sulfuric acid acidulated products, the percentage degradation was relatively high, especially for the undried product. For example, the percentage degradation of dried (Run MSR 1002) and undried (Run MSR 1002-A) products were 7.2% and 16.2%, respectively. The moisture absorption properties of all products were favorable, and no measurable penetration of atmospheric moisture into an exposed sample (after 72 hours at 80% relative humidity and 30°C) was detected.

Experimental Materials for Field Trials in India

According to the terms of the contract, promising experimental products were sent to India for field trials. These materials were selected on the basis of the greenhouse and soil incubation studies and through discussions with the PPCL representatives who visited IFDC in March 1984. Additionally, PPCL requested that other products not evaluated in the greenhouse study also be sent to India, especially those produced from Mussoorie phosphate concentrate (prepared by Sala International, Sweden). The type and amount of experimental products airfreighted to India were as follows:

Sample Number	Sample Description	Amount (kg)
	ROM Mussoorie Phosphate Rock	
MSR 301	Minigranular (sulfuric acid binder--pinmixer)	25
MSR 400-A	Minigranular (phosphoric acid binder--pinmixer)	20
MSR 817[a]	ROP[b,c] (phosphoric acid binder--pug mill)	25
MSR 605	Granular PAPR using sulfuric acid (≅40% water solubility)	40
MSR 816[a]	Granular PAPR using phosphoric acid (≅25% water solubility)	25
MSR 702	Granular PAPR using phosphoric acid (≅50% water solubility)	25
	Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden)	
R231.74	Ground Mussoorie phosphate concentrate	30
MSR 809-S[a]	ROP[b] PAPR using sulfuric acid (≅50% water solubility)	25
MSR 810-C-S[a]	Granular PAPR using sulfuric acid (≅50% water solubility)	30
MSR 813-S[a]	Granular PAPR using phosphoric acid (≅25% water solubility)	25
MSR 812-S[a]	Granular PAPR using phosphoric acid (≅50% water solubility)	25

a. Not evaluated in the greenhouse studies.
b. Run of pile.
c. Contains a mixture of granules and minigranules.

The chemical analysis of a representative sample of each product is shown in Table 36.

Conclusions and Recommendations

The ROM Mussoorie phosphate rock is a low- to medium-grade (15%-18% P_2O_5) carbonate-fluorapatite with calcite being the principal diluent and with significantly lesser amounts of dolomite. The chemical quality of the ore is further diminished by the presence of pyrite (5%) and dolomite (5%).

Attrition scrubbing of this ore in an acid medium to remove carbonates seems technically feasible. Of the acid-media tested (5% HCl, 5% HNO_3, 2% HNO_3, 5% HNO_3 + 5% H_2SO_4, 2% HNO_3 + 5% H_2SO_4, and 5% H_2SO_4) 5% HNO_3 solution seems to be the most attractive; however, the rock feed needs to be finely ground, and the acid consumption is relatively high. Best results are obtained when the ore is ground to 80% (by weight) smaller than 0.075 mm (200-mesh, Tyler). To reduce the CO_2 content from about 14% (ROM rock) to about 4%, the acid consumption (on 100% basis) is around 576 kg/mt product, an amount that is quite high. Thus, unless a relatively cheap source of acid is available, the attrition scrubbing process may not be economically attractive. Nevertheless, a cost:benefit analysis is required to assess the economic viability of this process.

The physical properties (less dusty and free flowing) of the ROM finely ground Mussoorie phosphate rock (being sold as a direct-application fertilizer) can be improved through minigranulation using such binders as urea solution, potassium chloride solution, sulfuric acid solution, phosphoric acid solution, and urea plus nitric acid solution. From an operational viewpoint the potassium chloride, sulfuric acid, and phosphoric acid solutions are more attractive. The pinmixer granulator used for minigranulation in the laboratory-scale operation appears to be suitable, but the extent of pin wear and caking in the granulator housing cause concern. Further, the extremely small size of minigranules (0.300 to 0.106 [minus 48- plus 150-mesh, Tyler]) tends to plug the screens and thus reduce the screening efficiency. In a larger scale operation a combination of a scalping screen (to remove big lumps) and an air-classification system may be a better alternative than conventional screening. Hence, it is recommended that the minigranulation process be further studied in a pilot plant to evaluate some of these options and obtain operating data to scale up to an industrial-scale operation. The pilot-plant capacity should be around 1 mtph, and the design should be flexible enough to allow evaluation of other types of granulators, such as a pug mill (or any modifications of it) and a fluid-bed dryer. This pilot plant can also be used to produce products for agronomic trials where the effect of different granule size ranges of products, other than 0.300 to 0.106 mm (minus 48- plus 150-mesh, Tyler), on crop response can be studied. Ultimately, the pilot-plant data would provide a more reliable basis for estimating the investment and production costs. Incidentally, it is reported that a company in New Zealand recently demonstrated, in a pilot plant (4-6 mtph), the production of granulated phosphate rock using a pelletizer (hybrid of pug mill and pinmixer) (18).

The SSAG process using ROM Mussoorie phosphate rock and sulfuric acids of 73% and 93% concentrations are difficult to control at 50% product water solubility because of stickiness, which causes buildup in the granulator, dryer, screens, and crusher. A reduction in the amount of acid used for acidulation improves the operation but produces a weak granule. For example, with 93% sulfuric acid the product water solubility is 30% and the operation is controllable; the product is free flowing but weak due to a low crushing strength (about 0.5 kg/granule). The operation and the product crushing strength can be improved by pretreatment of the ROM rock with phosphoric acid followed by acidulation with sulfuric acid.

In contrast to acidulating the ROM rock with sulfuric acid, the use of phosphoric acid in the SSAG is quite simple and trouble free. However, to achieve 50% product water solubility, about 56% of the P_2O_5 has to be derived from phosphoric acid. Thus, more than 50% of the P_2O_5 in the product has to be imported (from India or other sources); this makes phosphoric acid acidulation questionable and forms the basis for recommending an economic review by PPCL.

In comparison with the ROM rock, the attrition-scrubbed material (prepared by using 5% HNO_3 solution) is well suited for the SSAG process using either acid (sulfuric or phosphoric). Because of a lower carbonate content of the scrubbed rock, the acid consumption (either sulfuric or phosphoric) is lower than that for the ROM rock. The use of attrition-scrubbed material is attractive provided that attrition scrubbing is economical.

The Mussoorie phosphate concentrate prepared by Sala International, Sweden, using the heavy-media separation technique, is reasonably easy to acidulate with 83% sulfuric acid in the SSAG process to produce a granular product containing about 50% water solubility. However, with a 93% sulfuric acid, the operation is difficult to control unless the quantity of acid is reduced to a level where the product water solubility is 30%.

In addition to its use with the SSAG process, the above concentrate is also suitable for production of PAPR in an ROP form, which is semigranular and nondusty. The ROP PAPR process is relatively simple, and the product is likely to be cheaper to produce than the granular material produced by the SSAG process. However, detailed investment and production cost studies are needed and recommended.

On the basis of the laboratory tests with the Mussoorie rock (ROM and concentrate), it is recommended that PPCL consider the production of PAPR. However, prior to commercial production, it is recommended that PPCL set up a demonstration-scale plant where both ROM rock and concentrate can be evaluated using either sulfuric or phosphoric acid or both. The demonstration plant can be used to confirm the laboratory test results and also to obtain enough information to do a detailed production economics study. The demonstration plant should have a capacity of 3-5 mtph of production and should be designed with sufficient flexibility to evaluate various process options. The operation of the demonstration plant will provide the needed experience for the operators and may be viewed as the training ground for PPCL engineers who may later be involved in the operation of the commercial-scale plant, if PPCL decides to proceed in that direction. Even when a commercial-scale plant is constructed, the demonstration plant can be used to solve any technical problems that may arise. Further, the demonstration plant can be used to evaluate other indigenous phosphate rocks for PAPR production and also to develop other product types, including compound fertilizers. Ultimately, the PAPR products produced in the demonstration plant can be used for field trials and market acceptance studies.

IFDC has demonstrated the SSAG and ROP PAPR processes using central Florida phosphate rock in pilot-plant scale (≅250-500 kg/hour production capacity). Although the central Florida phosphate rock is more reactive and has a lower content of free calcite than the ROM Mussoorie rock and concentrate prepared by Sala International, Sweden, it is felt that the Mussoorie rock would be suitable for production of PAPR on a larger scale. It should be mentioned, however, that a reduced level of free calcite content in the ROM rock and concentrate prepared by Sala International, Sweden, would improve the plant operation and decrease the sulfuric acid consumption.

A preliminary list of battery-limits equipment for a demonstration-scale plant (3-5 mtph capacity), along with a brief process description and pollution control requirements, is included in Appendix B. Abbreviated equipment specifications are also included based on IFDC pilot-plant runs using central Florida phosphate rock. It would be helpful to confirm these specifications through pilot-plant test runs using ROM Mussoorie rock and concentrate prepared by Sala International, Sweden.

References

1. Pyrites, Phosphates & Chemicals Ltd. 1982. Mussoorie-Phos--A Phosphate Fertilizer for Direct Application.
2. Bond, F. C. 1954. "Crushing and Grinding Calculations," Canadian Mining and Metallurgical Bulletin, July, 47(507):446-472.
3. Livingston, O. W. 1978. "Minigranulation--A Method for Improving the Properties of Phosphate Rock for Direct Application," IN Seminar on Phosphate Rock for Direct Application, IFDC-SP-1, pp. 367-377.
4. Livingston, O. W. 1981. "Technology of Production of Phosphate Rock Fertilizers," IN Proceedings of the International Conference on Phosphorus and Potassium in the Tropics, The Malaysian Society of Soil Science, Kuala Lumpur, Malaysia, pp. 545-555.
5. Driscoll, R. E. October 20, 1970. "Process for Producing Improved Pellets of a Powder," U.S. Patent 3,535,412.
6. Frye, J. A., W. C. Newton, and W. H. Engelleitner. 1975. "The Pinmixer--A Novel Agglomeration Service," Paper presented at the 1975 IBA Conference, Massachusetts.
7. Raistrick, B. December 5, 1961. "Apparatus for Granulating Fertilizer," U.S. Patent 3,011,876.
8. Tennessee Valley Authority. 1970. TVA Procedures for Determining Physical Properties of Fertilizers, Special Report No. S-444, National Fertilizer Development Center (NFDC), Muscle Shoals, Alabama 35660.
9. Unpublished report, IFDC.
10. Venkatramanan, K., and M. T. Sebastian. 1983. "Flow Property of Indian Rock Phosphate and Application to Plant Design," Fertilizer News, December, pp. 102-106.
11. Lanzon, M. 1983. "How to Avoid Flow Problems in Hoppers and Feeders," Canadian Chemical Processing, 67(4):31-32.
12. Kuhnemund, B. 1984. "Bin Storage of Bulk Materials," Pit and Quarry, 76(8):57-59, 62.
13. Carr, R. L., Jr. 1965. "Evaluating Flow Properties of Solids," Chem. Eng., No. 2, pp. 163-168.
14. Personal communications, Werner Ramin, Giulini Chemie GmbH, Federal Republic of Germany.
15. Personal communications, Mario Torres, Fertisul, S.A., Brazil.

16. Peng, P. H., and L. L. Hammond. 1979. "Ground and Granulated Phosphate Rocks for Direct Application," Paper presented at New Zealand Fertiliser Manufacturers' Research Association meeting, University of Auckland, New Zealand, November 21-23.

17. Personal communications, Nelson Pagnanelli, Fertilizantes Fosfatados S.A., Uberaba, Brazil.

18. Personal communications, David J. Udy, Winston Limited, Auckland, New Zealand.

Table 1. Chemical Analyses of Run-of-Mine, Ground and Crushed Mussoorie Phosphate Rock Used for Minigranulation, Attrition Scrubbing, and Partial Acidulation/Granulation Studies[a]

	Ground[b]	Crushed[c]
	(wt %)	
P_2O_5	18.6	17.9
CaO	43.8	42.3
SiO_2	15.4	15.7
F	1.8	1.7
Al_2O_3	1.7	1.8
Fe_2O_3	4.0	3.6
Na_2O	0.26	0.21
MgO	1.4	1.6
K_2O	0.45	0.44
S	2.3	2.3
Cl	0.013	0.013
CO_2	13.6	13.6
Organic carbon	1.4	1.4
Loss on ignition	10.8	10.9
H_2O	0.17	0.48

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a. Rock received on May 12, 1983.

b. Composite of ground sample, designated as IFDC inventory No. R231.61.

c. Composite of crushed sample, designated as IFDC inventory No. R231.62.

Table 2. Chemical Analysis of the Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden) Used for the Partial Acidulation Process Demonstration Runs[a]

	Wt %
P_2O_5	25.0
CaO	45.3
SiO_2	5.1
F	2.5
Al_2O_3	0.55
Fe_2O_3	5.0
Na_2O	0.19
MgO	1.2
K_2O	0.15
S	3.3
Cl	0.02
CO_2	10.0
Organic carbon	1.8
Loss on ignition	5.4
H_2O	0.16

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a. Concentrate received on January 11, 1984, designated as IFDC inventory No. R231.74.

Table 3. Chemical Analysis of a Mussoorie Ore Sample Used for a Characterization Study[a]

	Wt %
P_2O_5	15.2
CaO	46.0
SiO_2	11.6
Al_2O_3	1.4
Fe_2O_3	4.1
Na_2O	0.21
MgO	2.1
K_2O	0.3
S	2.9
Cl	0.015
F	1.45
C	1.23
CO_2	17.3
Loss on ignition	17.9
NAC-soluble P_2O_5[b]	1.0

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a. 10-kg sample received January 20, 1983, designated as IFDC inventory No. R231.50.

b. Determined on a carbonate-free sample.

Table 4. Mussoorie Phosphate Ore Liberation Study Based on Point-Counting--500 Points for Each Size Fraction[a]

	Percent of Total in Size Fraction			
	Free Carbonate	Free Apatite	Complex Locked	Simple Locked
-48 Tyler +60 U.S. (60 Tyler)	26	35.4	36.2	2.4
-60 +80 U.S.	24.8	48.0	21.6	5.6
-80 +100 U.S.	30.0	44.8	21.4	3.4
-100 +200 U.S.	24.4	57.6	18.0	

a. Tyler mesh equivalents:

U.S. (mesh)	Tyler (mesh)	Opening (mm)
-	48	0.300
60	60	0.250
80	80	0.180
100	100	0.150
200	200	0.075

Table 5. Chemical Analysis of Run-of-Mine Mussoorie Phosphate Rocks Used for the Attrition Scrubbing Tests

Sample	P_2O_5	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	CO_2	S	F
	(wt %)								
Jaw crushed	17.7	42.8	1.41	13.40	4.19	1.84	13.8	2.0	2.4
As-received ground	17.2	43.3	1.50	13.1	3.40	2.42	15.4	1.5	1.8

Table 6. Size Distribution of Run-of-Mine Mussoorie Phosphate Rock Used for the Attrition Scrubbing Tests

Sample	Size Mesh, Tyler[a]	Wt %
Jaw crushed	-6 +10	9.88
	-10 +35	57.56
	-35 +48	6.59
	-48 +65	4.06
	-65 +150	6.46
	-150 +200	3.49
	-200 +325	2.16
	-325	9.80
		100.00
As-received ground	-150 +200	24.06
	-200 +270	13.78
	-270 +325	7.27
	-325 +400	4.76
	-400	50.13
		100.00

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a. Tyler mesh equivalents:

Tyler (mesh)	Opening (mm)
6	3.35
10	1.70
35	0.425
48	0.300
65	0.212
150	0.106
200	0.075
270	0.053
325	0.045
400	0.038

Table 7. Chemical Analyses of the Different Size Fractions of the Run-of-Mine, Jaw-Crushed Mussoorie Phosphate Rock Used for the Attrition Scrubbing Tests

Size Mesh, Tyler[a]	Wt % of Total Sample	P_2O_5	CaO	MgO	CO_2	SiO_2	Fe_2O_3	Al_2O_3	S
		(wt %)							
-6 +10	9.88	17.40	45.30	1.50	14.50	13.60	4.20	1.60	1.98
-10 +35	57.56	19.90	45.90	1.45	14.90	13.90	3.91	1.68	2.17
-35 +48	6.59	19.30	44.92	1.30	13.70	13.32	3.94	1.60	1.80
-48 +65	4.06	19.50	44.08	1.30	12.40	12.90	4.00	1.64	1.74
-65 +150	6.46	18.80	43.20	1.40	12.10	13.62	3.80	1.70	1.80
-150 +200	3.49	17.40	42.50	1.50	13.20	13.92	4.82	1.90	1.94
-200 +325	2.16	13.20	40.10	1.70	14.80	18.14	6.30	3.48	2.53
-325	9.80	11.50	42.31	1.90	15.67	19.40	6.39	3.74	2.54
Total Calc.	100.00	18.47	44.93	1.49	14.40	4.26	4.30	1.91	2.12

a. Tyler mesh equivalents:

Tyler (mesh)	Opening (mm)
6	3.35
10	1.70
35	0.425
48	0.300
65	0.210
150	0.106
200	0.075
325	0.045

Table 8. Effect of Ball Mill Grinding on the Size Distribution of the Run-of-Mine, Jaw-Crushed Mussoorie Phosphate Rock Used for the Attrition Scrubbing Tests

Size Mesh, Tyler[a]	Unground	1.5 Minutes	3 Minutes	6 Minutes	12 Minutes
	(wt %)				
-6 +10	9.88	-	-	-	-
-10 +35	57.56	-	-	-	-
-35 +48	6.59	20.10	-	-	-
-48 +65	4.06	27.05	23.96	-	-
-65 +150	6.46	18.35	24.31	17.26	-
-150 +200	3.49	8.99	17.83	22.14	22.70
-200	11.96	25.51	33.90	60.60	77.30
Total Calc.	100.00	100.00	100.00	100.00	100.00

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a. Tyler mesh equivalents:

Tyler (mesh)	Opening (mm)
6	3.35
10	1.70
35	0.425
48	0.300
65	0.210
150	0.106
200	0.075

Table 9. Attrition Scrubbing of the Prepared Ground Sample From the Run-of-Mine, Jaw-Crushed Mussoorie Phosphate Rock in 2% HNO_3

Size Mesh, Tyler[a]	Wt %	Assay %								Distribution %								pH of the Pulp
		P_2O_5	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	CO_2	S	P_2O_5	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	CO_2	S	
-10 +48	72.38	18.4	39.9	1.20	19.1	2.6	1.90	6.40	1.9	69.22	75.66	83.62	74.77	69.56	67.51	80.37	69.41	3.6
-48 +100	8.90	19.2	38.2	0.64	18.0	2.9	1.80	5.32	2.1	8.88	8.91	5.49	8.66	9.54	7.86	8.21	9.44	
-100 +200	3.75	20.5	33.7	0.78	21.8	3.5	2.20	3.87	2.0	4.00	3.31	2.82	4.42	4.85	4.05	2.53	3.78	
-200	14.97	23.0	30.9	0.56	15.0	2.9	2.80	3.42	2.3	17.90	12.12	8.07	12.15	16.05	20.58	8.89	17.37	
Total Calc.	100.00	19.24	38.17	1.04	18.49	2.71	2.04	5.76	1.98	100	100	100	100	100	100	100	100	

a. Tyler mesh equivalents:

Tyler (mesh)	Opening (mm)
10	1.700
48	0.300
100	0.150
200	0.075

Table 10. Attrition Scrubbing of the Run-of-Mine, Jaw-Crushed Mussoorie Phosphate Rock Ground in a Batch-Type Ball Mill for 12 Minutes (80% Minus 0.075 mm [200-Mesh, Tyler]) in Various Acids

Acid Used	Solid Content (wt %)	Pulp (pH)	Materials	P_2O_5	CaO	MgO	CO_2	Fe_2O_3	Al_2O_3	SiO_2	S
				(wt %)							
2% HNO_3; 100% of stoichiometry[a]	4.8	4.12	Product	19.50	35.6	1.7	3.86	4.6	3.2	19.20	2.1
			Filtered solution	0.40	2.4	0.1	-	<0.01	<0.01	<0.01	0.02
5% HNO_3; 100% of stoichiometry[b]	11.2	3.37	Product	22.30	34.7	1.4	3.68	3.9	2.4	18.80	2.1
			Filtered solution	0.70	2.8	0.1	-	<0.01	<0.01	<0.1	0.02
5% H_2SO_4; 100% of stoichiometry[c]	14.1	2.40	Product	13.10	40.3	1.1	2.97	3.3	1.9	18.00	8.9
			Filtered solution	0.90	0.3	0.1	-	<0.01	<0.01	<0.1	0.04
2% HNO_3 + 5% H_2SO_4; 100% of stoichiometry (1:1 ratio)[d]	7.2	2.7	Product	14.60	38.8	0.97	3.59	3.4	2.0	14.10	6.9
			Filtered solution	0.50	1.40	0.1	-	<0.01	<0.01	<0.1	0.03
5% HNO_3 + 5% H_2SO_4; 100% of stoichiometry (1:1 ratio)[e]	12.5	2.84	Product	15.0	35.2	1.2	3.40	3.2	1.9	12.10	6.2
			Filtered solution	0.65	1.90	0.1	-	<0.01	<0.01	<0.1	0.03
5% HCl; 100% of stoichiometry[f]	17.9	2.50	Product	23.10	31.4	1.5	2.86	4.6	3.3	22.60	2.5
			Filtered solution	2.8	6.8	0.1	-	<0.01	<0.01	<0.1	0.04

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a. Acid quantity (kg/mt product; 100% acid basis)--575.7.
b. Acid quantity (kg/mt product; 100% acid basis)--575.7.
c. Acid quantity (kg/mt product; 100% acid basis)--447.7.
d. Acid quantity (kg/mt product; 100% acid basis)--511.7 (287.9 HNO_3 + 223.8 H_2SO_4).
e. Acid quantity (kg/mt product; 100% acid basis)--511.7 (287.9 HNO_3 + 223.8 H_2SO_4).
f. Acid quantity (kg/mt product; 100% acid basis)--333.5.

Table 11. Attrition Scrubbing of the Run-of-Mine, As-Received, Ground Mussoorie Phosphate Rock in Various Acids

Acid Used	Solid Content (wt %)	Pulp (pH)	Materials	P_2O_5	CaO	MgO	CO_2	Fe_2O_3	Al_2O_3	SiO_2	S
							(wt %)				
5% HNO_3; 100% of stoichiometry[a]	10.2	3.15	Product	21.9	32.4	1.6	3.77	5.4	2.57	19.8	1.3
			Filtered solution	0.7	3.0	0.09	-	0.002	0.03	0.02	<0.1
5% HCl; 100% of stoichiometry[b]	16.4	2.45	Product	22.5	31.2	1.3	2.58	5.0	2.57	20.5	2.5
			Filtered solution	2.7	2.0	0.12	-	0.004	0.02	0.02	<0.1
5% H_2SO_4; 100% of stoichiometry[c]	12.7	2.50	Product	12.7	36.8	0.9	2.19	2.7	2.31	9.1	9.9
			Filtered solution	0.82	3.5	0.14	-	0.005	0.01	0.04	<0.1
5% HNO_3 + 5% H_2SO_4; 100% of stoichiometry (1:1 ratio)[d]	11.3	2.84	Product	14.2	34.4	1.0	2.64	3.1	2.43	10.9	6.7
			Filtered solution	0.74	2.0	0.14	-	0.003	<0.01	0.03	<0.1

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a. Acid quantity (kg/mt product; 100% acid basis)--678.5.
b. Acid quantity (kg/mt product; 100% acid basis)--393.8.
c. Acid quantity (kg/mt product; 100% acid basis)--527.7.
d. Acid quantity (kg/mt product; 100% acid basis)--603.1 (339.3 HNO_3 + 263.8 H_2SO_4).

Table 12. Attrition Scrubbing of the Prepared Ground Sample From the Run-of-Mine, Jaw-Crushed Mussoorie Phosphate Rock in 5% H_2SO_4

Size Mesh, Tyler[a]	Wt %	Assay %								Distribution %								pH of the Pulp
		P_2O_5	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	CO_2	S	P_2O_5	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	CO_2	S	
-10 +48	70.44	16.8	43.8	1.40	16.8	2.7	2.0	5.89	2.1	88.25	75.68	83.31	71.36	68.84	66.22	89.41	33.17	2.45
-48 +100	7.35	14.5	42.2	0.73	15.4	2.9	1.8	4.12	5.5	7.95	7.61	4.57	6.82	7.72	6.20	6.53	9.07	
-100 +200	4.29	10.7	36.4	0.80	20.0	3.4	2.4	3.18	7.4	3.42	3.83	2.88	5.18	5.28	4.84	2.94	7.12	
-200	17.92	0.32	29.3	0.60	15.4	2.8	2.7	0.29	12.6	0.38	12.88	9.24	16.64	18.16	22.74	1.12	50.64	
Total Calc.	100.00	13.41	40.77	1.18	16.58	2.76	2.13	4.64	4.46	100	100	100	100	100	100	100	100	

---

[a] Tyler mesh equivalents:

Tyler (mesh)	Opening (mm)
10	1.700
48	0.300
100	0.150
200	0.075

Table 13. Attrition Scrubbing of the Prepared Ground Sample From the Run-of-Mine, Jaw-Crushed Mussoorie Phosphate Rock in 2% HNO_3 + 5% H_2SO_4 (at 1:1 Ratio)

Size Mesh, Tyler[a]	Wt %	Assay %								Distribution %								pH of the Pulp
		P_2O_5	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	CO_2	S	P_2O_5	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	CO_2	S	
-10 +48	63.77	21.1	40.5	1.20	18.6	2.9	1.8	5.29	1.7	77.15	67.18	70.34	63.70	55.58	53.40	84.52	26.47	3.00
-48 +100	11.16	21.6	40.4	0.97	18.3	3.5	2.1	3.65	3.0	13.83	11.73	9.95	10.96	11.74	10.90	10.20	8.17	
-100 +200	4.89	19.8	34.2	0.96	20.1	4.9	2.9	1.88	4.4	5.55	4.35	4.31	5.28	7.21	6.60	2.30	5.25	
-200	20.18	3.0	31.9	0.83	18.5	4.2	3.1	0.59	12.2	3.47	16.74	15.40	20.06	25.47	29.10	2.98	60.11	
Total Calc.	100.00	17.43	38.45	1.09	18.62	3.33	2.15	3.99	4.10	100	100	100	100	100	100	100	100	

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[a] Tyler mesh equivalents:

Tyler (mesh)	Opening (mm)
10	1.700
48	0.300
100	0.150
200	0.075

Table 14. Chemical Analysis of Attrition-Scrubbed Mussoorie Phosphate Ore in 5% HNO_3 (Pilot Plant)

	Wt %
P_2O_5	21.60
CO_2	3.50
C.S. P_2O_5	3.50
W.S. P_2O_5	0.60
CaO	35.60
MgO	2.00
SiO_2	19.10
Al_2O_3	2.30
Fe_2O_3	5.00
F	2.60
K_2O	0.65
Na_2O	0.23
S	3.30
Cl	0.12
C (organic)	2.20
Loss on ignition	10.70

Table 15. Chemical Analysis and Size Distribution of the Run-of-Mine, As-Received, Ground Mussoorie Phosphate Rock Used for the Minigranulation Studies

Chemical Composition							
P_2O_5	CaO	SiO_2	F	Al_2O_3	Fe_2O_3	MgO	CO_2
(wt %)							
18.6	43.8	15.4	1.8	1.7	4.0	1.4	13.6

Size Distribution Analysis, Percent of Total Feed in Tyler Mesh Fractions Shown[a]						
+65	-65 +100	-100 +150	-150 +200	-200 +270	-270 +400	-400
1.5	4.0	6.2	10.9	10.0	14.0	53.4

a. Tyler mesh equivalents:

Tyler (mesh)	Opening (mm)
65	0.212
100	0.150
150	0.106
200	0.075
270	0.053
400	0.038

Table 16. Summary of Operating Data--Minigranulation of Run-of-Mine, As-Received, Ground Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit

Test number	MSR 105-AA	MSR 200-A	MSR 301	MSR 400-A	MSR 501-A
Binder type	Urea	Potassium chloride	Sulfuric acid	Phosphoric acid[a]	Urea + nitric acid
Binder concentration, wt %	50	13.5	50	40[b]	48; 2[c]
Actual production rate, kg/hour[d]	11.82	11.49	17.30	11.11	14.48
Pinmixer					
Rock feed rate, kg/hour	12.17	12.11	18.36	11.96	15.28
Binder feed rate, kg/hour	1.92	3.0	3.25	2.48	1.686
Water feed rate, kg/hour	0.45	0.21	1.2	1.5	-
Nitric acid feed rate (2% by weight), kg/hour	-	-	-	-	1.05
Temperature of binder, °C	105	25	25	25	105
Recycle feed rate, kg/hour	14.00	18.24	9.19	18.02	15.29
Recycle ratio, kg/kg[e]	1.08	1.45	0.46	1.4	0.95
Temperature of recycle, °C	27	27	27	27	27
Particle size of recycle:					
Oversize (larger than 0.295 mm [+48 mesh, Tyler]), %	0	0	0	0	0
Product (between 0.106 and 0.295 mm [-48 +150 mesh, Tyler]), %	13.4	14.8	15.5	18.7	25.5
Undersize (smaller than 0.106 mm [-150 mesh, Tyler])	86.6	85.2	84.5	81.3	74.5
Discharge temperature, °C	74	76	52	44	60
Average revolutions, rpm; tip speed (m/second)	1,000; 6.4	870; 5.6	840; 5.4	850; 5.4	850; 5.4
Discharge moisture content, %	3.5	4.5	7.5	7.5	5.5
Average pin wear, mm/kg of product	0.26	0.21	0.066	0.034	0.26
Power consumption, kWh/mt of product[f]	45	54	35	50	40
Dryer					
Angle, degree	2.5	2.5	2.5	2.5	2.5
Revolution, rpm	6	6	6	6	6
Air discharge temperature, °C	85	74	70	65	69
Material discharge temperature, °C	75	66	64	57	60

(Continued)

Table 16. Summary of Operating Data--Minigranulation of Run-of-Mine, As-Received, Ground Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit (Continued)

Test number	MSR 105-AA	MSR 200-A	MSR 301	MSR 400-A	MSR 501-A
Binder type	Urea	Potassium chloride	Sulfuric acid	Phosphoric acid[a]	Urea + nitric acid
Binder concentration, wt %	50	13.5	50	40[b]	48; 2[c]
Actual production rate, kg/hour[d]	11.82	11.49	17.30	11.11	14.48
Analysis of Product					
Total P_2O_5, %	16.8	16.5	15.9	24.0	16.4
Water-soluble P_2O_5, %	-	-	0.3	0.9	-
Available P_2O_5, %[g]	0.3	0.3	0.8	4.9	0.4
Free acid, as % P_2O_5	-	-	0.0	0.1	-
N, %	2.6	-	-	-	2.6
K_2O, %	-	2.8	-	-	-
Moisture, %[h]	<1.0	<1.0	<1.0	<1.0	<1.0
Availability, % of total P_2O_5	1.8	1.8	5.0	20.0	2.4
Raw Materials Consumption					
Urea:product ratio[i]	0.073	-	-	-	0.047
Potassium chloride:product ratio[i]	-	0.032	-	-	-
Sulfuric acid:product ratio[i]	-	-	0.076	-	-
Phosphoric acid:product ratio[j]	-	-	-	0.137	-
Nitric acid:product ratio[i]	-	-	-	-	0.001
Rock:product ratio	0.927	0.968	0.859	0.892	0.882

---

a. Wet-process acid.

b. Expressed as P_2O_5.

c. 48% urea and 2% nitric acid.

d. Due to loss of material during in-process handling, the actual production rate is lower when compared with the feed rate of raw materials (phosphate rock and binder).

e. Defined as the weight ratio of total recycle to phosphate rock plus binder fed to the pinmixer on a dry basis. Under ideal operating conditions, this ratio would correspond to the recycle fed to the granulator and the amount of product produced.

f. Approximate. Relative to empty pinmixer operation.

g. Expressed as summation of water-soluble and citrate-soluble P_2O_5 where citrate-soluble P_2O_5 is measured by AOAC neutral ammonium-citrate method.

h. AOAC vacuum desiccation method.

i. Based on 100% concentration (i.e., KCl, H_2SO_4, HNO_3).

j. Based on 54% P_2O_5 phosphoric acid concentration.

Table 17. Physical Properties of Minigranulated Products Prepared From Run-of-Mine, As-Received, Ground Mussoorie Phosphate Rock[a]

Sample Number[b]	Binder Type[c]	Bulk Density[d]		Angle of Repose[e]	Porosity	Abrasion Resistance, % Degradation[f]	Disintegration in Water	
		kg/m³	lb/ft³	(degree)	(%)		5 minutes (%)	15 minutes (%)
MSR 105-AA	Urea	1,111	69.4	30.0	4.3	8.0	73	78
MSR 200-A	Potassium chloride	1,122	70.1	28.5	4.3	13.1	84	85
MSR 301	Sulfuric acid	1,132	70.7	32.0	5.9	6.5	18	47
MSR 400-A	Phosphoric acid	1,076	67.2	32.0	2.5	11.3	3	3
MSR 501-A	Urea plus nitric acid	1,065	66.5	32.0	4.3	6.8	89	89

---

a. Porosity and disintegration in water were determined according to the procedure developed by IFDC; all other tests were performed according to the procedures outlined in the TVA Special Report No. S-444 (8).

b. Corresponds to the test numbers shown in Table 16.

c. Refer to Table 16 for binder concentration in the product.

d. Bulk density of finely ground Mussoorie phosphate rock--1,290 kg/m³ (80.6 lb/ft³).

e. Angle of repose of finely ground Mussoorie phosphate rock--42°.

f. Under simulated handling.

Table 18. Hygroscopicity of Minigranulated Products Prepared From Run-of-Mine, As-Received, Ground Mussoorie Phosphate Rock[a]

Sample Number[b]	Binder Type[c]	Hygroscopicity (72 Hours' Exposure Time at 80% Relative Humidity and 30°C) Moisture Absorption (mg/cm^2)	Moisture Penetration (cm)	Moisture-Holding Capacity (mg/cm^3)	Moisture-Holding Capacity (%)	Physical Condition[d]
MSR 105-AA	Urea	96.5	1.0	96.5	8.6	(A) Damp with light-to-medium set after 48 hours (B) Same as A
MSR 200-A	Potassium chloride	61.7	0.0	-[e]	-[e]	(A) Dry with very light set after 48 hours (B) Same as A
MSR 301	Sulfuric acid	24.1	0.0	-[e]	-[e]	(A) Dry and free flowing (B) Same as A
MSR 400-A	Phosphoric acid	5.4	0.0	-[e]	-[e]	(A) Dry and free flowing (B) Same as A
MSR 501-A	Urea plus nitric acid	123.3	2.6	47.4	4.3	(A) Damp with medium set after 48 hours (B) Same as A

---

a. Determined according to the procedure outlined in TVA Special Report No. S-444 (8).
b. Corresponds to the test numbers shown in Table 16.
c. Refer to Table 16 for binder concentration in the product.
d. Condition: (A) periodically checked during the test period; (B) checked after test period.
e. Moisture-holding capacity cannot be calculated without some evidence of moisture penetration.

Table 19. Chemical Analyses and Size Distribution of the Run-of-Mine and Attrition-Scrubbed Mussoorie Phosphate Rock Used for Partial Acidulation/Granulation Studies

	Chemical Composition							
	P_2O_5	CaO	SiO_2	F	Al_2O_3	Fe_2O_3	MgO	CO_2
	(wt %)							
Run of mine	18.6	43.8	15.4	1.8	1.7	4.0	1.4	13.6
Attrition scrubbed[a]	21.6	35.6	19.1	2.6	2.3	5.0	2.0	3.5

	Size Distribution Analysis Percentage of Total Feed in Tyler Mesh Fraction Shown[b]						
	+65	-65 +100	-100 +150	-150 +200	-200 +270	-270 +400	-400
Run of mine	1.5	4.0	6.2	10.9	10.0	14.0	53.4
Attrition scrubbed	-	6.8	7.8	14.3	12.3	11.1	47.7

---

a. The run-of-mine rock was attrition scrubbed with 5% HNO_3 (refer to Beneficiation section of this report).

b. Tyler mesh equivalents:

Tyler (mesh)	Opening (mm)
65	0.212
100	0.150
150	0.106
200	0.075
270	0.053
400	0.038

Table 20. Summary of Operating Data--Partial Acidulation/Granulation of the Run-of-Mine Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit (Continued)

Test number	MSR 604	MSR 605	MSR 608	MSR 702[a]
Acid type	Sulfuric acid	Sulfuric acid	Sulfuric acid	Phosphoric acid
Actual production rate, kg/hour[b]	13.76	10.33	11.8	17.91
Analysis of Product				
Total P_2O_5, %	14.5	13.9	12.6	32.6
Water-soluble P_2O_5, %	3.9	4.5	5.0	15.5
Available P_2O_5, %[h]	4.1	4.7	5.3	19.6
K_2O, %	-	-	2.4	-
CO_2, %	5.1	4.0	1.9	5.0
Free acid, as % P_2O_5	2.1	3.9	6.3	0.8
Moisture, %[i]	1.9	2.6	2.2	2.5
Fluorine, %	1.1	1.1	0.9	1.1
Water solubility, % of total P_2O_5	26.8	32.4	39.6	47.5
Availability, % of total P_2O_5	28.3	33.8	42.0	60.1
Raw Materials Consumption				
Acid:rock ratio	0.325[j]	0.356[j]	0.423[j]	0.436[k]
Acid:product ratio	0.254[j]	0.266[j]	0.287[j]	0.337[k]
Rock:product ratio	0.780	0.747	0.677	0.774
Potassium chloride:product ratio	-	-	0.034	-

---

a. Pretreatment step not required.

b. Due to the evolution of gases (mainly CO_2 and fluorine compounds) and loss of material during "in-process" handling, the actual production rate is lower when compared with the feed rate of raw materials (phosphate rock and acid).

c. Determined using Chittick gasometric apparatus.

d. Critical speed is that speed at which the centrifugal force balances the gravitational force and the granules cease to roll. The numerical value is: $\frac{60}{\Pi}\sqrt{\frac{g \sin \theta}{2D}}$; where g is the gravity constant (9.81 m/s^2), θ is the pan angle (degrees) from the horizontal, D is the pan diameter (meters).

e. As H_2SO_4.

f. As P_2O_5.

g. Defined as the weight ratio of total recycle to phosphate rock plus acid feed to the granulator on a dry basis. Under ideal operating conditions, this ratio would correspond to the recycle fed to the granulator and the amount of product produced.

h. Expressed as summation of water-soluble and citrate-soluble P_2O_5 where citrate-soluble P_2O_5 is measured by AOAC neutral ammonium citrate method.

i. AOAC vacuum desiccation method.

j. Based on 100% H_2SO_4 sulfuric acid concentration.

k. Based on 54% P_2O_5 phosphoric acid concentration.

Table 20. Summary of Operating Data--Partial Acidulation/Granulation of the Run-of-Mine Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit

Test number	MSR 604	MSR 605	MSR 608	MSR 702[a]
Acid type	Sulfuric acid	Sulfuric acid	Sulfuric acid	Phosphoric acid
Actual production rate, kg/hour[b]	13.76	10.33	11.8	17.91
Acidulator for Pretreatment				
Type	Pinmixer	Pinmixer	Pinmixer	-
Revolution, rpm; tip speed (m/second)	750; 4.8	750; 4.8	750; 4.8	-
Rock feed rate, kg/hour	12.15	9.17	9.13	-
Acid concentration, % H_2SO_4	93	93	93	-
Acid feed rate, kg/hour	1.5	1.14	1.14	-
Material discharge temperature, °C	52	50	50	-
Material discharge moisture content, %	6.0	6.0	6.0	-
Material discharge CO_2 content, %[c]	9.6	9.7	9.3	-
Granulator				
Type	Pan	Pan	Pan	Pan
Angle, degree from the horizontal	43	43	43	43
Revolution, rpm; % of critical speed[d]	19; 36	19; 36	19; 36	19; 36
Rock feed rate, kg/hour	-	-	-	16.13
Potassium chloride feed rate, kg/hour	-	-	0.46	-
Acid concentration, %	73[e]	73[e]	73[e]	55.3[f]
Acid feed rate, kg/hour	3.5	3.02	4.15	6.86
Water feed rate, kg/hour	0.7	1.7	1.17	0.94
Recycle temperature, °C	30	30	30	30
Recycle feed rate, kg/hour	13.66	26.66	24.13	5.98
Bed temperature, °C	46	51	44	38
Recycle ratio, kg/kg[g]	0.80	2.10	1.70	0.30
Discharge moisture content, %	7.5	8.5	12.5	13.0
Dryer				
Angle, degree	2.5	2.5	2.5	2.5
Revolution, rpm	6	6	6	6
Air discharge temperature, °C	115	129	136	104
Material discharge temperature, °C	94	102	93	84

(Continued)

Table 21. Summary of Operating Data--Partial Acidulation/Granulation of Attrition-Scrubbed Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit

Test number	MSR 801	MSR 901
Acid type	Phosphoric acid	Sulfuric Acid
Actual production rate, kg/hour[a]	19.11	16.81
Granulator		
Type	Pan	Pan
Angle, degree from the horizontal	43	43
Revolution, rpm; % of critical speed[b]	19; 36	19; 36
Rock feed rate, kg/hour	18.35	15.13
Acid concentration, %	55.3[c]	73[d]
Acid feed rate, kg/hour	5.38	5.47
Water feed rate, kg/hour	0.94	1.87
Recycle temperature, °C	25	25
Recycle feed rate, kg/hour	8.17	19.85
Bed temperature, °C	34	43
Recycle ratio, kg/kg[e]	0.38	1.1
Discharge moisture content, %	12.2	13.4
Dryer		
Angle, degree	2.5	2.5
Revolution, rpm	6	6
Air discharge temperature, °C	95	106
Material discharge temperature, °C	69	72
Analysis of Product		
Total P_2O_5, %	30.3	17.6
Water-soluble P_2O_5, %	13.1	8.5
Available P_2O_5, %[f]	17.4	10.4
CO_2, %[g]	2.9	1.0
Free acid, as % P_2O_5	2.2	3.5
Moisture, %[h]	2.1	2.2
Fluorine, %	1.4	1.6
Water solubility, % of total P_2O_5	43.2	48.2
Availability, % of total P_2O_5	57.4	59.0

(Continued)

Table 21. Summary of Operating Data--Partial Acidulation/Granulation of Attrition-Scrubbed Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit (Continued)

Test number	MSR 801	MSR 901
Acid type	Phosphoric acid	Sulfuric Acid
Actual production rate, kg/hour[a]	19.11	16.81
Raw Materials Consumption		
Acid:rock ratio	0.300[i]	0.264[j]
Acid:product ratio	0.240[i]	0.215[j]
Rock:product ratio	0.802	0.815

---

a. Due to the evolution of gases (mainly CO_2 and fluorine compounds) and loss of material during in-process handling, the actual production rate is lower when compared with the feed of raw materials (phosphate rock and acid).

b. Critical speed is that speed at which the centrifugal force balances the gravitational force and the granules cease to roll. The numerical value is: $\frac{60}{\pi}\sqrt{\frac{g \sin \theta}{2D}}$; where g is the gravity constant (9.81 m/s^2), θ is the pan angle (degrees) from the horizontal, D is the pan diameter (meters).

c. As P_2O_5.

d. As H_2SO_4.

e. Defined as the weight ratio of total recycle to phosphate rock plus acid fed to the granulator on a dry basis. Under ideal operating conditions, this ratio would correspond to the recycle fed to the granulator and the amount of product produced.

f. Expressed as summation of water-soluble and citrate-soluble P_2O_5 where citrate-soluble P_2O_5 is measured by AOAC neutral ammonium citrate method.

g. Determined using Chittick gasometric apparatus.

h. AOAC vacuum desiccation method.

i. Based on 54% P_2O_5 phosphoric acid concentration.

j. Based on 100% H_2SO_4 sulfuric acid concentration.

Table 22. Physical Properties of Partially Acidulated/Granulated Products Prepared From Run-of-Mine and Attrition-Scrubbed Mussoorie Phosphate Rocks[a]

Sample No.[b]	Rock Type[c]	Acid Type	Additive	Bulk Density kg/m^3	Bulk Density lb/ft^3	Angle of Repose (degree)	Porosity (%)	Average Crushing Strength (kg/granule)	Abrasion Resistance,[d] % Degradation	Disintegration in Water 5 Minutes (%)	Disintegration in Water 15 Minutes (%)
MSR 604	Run of mine	Sulfuric	-	990	61.8	35.7	2.3	0.21	61.5	99	99
MSR 605	Run of mine	Sulfuric	-	1,090	68.0	36.2	3.7	0.34	27.9	99	100
MSR 608	Run of mine	Sulfuric	KCl	930	58.1	36.7	6.1	0.73	27.5	61	95
MSR 702	Run of mine	Phosphoric	-	910	56.6	36.2	6.9	1.77	9.2	85	96
MSR 801	Attrition scrubbed	Phosphoric	-	930	58.1	37.2	1.3	1.50	2.8	99	100
MSR 901	Attrition scrubbed	Sulfuric	-	920	57.4	35.8	1.3	0.72	21.6	30	56

---

a. Porosity and disintegration in water were determined according to the procedure developed by IFDC; all other tests were performed according to the procedures outlined in the TVA Special Report No. S-444 (8).
b. Corresponds to the test numbers shown in Tables 20 and 21.
c. Refer to Table 19 for chemical composition and size distribution analyses.
d. Under simulated handling.

Table 23. Hygroscopicity of Partially Acidulated/Granulated Products Prepared From Run-of-Mine and Attrition-Scrubbed Mussoorie Phosphate Rocks[a]

Sample No.[b]	Rock Type[c]	Acid Type	Additive	Hygroscopicity (72 Hours' Exposure Time at 80% Relative Humidity and 30°C) Moisture Absorption (mg/cm^2)	Moisture Penetration (cm)	Moisture-Holding Capacity (mg/cm^3)	Moisture-Holding Capacity (%)	Physical Conditions[d]
MSR 604	Run of mine	Sulfuric	-	139.4	2.8	49.8	5.2	(A) Granules slightly damp on surface after 3 hours (B) Granules slightly damp on surface after 3 hours
MSR 605	Run of mine	Sulfuric	-	190.3	3.5	54.4	5.0	(A) Granules slightly damp on surface after 3 hours (B) Granules slightly damp on surface after 3 hours
MSR 608	Run of mine	Sulfuric	KCl	158.2	1.8	87.9	9.2	(A) Granules dry and free flowing (B) Granules dry and free flowing
MSR 702	Run of mine	Phosphoric	-	91.2	1.0	91.2	10.0	(A) Granules dry and free flowing (B) Granules dry and free flowing
MSR 801	Attrition scrubbed	Phosphoric	-	128.7	1.0	128.7	13.9	(A) Granules dry and free flowing (B) Granules dry and free flowing
MSR 901	Attrition scrubbed	Sulfuric	-	83.1	1.0	83.1	9.1	(A) Granules dry and free flowing (B) Granules dry and free flowing

---

a. Determined according to the procedure outlined in TVA Special Report No. S-444 (8).
b. Corresponds to the test numbers shown in Tables 20 and 21.
c. Refer to Table 19 for chemical composition and size distribution analyses.
d. Condition: (A) periodically checked during the test period; (B) checked after test period.

Table 24. Summary of Operating Data--Minigranulation and Granulation of Run-of-Mine Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit--Demonstration Test Runs

Test number	MSR 205	MSR 206	MSR 817
Binder type	Potassium Chloride	Potassium Chloride	Phosphoric Acid[a]
Binder concentration, wt %	13.5	13.5	52.2[b]
Actual production rate, kg/hour[c]	13.60	15.63	18.35
Granulator			
Type	Pinmixer	Pug mill	Pug mill
Rock feed rate, kg/hour	15.09	14.89	18.12
Binder feed rate, kg/hour	3.14	3.85	4.47
Water feed rate, kg/hour	-	-	1.16
Temperature of binder, °C	24	24	24
Recycle feed rate, kg/hour	14.99	12.67	-
Recycle ratio, kg/kg[d]	0.97	0.82	-
Recycle temperature, °C	46	45	-
Particle size of recycle:			
Oversize, %	0[e]	0[f]	-
Product, %	18.4[g]	≈3[h]	-
Undersize, %	81.6[i]	≈97[j]	-
Discharge temperature, °C	72	NA[k]	40
Average revolution, rpm; tip speed (m/s)	850; 5.4	300; 1.2	300; 1.2
Discharge moisture content, %	6.5	10.6	8.0
Average pin wear, mm/kg of product	0.23	-	-
Power consumption, kWh/mt of product[l]	52	NA[k]	NA[k]
Den[m]			
Type	-	-	Box
Time, minutes	-	-	60
Temperature, °C, after 10 minutes	-	-	43.5
20 minutes	-	-	43.5
30 minutes	-	-	43.5
40 minutes	-	-	43.0
50 minutes	-	-	43.0
60 minutes	-	-	43.0
Moisture content after 60 minutes, %			4.8
Dryer			
Angle, degree	2.5	2.5	-
Revolutions, rpm	6	6	-
Air discharge temperature, °C	112	101	-
Material discharge temperature, °C	100	78	-
Analysis of Product			
Total P_2O_5, %	16.4	16.1	26.1
Water soluble P_2O_5, %	-	-	8.2
Available P_2O_5, %[n]	0.2	0.1	11.0
Free acid, as % P_2O_5	-	-	1.2
K_2O, %	2.4	2.6	-
Moisture, %[o]	<1.0	<1.0	2.6
Availability, % of total P_2O_5	1.2	0.6	42.1

(Continued)

Table 24. Summary of Operating Data--Minigranulation and Granulation of Run-of-Mine Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit--Demonstration Test Runs (Continued)

Test number	MSR 205	MSR 206	MSR 817
Binder type	Potassium Chloride	Potassium Chloride	Phosphoric Acid[a]
Binder concentration, wt %	13.5	13.5	52.2[b]
Actual production rate, kg/hour[c]	13.60	15.03	18.35
Raw Materials Consumption			
Potassium chloride:product ratio[p]	0.027	0.034	-
Acid:product ratio[q]	-	-	0.198
Rock:product ratio	0.973	0.966	0.829

---

a. Wet-process acid.

b. Expressed as P_2O_5.

c. Due to loss of material during in-process handling, the actual production rate is lower when compared with the feed rate of raw materials (phosphate rock and binder).

d. Defined as the weight ratio of total recycle to phosphate rock plus binder fed to the granulator on a dry basis. Under ideal operating conditions, this ratio would correspond to the recycle fed to the granulator and the amount of product produced.

e. Larger than 0.300 mm (plus 48-mesh, Tyler).

f. Larger than 3.35 mm (plus 6-mesh, Tyler).

g. Between 0.300 and 0.106 mm (minus 48- plus 150-mesh, Tyler).

h. Between 3.35 and 0.212 mm (minus 6- plus 65-mesh, Tyler).

i. Smaller than 0.106 mm (minus 150-mesh, Tyler).

j. Smaller than 0.212 mm (minus 65-mesh, Tyler).

k. NA = not available.

l. Approximate. Relative to empty granulator operation.

m. For Run MSR 808, the material from the pug mill was denned for about 1 hour. The ex-den material was slightly wet but free flowing and was stored in a pile at room temperature (24°C) for 24 hours for further curing. The size distribution of the material after 24 hours is as follows:

Mesh, Tyler	+6	-6 +14	-14 +48	-48 +65	-65 +150	-150 +270	-270
Opening, mm	3.35	-3.35 +1.18	-1.18 +0.300	-0.300 +0.212	-0.212 +0.106	-0.106 +0.053	-0.053
Between sieves, %	12.67	21.31	30.74	12.50	8.64	8.56	5.58

n. Expressed as summation of water-soluble and citrate-soluble P_2O_5 where citrate-soluble P_2O_5 is measured by AOAC neutral ammonium citrate method.

o. AOAC vacuum desiccation method.

p. Based on 100% potassium chloride concentration.

q. Based on 54% P_2O_5 phosphoric acid concentration.

Table 25. Physical Properties of Minigranulated and Granulated Products Prepared From Run-of-Mine Mussoorie Phosphate Rock--Demonstration Test Runs[a]

Sample Number[b]	Binder Type[c]	Bulk Density[d]		Angle of Repose[e]	Porosity	Abrasion Resistance,[f] % Degradation	Disintegration in Water	
		kg/m^3	lb/ft^3	(degree)	(%)		5 minutes	15 minutes
							(%)	(%)
MSR 205	Potassium chloride	1,120	70.0	30	4.1	12.8	88	90
MSR 206	Potassium chloride	1,068	66.3	31	4.3	14.6	90	92
MSR 817[g]	Phosphoric acid	1,000	62.1	32	3.1	10.1	70	85

---

a. Porosity and disintegration in water were determined according to the procedure developed by IFDC; all other tests were performed according to the procedures outlined in the TVA Special Report No. S-444 (8).

b. Corresponds to the test numbers shown in Table 24.

c. Refer to Table 24 for binder concentration in the product.

d. Bulk density of finely ground Mussoorie phosphate rock--1,290 kg/m^3 (80.6 lb/ft^3).

e. Angle of repose of finely ground Mussoorie phosphate rock--42°.

f. Under simulated handling.

g. Physical properties determined on minus 3.35- plus 0.201-mm (minus 6- plus 65-mesh, Tyler) size fraction.

Table 26. Hygroscopicity of Minigranulated and Granulated Products Prepared From Run-of-Mine Mussoorie Phosphate Rock--Demonstration Test Runs[a]

Sample Number[b]	Binder Type[c]	Hygroscopicity (72 Hours' Exposure Time at 80% Relative Humidity and 30°C)				
		Moisture Absorption (mg/cm^2)	Moisture Penetration (cm)	Moisture-Holding Capacity (mg/cm^3)	Moisture-Holding Capacity (%)	Physical Condition[d]
MSR 205	Potassium chloride	63.0	0.0	-[e]	-[e]	(A) Dry with very light set after 48 hours (B) Same as A
MSR 206	Potassium chloride	68.0	0.0	-[e]	-[e]	(A) Same as MSR 205 (B) Same as MSR 205
MSR 817[f]	Phosphoric acid	12.6	0.0	-[e]	-[e]	(A) Dry and free flowing (B) Same as A

---

[a] Determined according to the procedure outlined in TVA Special Report No. S-444 (8).

[b] Corresponds to the test numbers shown in Table 24.

[c] Refer to Table 24 for binder concentration in the product.

[d] Condition: (A) periodically checked during the test period; (B) check after test period.

[e] Moisture-holding capacity cannot be calculated without some evidence of moisture penetration.

[f] Physical properties determined on minus 3.35- plus 0.212-mm (minus 6- plus 65-mesh, Tyler) size fraction.

Table 27. Size Distribution Analysis of the Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden) Used for the Partial Acidulation Process Demonstration Test Runs[a]

Percent of Total Feed in Tyler Mesh Fraction Shown[b]						
+65	-65 +100	-100 +150	-150 +200	-200 +270	-270 +400	-400
4.3	3.6	5.6	9.8	10.3	10.9	55.5

---

a. Refer to Table 2 for chemical composition. The material, received in the size range of 1 and 25 mm, was ground using a combination of a jaw crusher and a ball mill.

b. Tyler mesh equivalents:

Tyler (mesh)	Opening (mm)
65	0.212
100	0.150
150	0.106
200	0.075
270	0.053
400	0.038

Table 28. Summary of Operating Data--Partial Acidulation/Granulation of Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden) in the Continuous Laboratory-Scale Granulation Unit--Demonstration Test Runs

Test number	MSR 810-C-S	MSR 1001[a]	MSR 1001-A[b]
Acid type	Sulfuric	Sulfuric	Sulfuric
Actual production rate, kg/hour[c]	19.65	NA[d]	NA
Granulator			
Type	Drum	Pan	Pan
Angle, degree from horizontal	4	43	43
Revolutions, rpm; % of critical speed[e]	27; 36	18; 35	18; 35
Rock feed rate, kg/hour	7.614	9.312	9.312
Acid concentration, % H_2SO_4	83	92.8	92.8
Acid feed rate, kg/hour	3.961	3.127	3.127
Water feed rate, kg/hour	0.360	0.480	0.480
Recycle temperature, °C	45	NA	NA
Recycle feed rate, kg/hour	32.82	NA	NA
Bed temperature, °C	45	55	55
Recycle ratio, kg/kg[f]	3.0	NA	NA
Discharge moisture content, %	8.7	NA	NA
Dryer			
Angle, degree	2.5	2.5	-
Revolution, rpm	6	6	-
Air discharge temperature, °C	128	NA	-
Material discharge temperature, °C	92	NA	-
Analysis of Product @ 24 Hours			
Total P_2O_5, %	18.2	19.5	19.5
Water-soluble P_2O_5, %	9.0	6.5	6.4
Available P_2O_5, %[g]	10.0	6.7	6.6
CO_2, %[h]	0.86	NA	NA
Free acid, as % P_2O_5	3.7	4.0	5.0
Moisture, %[i]	3.3	2.0	4.1
Fluorine, %	1.1	1.4	1.4
Water solubility, % of total P_2O_5	49.5	33.3	32.8
Availability, % of total P_2O_5	54.9	34.4	33.8
Analysis of Product @ 1 Week			
Total P_2O_5, %	NA	20.0	20.2
Water-soluble P_2O_5, %	NA	6.4	6.9
Available P_2O_5, %[g]	NA	7.2	7.8
CO_2, %[h]	NA	NA	NA
Free acid, as % P_2O_5	NA	2.4	0.4
Moisture, %[i]	NA	2.0	2.6
Fluorine, %	NA	1.4	1.4
Water solubility, % of total P_2O_5	NA	32.0	34.2
Availability, % of total P_2O_5	NA	36.0	38.6

(Continued)

Table 28. Summary of Operating Data--Partial Acidulation/Granulation of Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden) in the Continuous Laboratory-Scale Granulation Unit--Demonstration Test Runs (Continued)

Test number	MSR 810-C-S	MSR 1001[a]	MSR 1001-A[b]
Acid type	Sulfuric	Sulfuric	Sulfuric
Actual production rate, kg/hour[c]	19.65	NA[d]	NA
Raw Materials Consumption			
Acid:rock ratio[j]	0.432	0.312	0.312
Acid:product ratio[j]	0.315	0.246	0.246
Rock:product ratio	0.728	0.789	0.789

---

a. The "green" (ex-granulator) material was dried in a rotary dryer with a cocurrent airflow that passed through a propane-fired combustion chamber located at the inlet (material feed end) of the dryer. The dryer discharge was screened hot.

b. The "green" (ex-granulator) material was pile cured for 1 week prior to screening.

c. Due to the evolution of gases (mainly CO_2 and fluorine compounds) and loss of material during in-process handling, the actual production rate is lower when compared with the feed rates of raw materials (phosphate rock and acid).

d. NA = not available.

e. Critical speed is that speed at which the centrifugal force balances the gravitational force and the granules cease to roll. Critical speed of the drum = $\frac{42.3}{\sqrt{D}}$ where D is the diameter of the drum in meters. Critical speed of the pan = $\frac{60}{\Pi} \sqrt{\frac{g \sin \Theta}{2D}}$; where g is the gravity constant (9.81 m/s^2), Θ is the pan angle (degrees) from the horizontal, D is the pan diameter (meters).

f. Defined as the weight ratio of total recycle and phosphate rock plus acid feed to the granulator on dry basis; under ideal operating conditions, this ratio would correspond to the recycle fed to the granulator and the amount of product produced.

g. Expressed as the summation of water-soluble and citrate-soluble P_2O_5 where citrate-soluble P_2O_5 is measured by AOAC neutral ammonium citrate method.

h. Determined using Chittick gasometric apparatus.

i. AOAC vacuum desiccation method.

j. Based on 100% acid concentration (H_2SO_4).

Table 29. Physical Properties of Partially Acidulated/Granulated Product Produced From Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden)--Single-Step Process--Demonstration Test Runs[a]

Sample No.[b]	Bulk Density		Angle of Repose	Porosity	Average Crushing Strength	Abrasion Resistance	Disintegration in Water	
	kg/m^3	lb/ft^3	(degree)	(%)	(kg/granule)	% Degradation[c]	5 Minutes (%)	15 Minutes (%)
MSR 810-C-S[d]	950	59.3	35.3	1.6	1.96	2.1	60	75
MSR 1001	NA[e]	NA	NA	NA	1.8	1.0	NA	NA
MSR 1001-A	NA	NA	NA	NA	0.4	14.4	NA	NA

---

a. Porosity and disintegration in water were determined according to the procedure developed by IFDC; all other tests were performed according to the procedures outlined in the TVA Special Report No. S-444 (8).

b. Corresponds to the test numbers shown in Table 28.

c. Under simulated handling.

d. Product size range 3.35 to 1.18 mm (minus 6- plus 14-mesh, Tyler).

e. NA = not available.

Table 30. Hygroscopicity of Partially Acidulated/Granulated Product Produced From Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden)--Single-Step Process--Demonstration Test Runs[a]

Sample No.[b]	Hygroscopicity (72 Hours' Exposure Time at 80% Relative Humidity and 30°C)				
	Moisture Absorption (mg/cm^2)	Moisture Penetration (cm)	Moisture-Holding Capacity (mg/cm^3)	Moisture-Holding Capacity (%)	Physical Condition[c]
MSR 810-C-S[d]	45.6	0	-[e]	-[e]	(A) Granules dry and free flowing (B) Granules dry and free flowing
MSR 1001	48.3	0	-[e]	-[e]	(A) Granules dry and free flowing (B) Granules dry and free flowing
MSR 1001-A	99.2	0	-[e]	-[e]	(A) Granules dry and free flowing (B) Granules dry and free flowing

---

a. Determined according to the procedure outlined in TVA Special Report No. S-444 (8).

b. Corresponds to the test numbers shown in Table 28.

c. Condition: (A) periodically checked during the test period; (B) checked after test period.

d. Prepared by single-step acidulation/granulation process. Product size fraction 3.35 to 1.18 mm (minus 6- plus 14-mesh, Tyler).

e. Moisture-holding capacity cannot be calculated without some evidence of moisture penetration.

Table 31. Summary of Operating Data--Partial Acidulation (Run-of-Pile) of Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden) in the Continuous Laboratory-Scale Unit--Demonstration Test Run

Test number	MSR 809-S
Acid type	Sulfuric
Actual production rate, kg/hour[a]	15.5
Acidulator	
Type	Pug mill
Average revolutions, rpm; tip speed (m/second)	90; 0.36
Rock feed rate, kg/hour	12.00
Acid concentration, % H_2SO_4	83
Acid feed rate, kg/hour	6.40
Discharge temperature, °C	108
Den	
Type	box
Time, minutes	60
Temperature, °C after 10 minutes	98
20 minutes	95
30 minutes	93
40 minutes	90
50 minutes	87
60 minutes	85
Moisture content of product after 60 minutes, %	4.5
Free acid in den product, as % P_2O_5	4.1
Analysis of Product[b]	
Total P_2O_5, %	18.4
Water-soluble P_2O_5, %	9.5
Available P_2O_5, %[c]	10.9
CO_2, %[d]	0.9
Free acid, as % P_2O_5	0.8
Moisture, %[e]	2.6
Fluorine, %	1.1
Water solubility, % of total P_2O_5	51.6
Availability, % of total P_2O_5	59.2
Product size fraction in 24-hour cured material, %[f]	40

(Continued)

Table 31. Summary of Operating Data--Partial Acidulation (Run-of-Pile) of Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden) in the Continuous Laboratory-Scale Unit--Demonstration Test Run (Continued)

Test number	MSR 809-S
Acid type	Sulfuric
Actual production rate, kg/hour[a]	15.5
Raw Materials Consumption	
Acid:rock ratio[g]	0.443
Acid:product ratio[g]	0.326
Rock:product ratio	0.736

---

a. Due to the evolution of gases (mainly CO_2 and fluorine compounds) and loss of material during in-process handling, the actual production rate is lower when compared with the feed rates of raw materials (phosphate rock and acid).

b. 24-hour cured sample.

c. Expressed as the summation of water-soluble and citrate-soluble P_2O_5 where citrate-soluble P_2O_5 is measured by AOAC neutral ammonium citrate method.

d. Determined using Chittick gasometric apparatus.

e. AOAC vacuum desiccation method.

f. Size fraction: 3.35 to 1.18 mm (minus 6- plus 14-mesh, Tyler). Includes crushed oversize.

g. Based on 100% acid concentration (H_2SO_4).

Table 32. Physical Properties of Partially Acidulated Product Produced From Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden)--Run-of-Pile Process--Demonstration Test Run[a]

Sample No.[b]	Bulk Density[c]		Angle of Repose[c] (degree)	Porosity[d] (%)	Average Crushing Strength[d] (kg/granule)	Abrasion Resistance,[d,e] % Degradation	Disintegration in Water[d]	
	kg/m^3	lb/ft^3					5 Minutes (%)	15 Minutes (%)
MSR 809-S	930	58.1	34.3	6.3	1.41	8.7	70	90

---

a. Porosity and disintegration in water were determined according to the procedure developed by IFDC; all other tests were performed according to the procedures outlined in the TVA Special Report No. S-444 (8).

b. Corresponds to the test number shown in Table 31.

c. Of the RCP sample (unscreened).

d. Of product size fraction (3.35 to 1.18 mm [minus 6- plus 14-mesh, Tyler]).

e. Under simulated handling.

Table 33. Hygroscopicity of Partially Acidulated Products Produced From Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden)--Run-of Pile Process--Demonstration Test Run[a]

Sample No.[c]	Hygroscopicity (72 Hours' Exposure Time at 80% Relative Humidity and 30°C)[b]				
	Moisture Absorption (mg/cm^2)	Moisture Penetration (cm)	Moisture-Holding Capacity (mg/cm^3)	Moisture-Holding Capacity (%)	Physical Condition[d]
MSR 809-S	34.9	0	-[e]	-[e]	(A) Granules dry and free flowing (B) Granules dry and free flowing

---

a. Determined according to the procedure outlined in TVA Special Report No. S-444 (8).

b. Of product size fraction (3.35 to 1.18 mm [minus 6- plus 14-mesh, Tyler]).

c. Corresponds to the test number shown in Table 31.

d. Condition: (A) periodically checked during the test period; (B) checked after test period.

e. Moisture-holding capacity cannot be calculated without some evidence of moisture penetration.

Table 34. Summary of Operating Data--Partial Acidulation/Granulation of Run-of-Mine Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit--Demonstration Test Runs

Test number	MSR 1000	MSR 1002[a]	MSR 1002-A[b]
Acid type	Phosphoric/Sulfuric	Sulfuric	Sulfuric
Actual production rate, kg/hour	NA[c]	NA	NA
Acidulator for Pretreatment			
Type	Pinmixer	-	-
Revolutions, rpm; tip speed (m/second)	875; 5.6	-	-
Rock feed rate, kg/hour	15.264	-	-
Acid concentration (phosphoric), % P_2O_5	43.4	-	-
Acid feed rate, kg/hour	2.673	-	-
Material discharge temperature, °C	32	-	-
Material discharge moisture content, %	NA	-	-
Material discharge CO_2 content, %	NA	-	-
Granulator			
Type	Pan	Pan	Pan
Angle, degree from horizontal	43	43	43
Revolutions, rpm; % of critical speed[d]	16; 31	18; 35	18; 35
Rock feed rate, kg/hour	-	13.326	13.326
Acid concentration (sulfuric), % H_2SO_4	92.8	92.8	92.8
Acid feed rate, kg/hour	4.154	4.200	4.200
Water feed rate, kg/hour	0.48	0.46	0.46
Recycle temperature, °C	NA	NA	NA
Recycle feed rate, kg/hour	NA	NA	NA
Bed temperature, °C	52	60	60
Recycle ratio, kg/kg	NA	NA	NA
Discharge moisture content, %	NA	NA	NA
Dryer			
Angle, degree	2.5	2.5	-
Revolutions, rpm	6	6	-
Air discharge temperature, °C	114	130	-
Material discharge temperature, °C	80	82	-
Analysis of Product @ 24 Hours			
Total P_2O_5, %	19.5	15.4	15.1
Water-soluble P_2O_5, %	8.0	4.4	4.6
Available P_2O_5, %[e]	9.0	5.2	5.3
CO_2, %	NA	NA	NA
Free acid, as % P_2O_5	3.0	4.6	4.9
Moisture, %[f]	2.3	2.1	4.6
Fluorine, %	1.3	1.6	1.5
Water solubility, % of total P_2O_5	41.0	28.6	30.5
Availability, % of total P_2O_5	46.2	33.8	35.1

(Continued)

Table 34. Summary of Operating Data--Partial Acidulation/Granulation of Run-of-Mine Mussoorie Phosphate Rock in the Continuous Laboratory-Scale Granulation Unit--Demonstration Test Runs (Continued)

Test number	MSR 1000	MSR 1002[a]	MSR 1002-A[b]
Acid type	Phosphoric/Sulfuric	Sulfuric	Sulfuric
Actual production rate, kg/hour	NA[c]	NA	NA
Analysis of Product @ 1 Week			
Total P_2O_5, %	19.5	15.5	15.3
Water-soluble P_2O_5, %	8.3	4.5	4.7
Available P_2O_5, %[e]	10.0	5.4	5.4
CO_2, %	NA	NA	NA
Free acid, % P_2O_5	0.7	1.6	0.6
Moisture, %[f]	2.0	2.0	3.3
Fluorine, %	1.2	1.2	1.3
Water solubility, % of total P_2O_5	42.6	29.0	30.7
Availability, % of total P_2O_5	51.3	34.8	35.3
Raw Materials Consumption			
Phosphoric acid:rock ratio[g]	0.129	-	-
Sulfuric acid:rock ratio[h]	0.248	0.328	0.328
Phosphoric acid:product ratio[g]	0.113	-	-
Sulfuric acid:product ratio[h]	0.195	0.272	0.272
Rock:product ratio	0.788	0.828	0.828

---

a. The "green" (ex-granulator) material was dried in a rotary dryer with a cocurrent airflow that passed through a propane-fired combustion chamber located at the inlet (material feed end) of the dryer. The dryer discharge was screened hot.

b. The "green" (ex-granulator) material was pile cured for 1 week prior to screening.

c. NA = not available.

d. Critical speed is that speed at which the centrifugal force balances the gravitational force and the granules cease to roll. The numerical speed value is: $\frac{60}{\Pi}\sqrt{\frac{g \sin \Theta}{2D}}$; where g is the gravity constant ($9.81\ m/s^2$), Θ is the pan angle (degrees) from the horizontal, D is the pan diameter (meters).

e. Expressed as the summation of water-soluble and citrate-soluble P_2O_5 where citrate-soluble P_2O_5 is measured by AOAC neutral ammonium citrate method.

f. AOAC vacuum desiccation method.

g. Based on 54% P_2O_5 phosphoric acid concentration.

h. Based on 100% H_2SO_4 sulfuric acid concentration.

Table 35. Physical Properties of Partially Acidulated/Granulated Product Produced From Run-of-Mine Mussoorie Phosphate Rock--Single-Step Process--Demonstration Test Runs[a]

			Hygroscopicity (72 Hours' Exposure Time at 80% Relative Humidity and 30°C)				
Sample No.[b]	Average Crushing Strength (kg/granule)	Abrasion Resistance, % Degradation	Moisture Absorption (mg/cm^2)	Moisture Penetration (cm)	Moisture-Holding Capacity (mg/cm^3)	Moisture-Holding Capacity (%)	Physical Condition[c]
MSR 1000	1.8	3.0	37.4	0	-[d]	-	(A) Granules dry and free flowing (B) Granules dry and free flowing
MSR 1002	0.5	7.2	21.4	0	-	-	(A) Granules dry and free flowing (B) Granules dry and free flowing
MSR 1002-A	0.4	16.2	112.6	0	-	-	(A) Granules dry and free flowing (B) Granules dry and free flowing

---

a. Determined according to the procedure outlined in TVA Special Report No. S-444 (8).
b. Corresponds to the test numbers shown in Table 34.
c. Condition: (A) Periodically checked during the test period; (B) checked after the test period.
d. Moisture-holding capacity cannot be calculated without some evidence of moisture penetration.

Table 36. Experimental Products Shipped to India for Field Trials

Sample No.	Sample Description	Chemical Composition Total P_2O_5	Water-Soluble P_2O_5	Available P_2O_5	CaO	F	SO_4	H_2O	Raw Materials Consumption Ratio Acid:Rock	Ratio Acid:Product	Ratio Rock:Product
		(wt %)									
		Run-of-Mine Mussoorie Phosphate Rock									
MSR 301[a]	Minigranular	16.2	0.5	1.3	36.3	1.7	7.0	0.1	0.089	0.076	0.855
MSR 400-A[a]	Minigranular	23.9	1.4	7.7	39.8	1.8	-	0.3	0.207	0.137	0.892
MSR 817[b]	ROP[c,d]	26.1	8.2	11.0	34.2	1.7	-	2.6	0.172	0.138	0.829
MSR 605[e]	Granular PAPR	14.1	3.8	5.5	31.3	1.0	26.6	2.1	0.356	0.266	0.747
MSR 816[f]	Granular PAPR	26.5	3.6	11.7	33.5	1.7	-	1.4	0.350	0.265	0.758
MSR 702[e]	Granular PAPR	32.3	14.8	19.5	31.2	1.6	-	0.4	0.325	0.258	0.774
		Mussoorie Phosphate Concentrate (Prepared by Sala International, Sweden)									
R231.74	Mussoorie phosphate concentrate	25.0	-	-	45.3	2.5	9.9	-	-	-	-
MSR 810-C-S[g]	Granular PAPR	18.2	9.0	10.0	32.3	1.1	30.7	2.4	0.432	0.315	0.728
MSR 809-S[h]	ROP PAPR[c]	18.4	9.5	10.9	34.3	1.1	31.6	4.1	0.443	0.326	0.736
MSR 813-S[g]	Granular PAPR	32.8	7.8	12.0	40.0	2.3	-	0.2	0.186	0.174	0.936
MSR 812-S[i]	Granular PAPR	36.3	20.0	21.5	33.4	1.9	-	1.5	0.348	0.288	0.829

---

a. Prepared under conditions similar to those corresponding to the same test number given in Table 16.
b. Prepared under conditions similar to those corresponding to the same test number given in Table 24.
c. Run of pile.
d. Contains a mixture of granules and minigranules.
e. Prepared under conditions similar to those corresponding to the same test number given in Table 20.
f. Prepared by the single-step acidulation granulation process using a pan granulator.
g. Prepared under conditions similar to those corresponding to the same test number given in Table 28.
h. Prepared under conditions similar to those corresponding to the same test number given in Table 31.
i. Prepared by the single-step acidulation granulation process using a pan granulator.

Figure 1. Polished Rock Fragments. Black Areas Are Apatite; Lighter Gray Areas Are Carbonate.

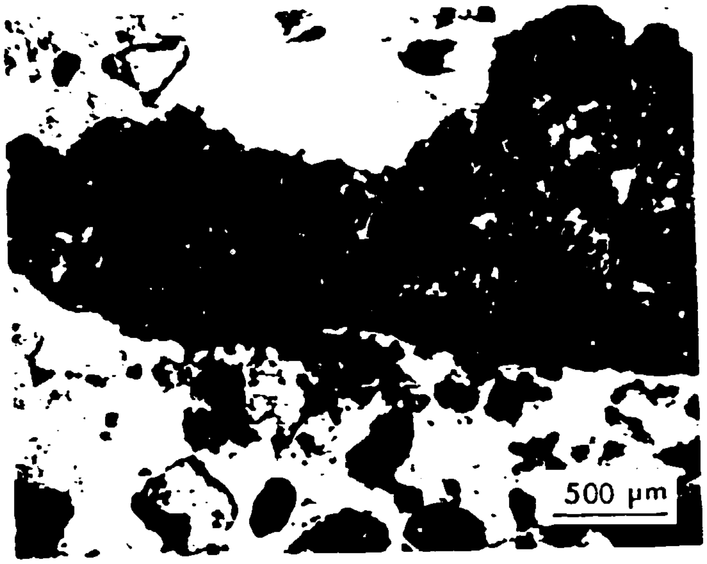

Figure 2. Plane Polarized Light View of Apatite Clasts (dark areas) in a Matrix of Calcite (light areas). Apatite Contains Small Quartz Inclusions.

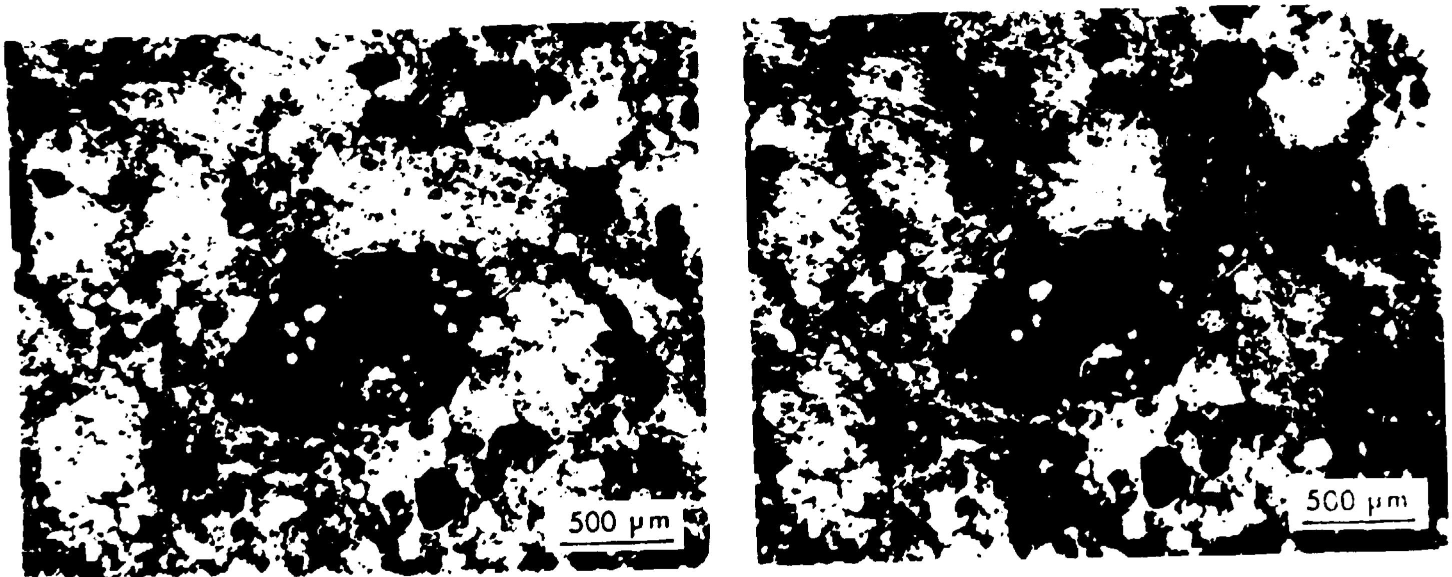

Figure 3. Plane Polarized Light View (left) of Apatite Pellets in Carbonate Matrix. In Crossed Polarized Light (right), Apatite Appears Isotropic (dark) With Birefringent Inclusions of Calcite and Quartz Endogangue. Carbonate Matrix Is Birefringent (white to gray).

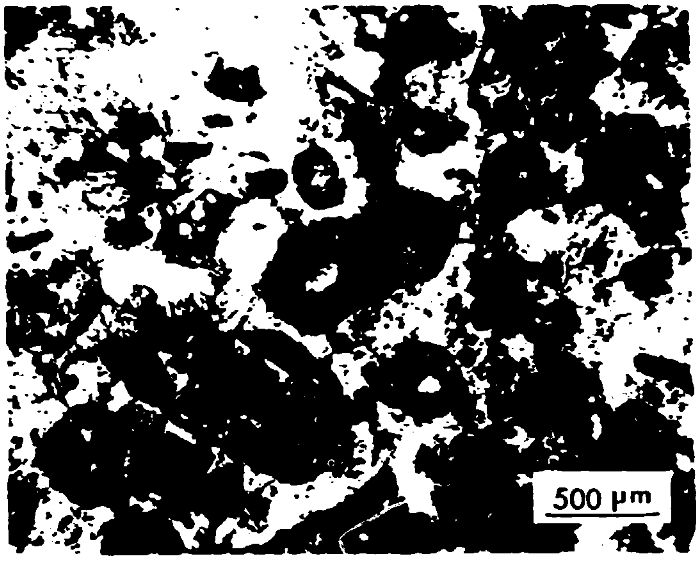

Figure 4. Plane Polarized Light View of Apatite Grains (dark) With Thin Overgrowths of Secondary Apatite. Matrix Is Calcite.

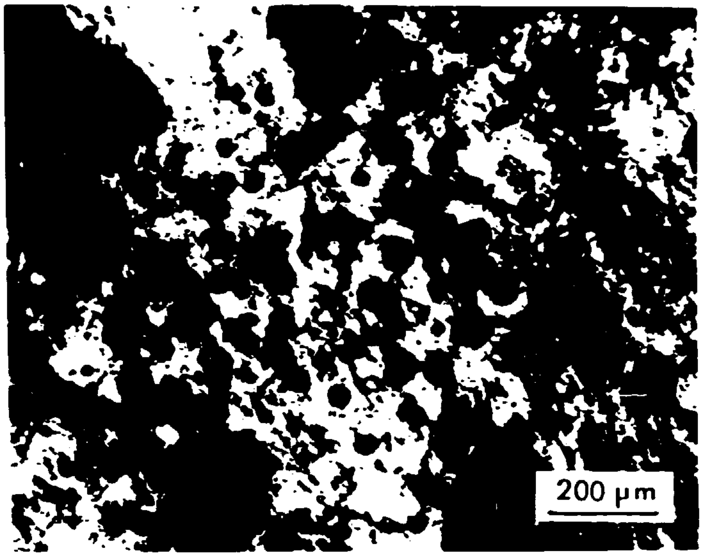

Figure 5. Plane Polarized Light View of Pyrite Grains (black, angular) and Apatite (larger, rounded dark grains) in Carbonate Matrix.

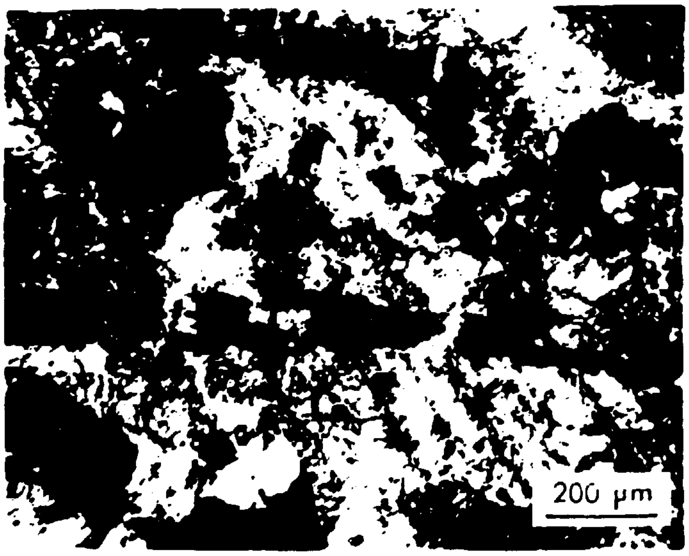

Figure 6. Plane Polarized Light View of Phosphatized Fossil Fragments (dark, angular) in Carbonate Matrix.

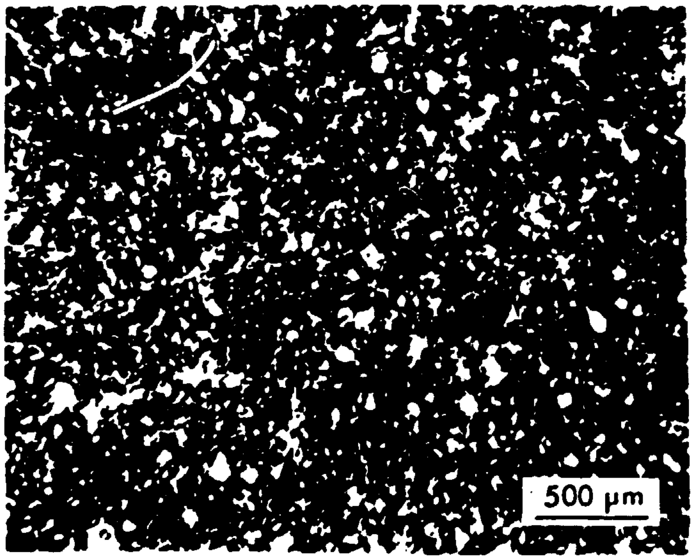

Figure 7. Plane Polarized Light View of Equigranular Intergrowth of Apatite, Carbonate, and Pyrite.

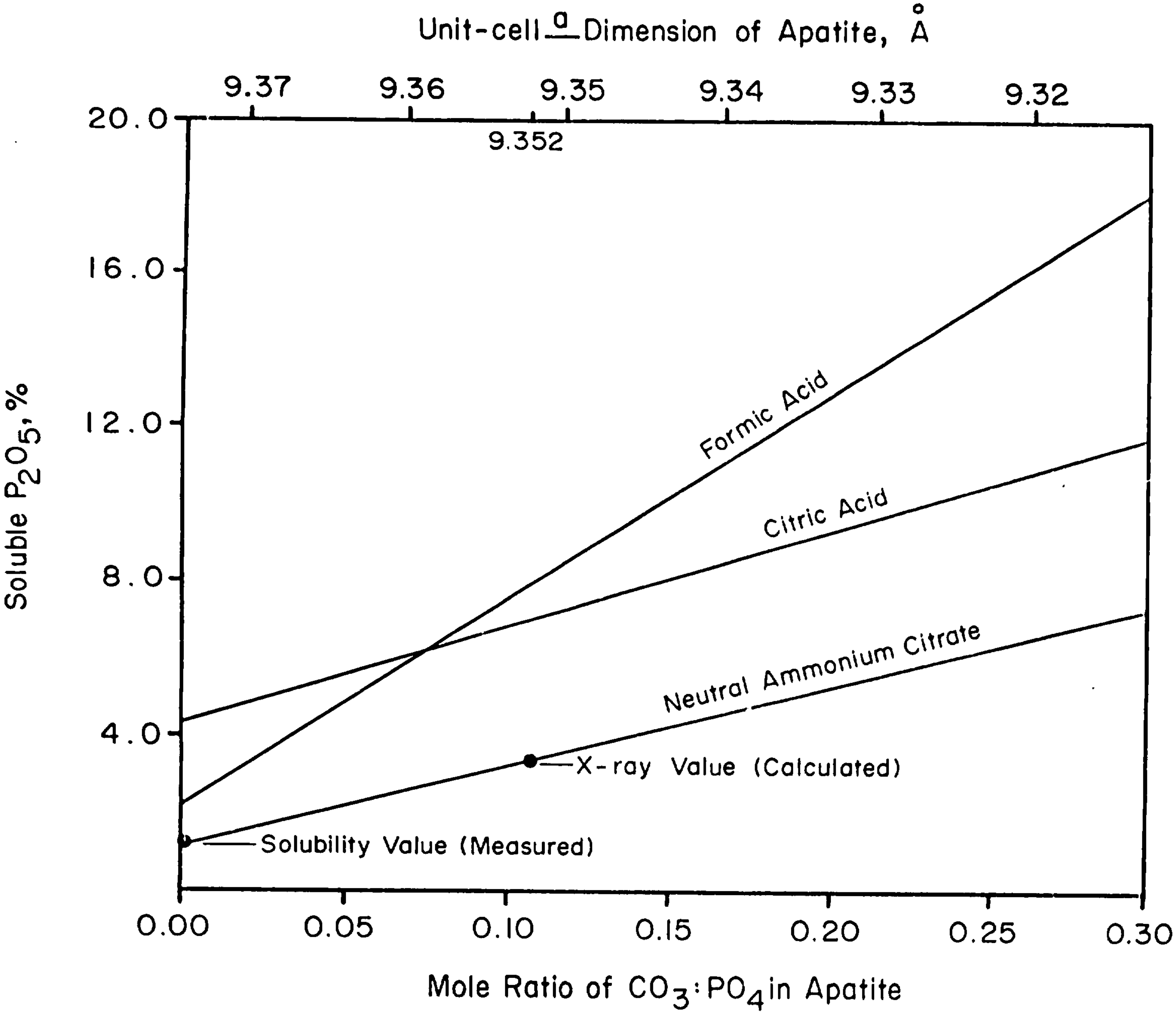

Figure 8. Solubility of P_2O_5 in Various Solvents as a Function of Apatite Composition.

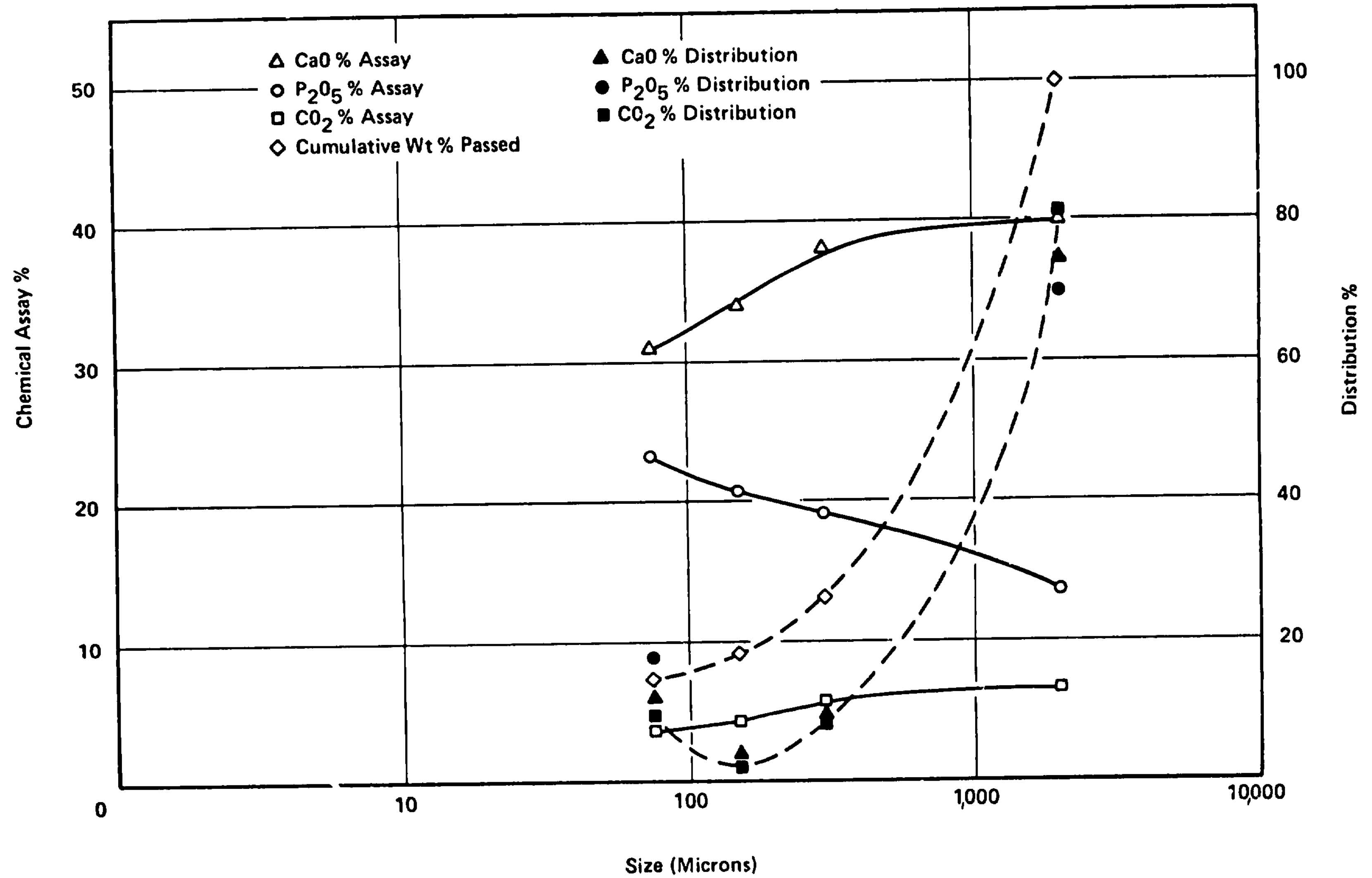

Figure 9. Size Distribution and Frequency Curves of the Main Components of the Crushed Mussoorie Phosphate Ore Scrubbed in 2% HNO_3.

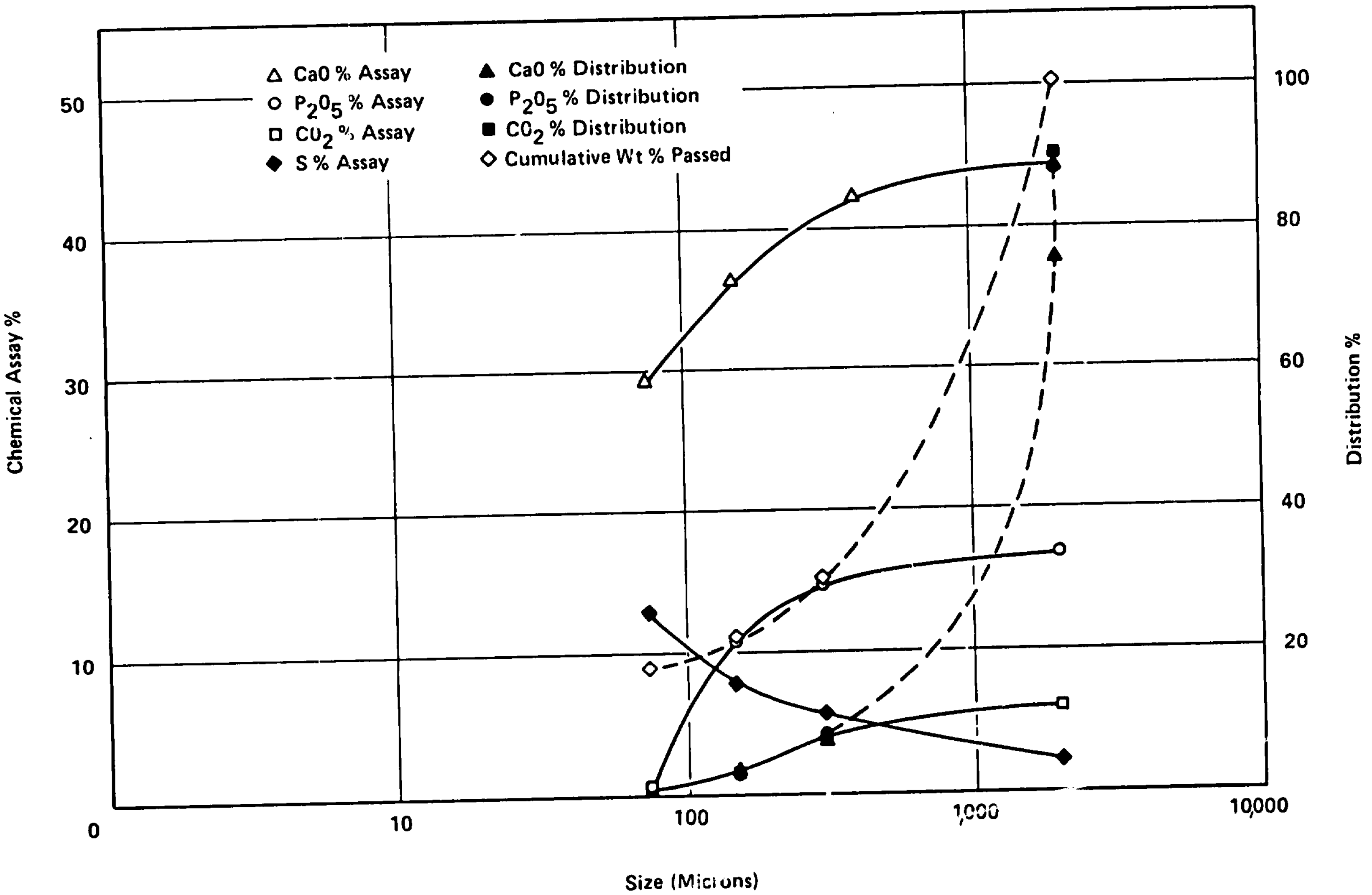

Figure 10. Size Distribution and Frequency Curves of the Main Components of the Crushed Mussoorie Phosphate Ore Scrubbed in 5% H_2SO_4.

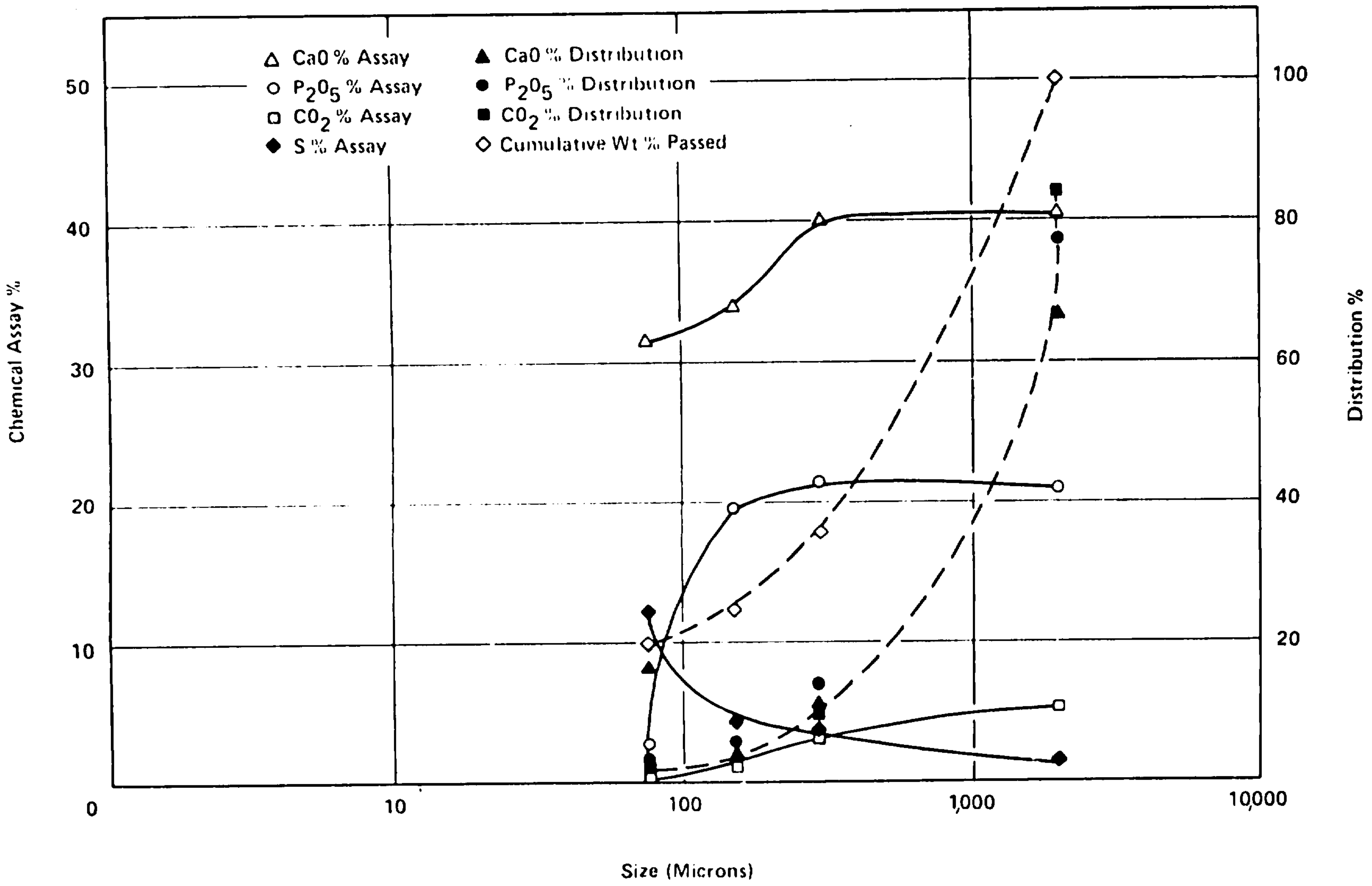

Figure 11. Size Distribution and Frequency Curves of the Crushed Mussoorie Phosphate Ore Scrubbed in a Mixture (1:1) of 2% HNO_3 + 5% H_2SO_4.

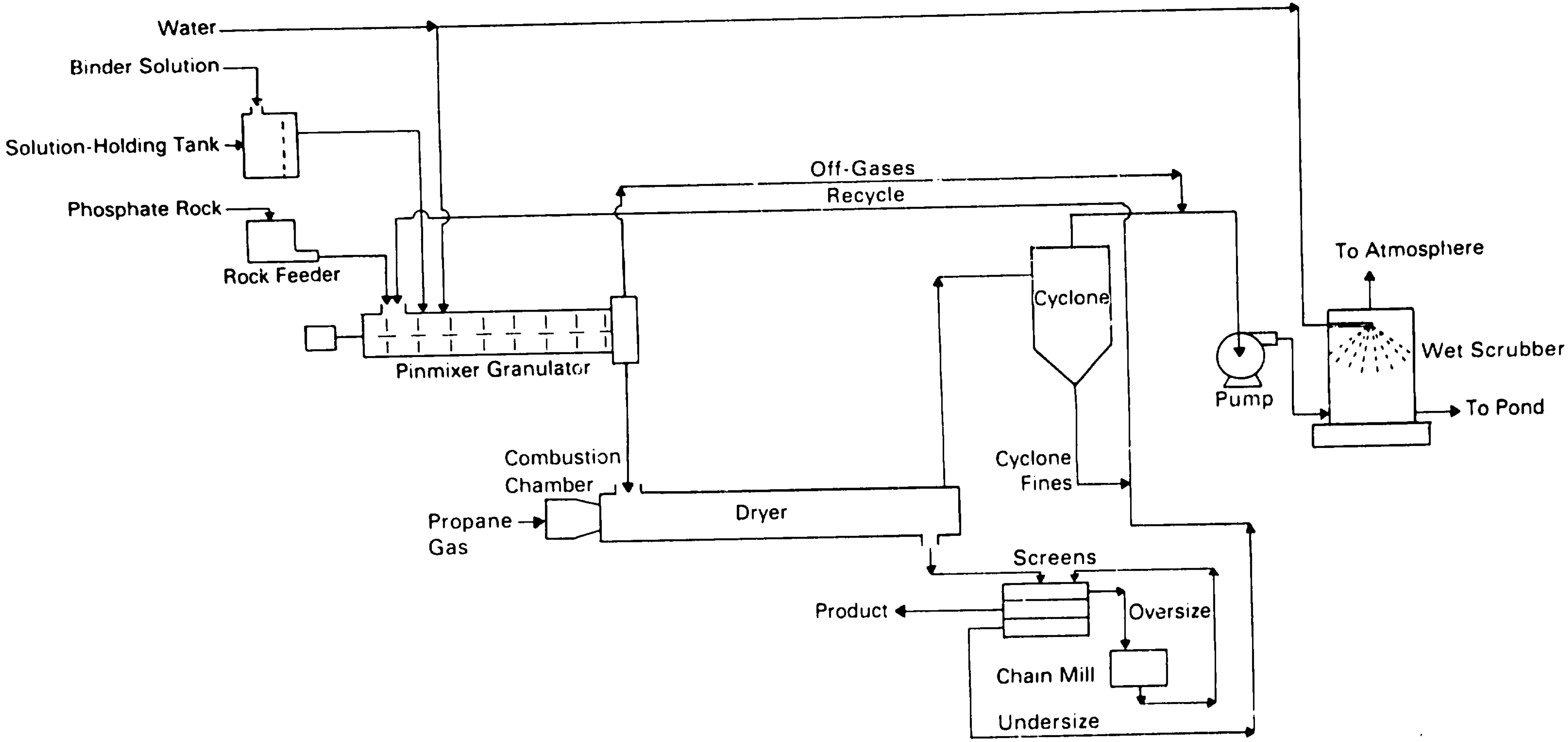

Figure 12. IFDC Continuous Laboratory-Scale Process for Minigranulation of Phosphate Rock.

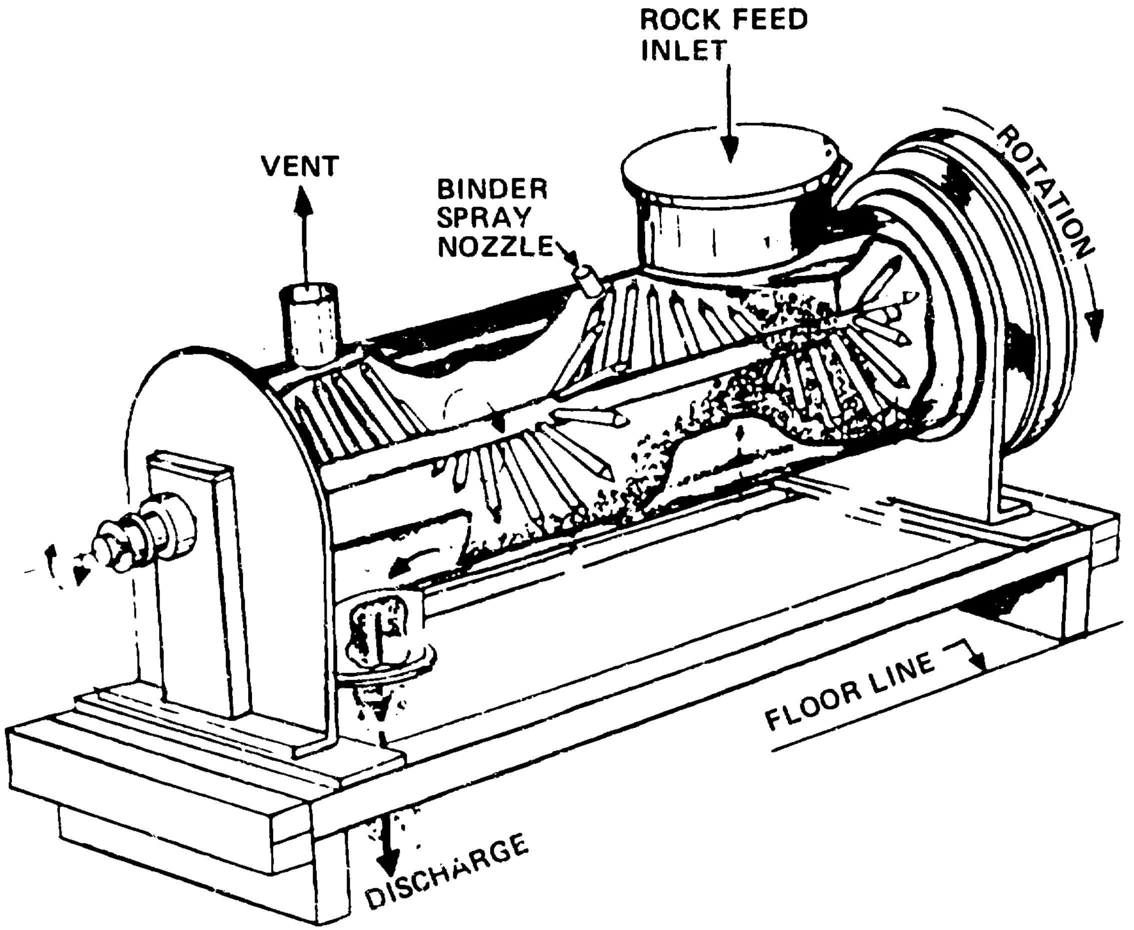

Figure 13. Perspective View of Pinmixer Used for Minigranulation of Phosphate Rock.

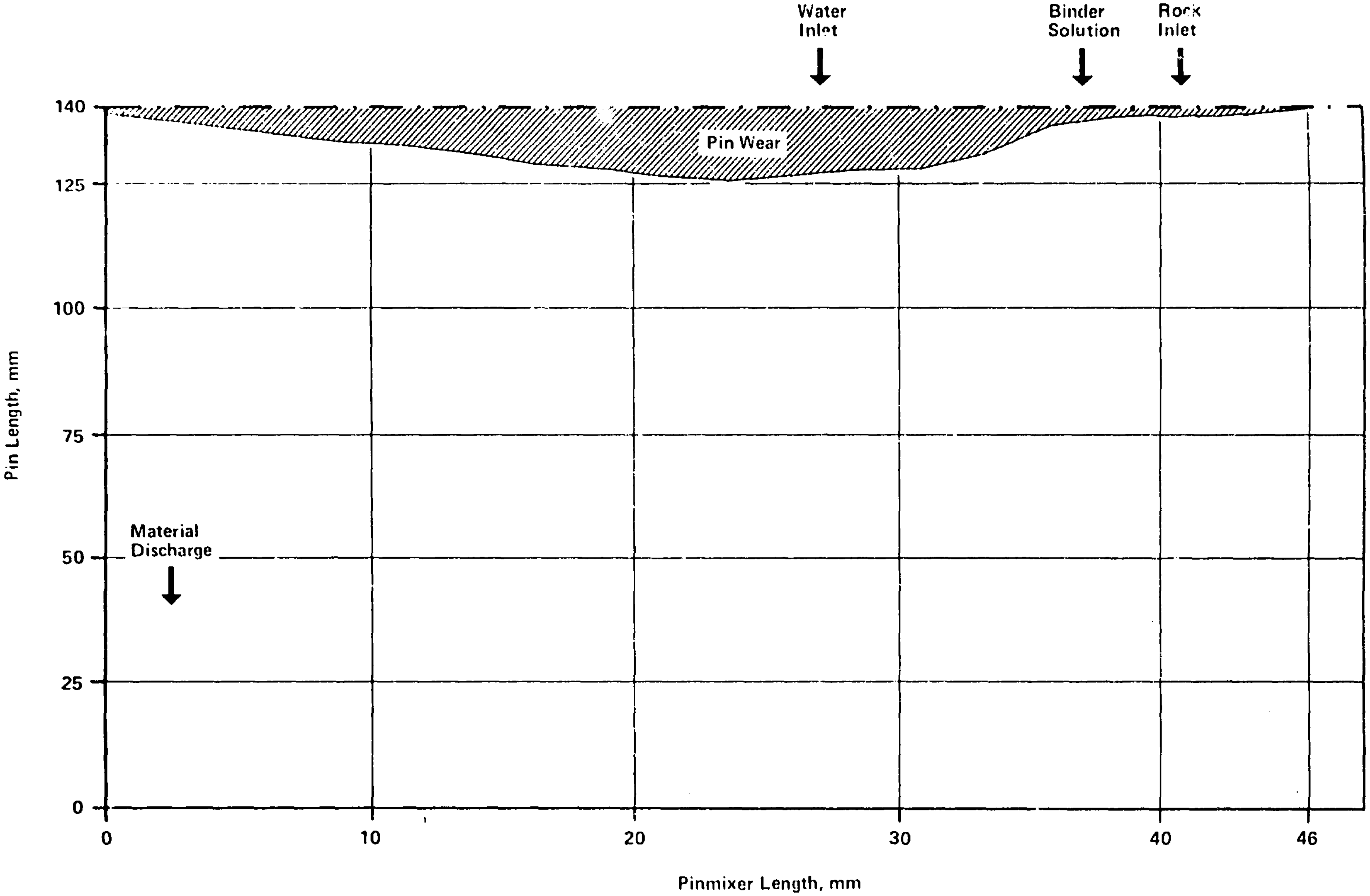

Figure 14. Typical Pin-Wear Profile for Minigranulation of Run-of-Mine, As- Received, Ground Mussoorie Phosphate Rock.

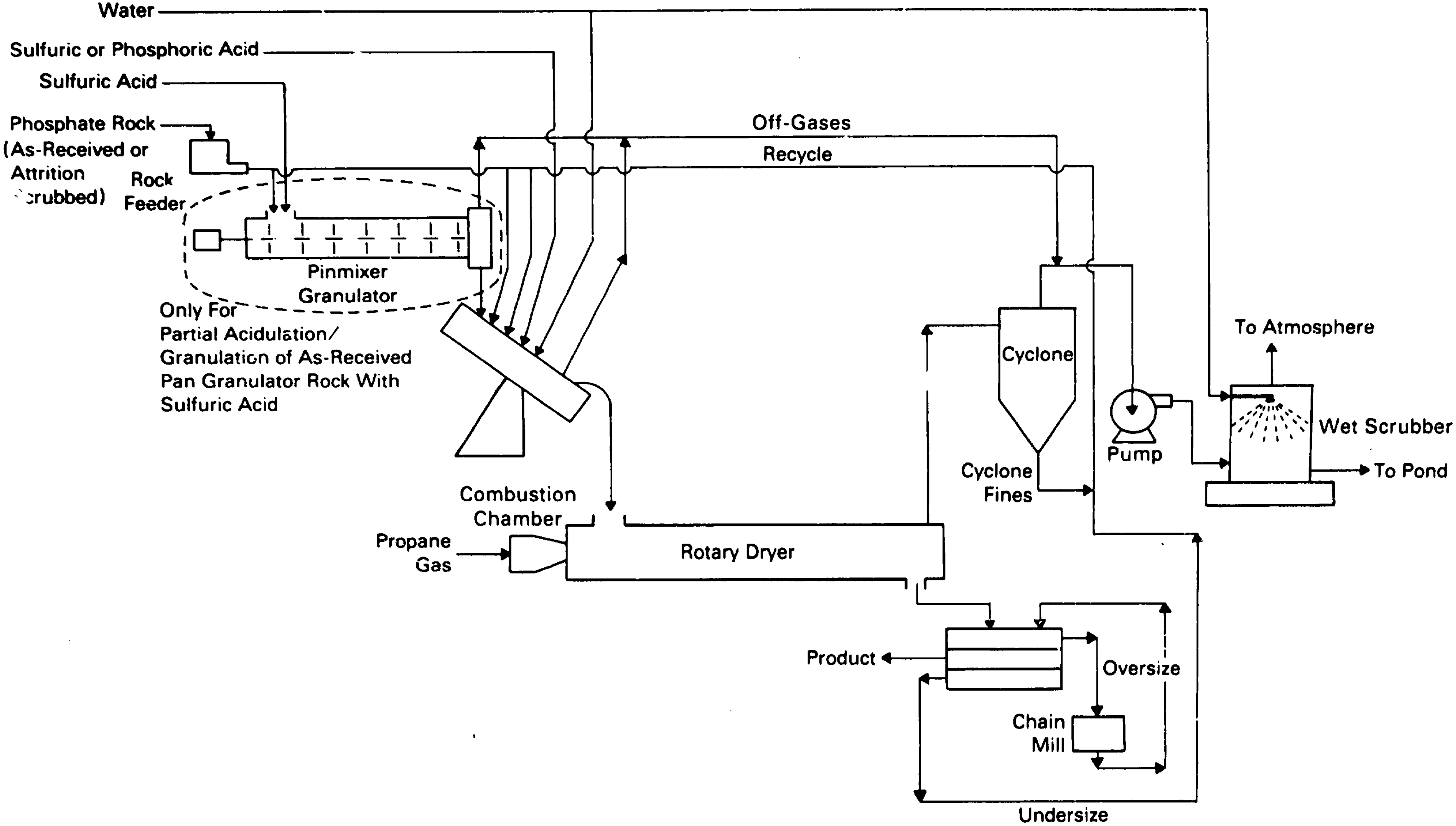

Figure 15. Schematic Diagram of IFDC Laboratory-Scale Equipment Setup for Continuous Partial Acidulation/Granulation of Mussoorie Phosphate Rock.

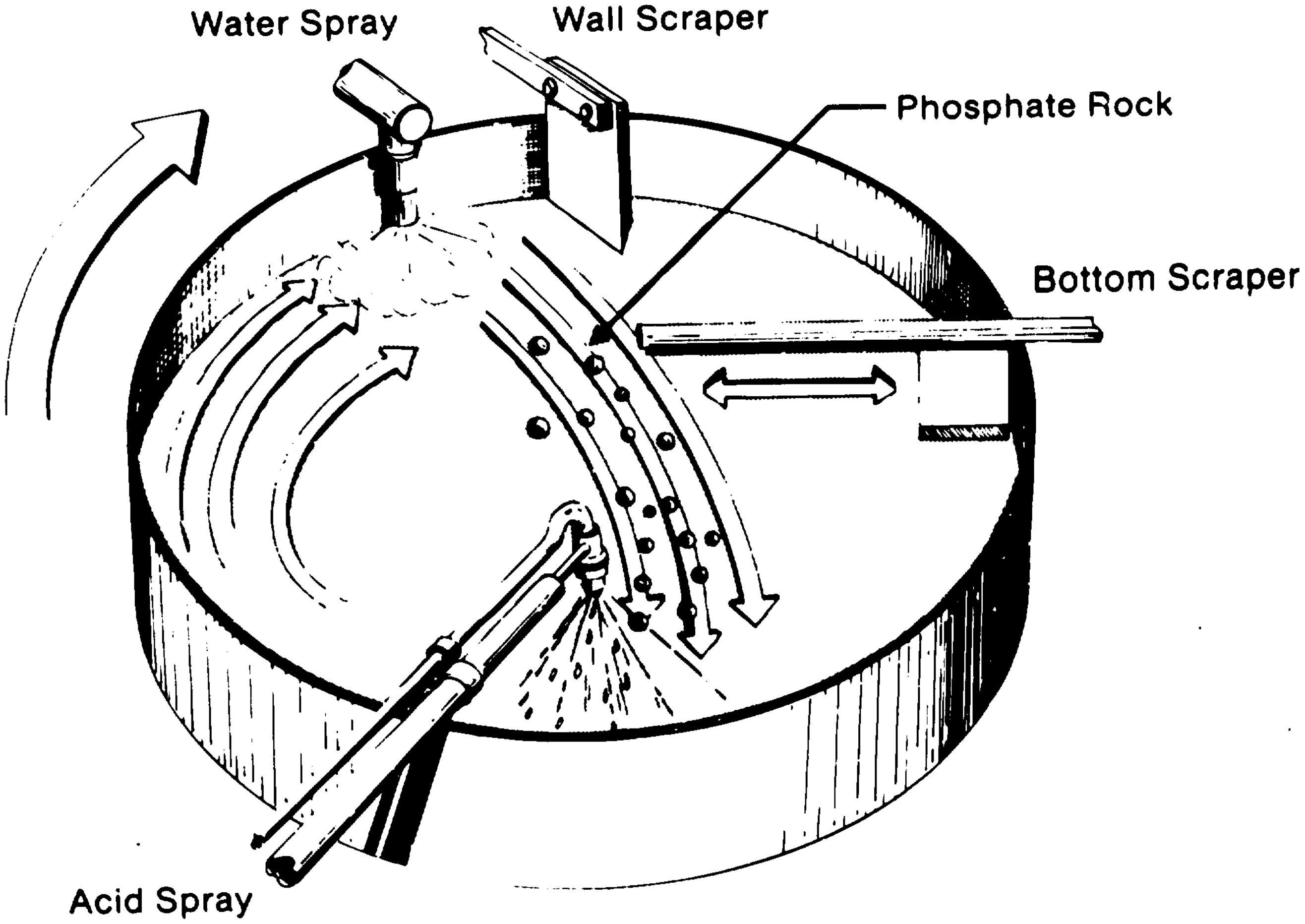

Figure 16. Pan Granulator for Single-Step Partial Acidulation/Granulation in IFDC Laboratory-Scale Unit Showing Relative Locations of Water and Acid Sprays.

APPENDIX A

X-RAY DIFFRACTION PATTERN OF MUSSOORIE PHOSPHATE ROCK

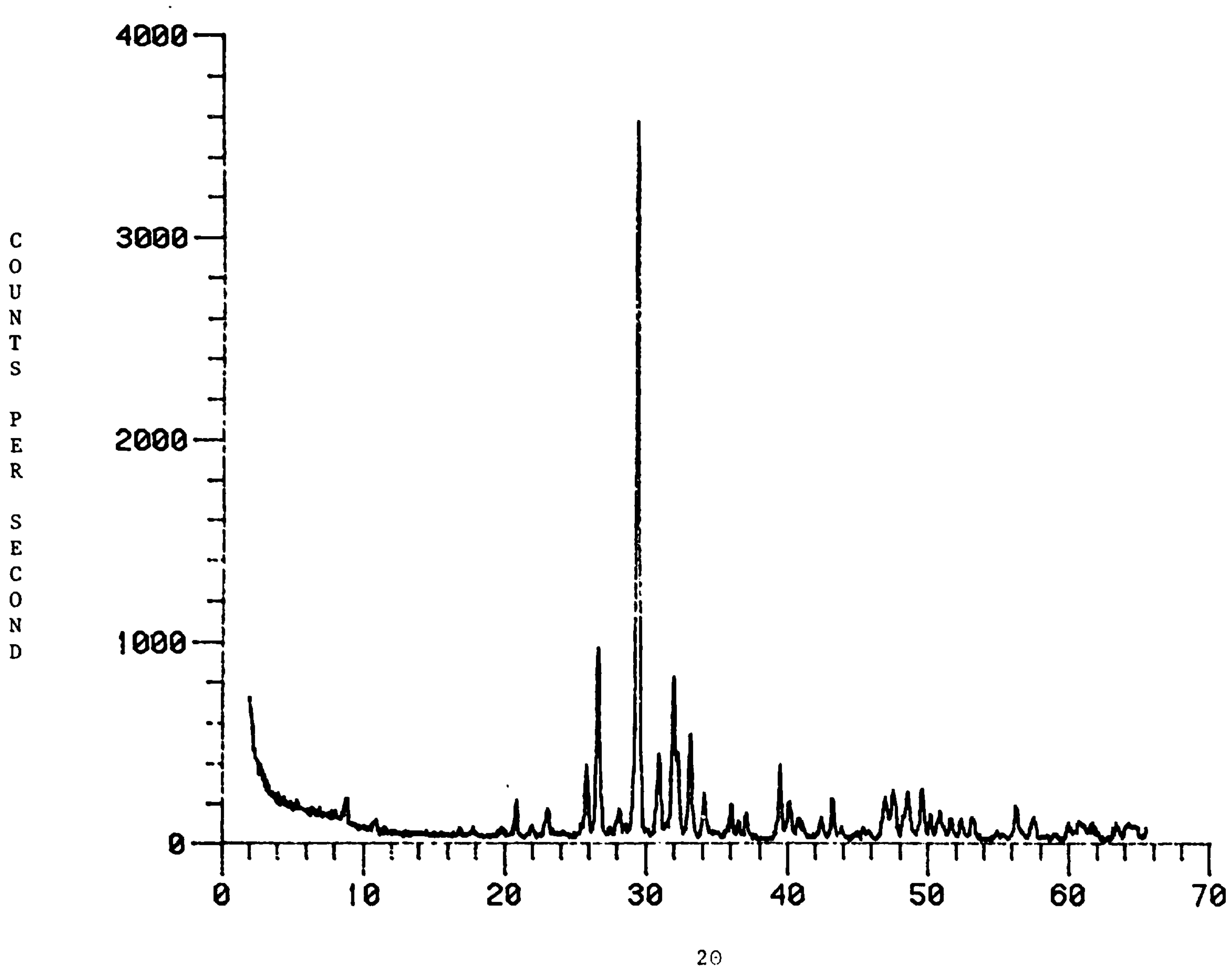

Figure A1. X-ray Diffraction Pattern of Mussoorie Phosphate Rock.

APPENDIX B

CONCEPTUAL PROCESSES FOR PRODUCTION OF PAPR FROM MUSSOORIE PHOSPHATE ROCK AND CONCENTRATE

CONCEPTUAL PROCESSES FOR PRODUCTION OF PAPR FROM MUSSOORIE PHOSPHATE ROCK AND CONCENTRATE

On the basis of the results of the process-demonstration trials with the ROM Mussoorie phosphate rock and concentrate (prepared by Sala International, Sweden) and IFDC pilot-plant runs (≃250-500 kg/hour of product) with the central Florida phosphate rock (unpublished reports), a conceptual process flow diagram was prepared (Figure B-1) for production of PAPR from either Mussoorie phosphate rock or concentrate. Additionally, on the basis of a desired 3-5 mtph capacity, preliminary estimates of the battery-limit process equipment[1] (including abbreviated specifications) for the demonstration plant were made. It should be noted that these are estimates only, and detailed engineering design would be required to confirm the suggested equipment sizes.

Description of the Process

The equipment configuration for the conceptual process is similar to that used for the process-demonstration runs and include the following options:

1. Single-step acidulation/granulation of either ROM Mussoorie rock or concentrate using either sulfuric or phosphoric acid.
2. Pretreatment of ROM rock with phosphoric acid followed by single-step acidulation/granulation using sulfuric acid.
3. In Options 1 and 2, the granulator discharge is not dried but pile cured prior to screening.

The SSAG process is a variation of a typical commercial granulation system used to produce granular TSP or NPK products and consists of the following basic steps (Option 1): acidulation/granulation of the phosphate rock with sulfuric or phosphoric acid and recycle fines, product drying, and screening.

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[1] The list does not include the following items:
   a. Coarse phosphate rock unloading, handling, and storage facilities.
   b. Phosphate rock grinding and ground rock storage facilities.
   c. Sulfuric or phosphoric acid receiving, storage, and pumping facilities.
   d. Bulk and bagged product storage facilities.
   e. Bagging equipment.
   f. Mobile equipment--payloaders, forklifts, utility trucks.
   g. Office, laboratory, maintenance shop and storeroom, weighbridge, potable and process water storage, fire protection system, and related plant site facilities.

The phosphate rock is transported by a bucket elevator to a surge bin. From the surge bin a weigh feeder is used to feed the rock continuously into the drum granulator. The sulfuric or phosphoric acid of desired concentration is pumped from the storage tank to the drum granulator. Recycle materials consisting of the undersize fraction (from the screening operation described later) and a portion of the onsize product are fed to the granulator. A recycle-to-product ratio of about 2 to 1 is maintained to facilitate good granulation. Water is added to the granulator to maintain a liquid phase level adequate for optimum granulation. The plastic material, usually at a temperature of 50°-60°C and containing 8%-10% moisture from the granulator, is discharged by gravity into a rotary dryer. The dryer is operated with a cocurrent flow of hot air that is heated in a combustion chamber directly fired with fuel oil. From the dryer, the material is discharged to an elevator and transferred to an oversize screen and a product screen connected in series to yield a product in the 1-4 mm size range. The oversize material (over 4 mm) is crushed in a chain mill and returned to the oversize screen. The undersize material (less than 1 mm) together with a fraction of product is recycled to the granulator as previously mentioned. The bulk product is conveyed to storage. Gases containing dust and fluorine from the granulator, dryer, screens, and other pieces of equipment are treated in cyclones and a wet-scrubber system using water as a scrubbing medium. From the scrubber the liquor is discharged to a settling and treatment pond. The pond water is treated with lime or limestone. The clarified water from the pond is recycled to the granulator.

When pretreatment of the ROM rock is required (Option 2), the ground rock is fed to a double-shaft pug mill where it is partly reacted with phosphoric acid. The moist material from the pug mill is discharged by gravity into the rotary-drum granulator where it is acidulated/granulated using sulfuric acid. Recycle material consisting of the undersize fraction and a portion of the onsize product are fed to the granulator. Water is added to the granulator to control granulation. The rest of the operation is similar to that described above.

When pile curing of the granulator discharge is used (Option 3), the combustion chamber of the dryer is turned off and the dryer is used as a cooler and conveyor of the granulator discharge to the curing pile. Depending on the desired length of curing (1-7 days), the material from the curing pile is recovered and screened. As before, the oversize is crushed and rescreened while the undersize is recycled to the granulator. Alternately, if a market exists, the undersize (minus 1 mm) can be a nonpremium-grade product.

Pollution Control

Fluorine is a common constituent in phosphate rock, and the acidulation of rock results in the release of some gaseous fluorine compounds. Fluorine gases, even in small quantities, are very toxic to plant and animal life. Removal of fluorine from process gas streams before they are exhausted to the atmosphere is essential and is closely monitored by pollution control authorities in many countries.

In laboratory-scale operations, because of the relatively small flow rates, actual fluorine measurements during acidulation and subsequent processing steps were not possible. However, analyses of products (granular and ROP) show that about 40% of the fluorine contained in the rock is lost during production of PAPR (Tables 27 and 30). Of this amount, about 40%-80% would be evolved during drying (for SSAG process) or denning (for ROP process), and the remainder would be evolved during the initial acidulation reactions. Hence, it is recommended that in a demonstration unit the off-gases from the reaction and drying or denning step be treated in a venturi-type wet scrubber before they are exhuasted to the atmosphere.

In addition to the gaseous pollutants (fluorine compounds), particulates (dust) generated during the handling of finely ground phosphate rock and during manufacturing and bagging operations are also of concern. Hence, every effort should be made to design and operate the system to minimize the escape of dust. Slow speed, positive or continuous discharge bucket elevators are essential for handling the dusty phosphate rock feed and recycle materials. Totally enclosed screw-, chain drag-, or belt-type conveyors are also well suited for use in these processes.

In the SSAG process, a cyclone-type dust collector is recommended for removing a relatively large quantity of particulate from the hot air exhausted from the dryer. A similar dust collector is also recommended for the fugitive dust collection system. The fugitive dust pickup system for the plant should be designed to ventilate the bucket elevators, conveyors, screens, crushers, and all dry material transfer points. Adequate ventilation of these units and material transfer points will ensure that a minimum of dust and fluorine escapes into the plant and work area. The dry collection systems are followed by the wet scrubber (mentioned earlier) to remove fluorine from the air before it is exhausted to the atmosphere.

The management and processing of the scrubber liquor discharged from the scrubber system usually depend upon local economics (availability and cost of water) and effluent control regulations. In India regulations prohibit discharge of contaminated water containing appreciable amounts of dissolved and suspended solids. Thus, an effluent pond (included in the auxiliary and support facilities) is recommended for settling suspended solids and for storage and recirculation of classified water back to the scrubber. Additionally, the pond water is also used to control granulation (in the drum granulator). This effluent pond system is simple, easy to control, and environmentally safe since the effluent pond serves as a "safety valve" in the event of a major process upset or spill that could otherwise be detrimental to the local waterways and environment. This type of wastewater management system also usually affords the most economic use of fresh makeup water.

It is anticipated that yearly dredging of settled solids would be required. These solids can be disposed of according to Indian environmental regulations.

A small fraction of the clarified water being recycled to the scrubber may need to be diverted to the local wastewater stream for disposal. A pH control system and a treatment system are recommended for this stream to ensure that it meets the acceptable criteria for discharge.

A pH control system is also recommended for the scrubber liquor system to protect the scrubber and related equipment from the attack of fluosilicic acid.

Table B-1 contains listings of the principal process equipment along with abbreviated equipment specifications.

Table B-1. Equipment List--3-5-mtph (10-mtph Throughput) Granulation Plant for Partially Acidulated Phosphate Rock[a]

Equipment Item Number (Refer to Figure B-1)	Description and Approximate Size or Capacity
1	Phosphate rock elevator--positive discharge, double chain, low speed, to feed elevated hopper, 15-mtph capacity, to be operated approximately 20% of the time.
2	Surge hopper--elevated to hold 2-hour supply of phosphate rock, vibrating cone bottom, rotary-vane discharge, 10 m^3 capacity.
3	Screw conveyor/weigh belt feeder assembly--capacity of 2-5 mtph of powdered phosphate rock.
4	Recycle bucket elevator--single chain, continuous discharge, 12-mtph capacity.
5	Double shaft pug mill, 0.6 m wide and 2.2 m long (mixing trough), complete with enclosed hood and fluorine vent duct.
6	Rotary drum granulator--2.0 m in diameter, 6.0 m long, with retaining dam 30 cm high located 1.0 m from discharge end, including water and acid distribution piping system, and rubber panel-type liner.
7	Pug mill and granulator exhaust fan--open material handling (OMH) type, stainless steel or FRP, 8,500 m^3/hour.
8	Fuel storage (heavy oil) for dryer--approximately 200 m^3 (60-day supply based on maximum consumption of 650,000 kcal/hour), including oil heating and pumping system.
9	Combustion control system to operate burner automatically or manually based on temperature of air discharged from dryer.
10	Rotary dryer (optional cooler) with cocurrent combustion system--1.52 m in diameter, 10.66 m long, ring gear and pinion drive, 200-kW motor and drive assembly, 800,000-kcal/hour burner to run at about 650,000 kcal/hour.
11	Dryer cyclone-type dust collector system--20,000 m^3/hour air at 100°C.
12	Dryer exhaust fan--one unit, OMH type, 20,000 m^3/hour, at 100°C, 38 cm pressure differential.
13	Dryer discharge and crusher discharge (screen feed) bucket elevator--single chain, continuous discharge, 20-mtph capacity.
14	Screens--inclined, vibratory, two single-deck units (one for oversize [+4 mm] and two for product size [+1 mm]), total maximum load 10 mtph, type 304SS square mesh on oversize screw, slotted (Ty-Rod) mesh on bottom (product) screen, 1.5 m^2 each screen surface.
15	Cage mill-type crusher, maximum of 3 mtph, 4-10 mm oversize crushing capacity.

(Continued)

Table B-1. Equipment List--3-5-mtph (10-mtph Throughput) Granulation Plant for Partially Acidulated Phosphate Rock[a] (Continued)

Equipment Item Number (Refer to Figure B-1)	Description and Approximate Size or Capacity
16	Recycle belt conveyor--to handle undersize material from product screens and dust collector, 10-mtph capacity, deep troughing idlers, 60 cm wide, enclosed to minimize dusting, length to fit layout of equipment.
17	Product belt conveyor--60 cm wide, length to fit layout of storage area.
18	Cyclone-type dust collector system for fugitive dust--20,000 m^3/hour.
19	Exhaust fan for fugitive dust system--OMH type, 20,000 m^3/hour at 30°C, 38 cm pressure differential.
20	Dryer, pug mill, and granulator wet scrubber--wood construction with slat packing, 10-m^2 total cross-section area, two compartments, 5 m^2 each (downflow and upflow), concrete sump, complete with pH (ammonia or calcium hydroxide) control system.
21 A,B	Scrubber recirculation pumps--two units, rubber-lined centrifugal, 55 m^3/hour at 3 kg/cm^3 total head each.
22 A,B	Scrubber liquor bleed pump for pumping to settling pong--two units (one in service and one spare), self-priming centrifugal, 2 m^3/hour each, total head dependent upon location of pond.
23 A,B	Pond water pumps--two units (one in service and one spare), rubber lined, for pumping to wet scrubber, granulator, and optional waste water treatment system, 2 m^3/hour, discharge head of pumps will be dependent upon location of pond.
24	Receiving, storage, and feeding system for material (ammonia or calcium hydroxide) to control pH of wet scrubber and pond effluent liquor.
25	Settling and scrubber liquor recovery pond, approximately 800-m^2 surface 3 m deep.

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[a] Does not include the following major items:
1. Coarse phosphate rock unloading, handling, and storage facilities.
2. Phosphate rock grinding and ground rock storage facilities.
3. Sulfuric and phosphoric acid receiving, storage, and pumping facilities.
4. Bulk and bagged product storage facilities.
5. Bagging equipment.
6. Mobile equipment--payloaders, forklifts, utility trucks.
7. Office, laboratory, maintenance shop and storeroom, weighbridge, potable and process water storage, fire protection system, and related plant site facilities.
8. Process instrumentation.

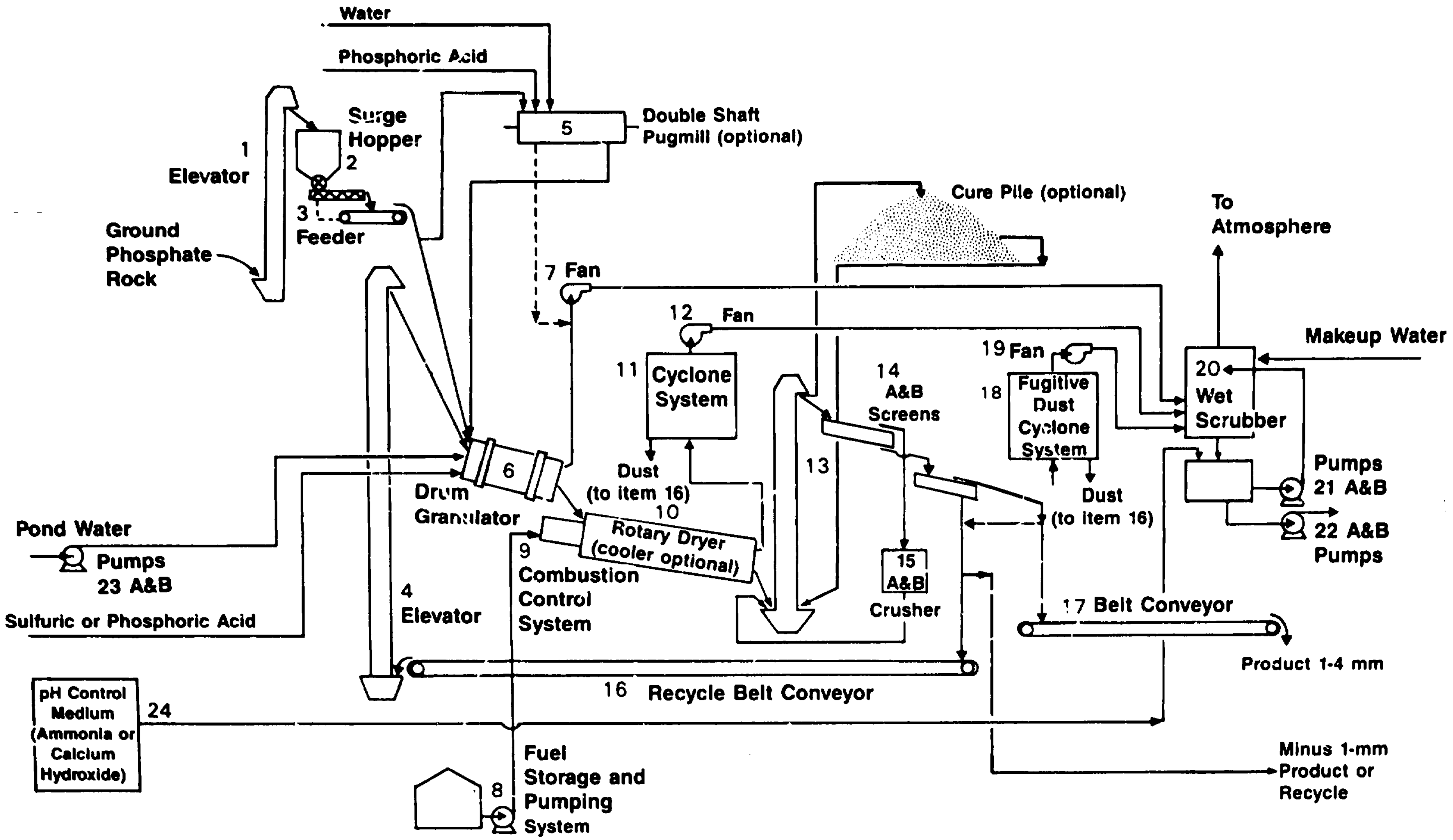

Figure B-1. Process Flow Diagram—Production of Granular Partially Acidulated Phosphate Rock With Minus 1-mm Product Option (Phosphoric and/or Sulfuric Acid).