or tubers from plots receiving 250 gallons per acre UF-85 was slightly higher than for those receiving 150 gallons per acre because the former treatment resulted in a greater percentage of russeted tubers. It is not definitely known whether the russeting observed was caused by *S. scarbies* or was a result of the high rate of UF-85 application. PCNB, applied at a rate of 50 pounds per acre, was also effective for controlling the pitted-type scab lesions.

1957 Results

High temperatures and near-drought conditions during July and August precluded optimum potato growth. However, these growing conditions were conducive to a higher incidence of scab than was reported for 1956.

There were no marked differences in tissue nitrogen between either amount or type of nitrogen fertilizer applied (Table III). This is in contrast to results of 1956 because of both a lack of leaching rains and the split application of the ammonium nitrate nitrogen. From a single application of UF-85, the urea nitrogen was apparently retained over the entire growing season and released at a rate which was not limiting for plant growth. The retention in the soil of the nitrogen from urea as UF-85 would suggest either an effective reduction of the nitrifying soil microorganism due to the free formaldehyde released or the presence of a series of urea-formaldehyde complexes which slowly break down to urea and formaldehyde.

Tuber yields were significantly higher for treatment numbers 4, 5, 6, and 9 than for the unfertilized potatoes. Lime at 2000 pounds per acre slightly reduced yields whereas at 500 pounds per acre, no effect on the yield was found. Tuber yields would have been considerably higher had the nitrogen, phosphorus, and potassium fertilizers been applied in the row instead of broadcast.

Dry soil conditions which prevailed during much of the 1957 growing season contributed toward a higher incidence of scab than was noted in 1956. Germination was not affected by a 150-gallon rate of UF-85 even though the potatoes were planted less than 2 hours after the UF-85 was applied. The data (Table III) show a definite and highly significant reduction of scab from UF-85 applied at a rate of 150 gallons per acre under conditions of low and high soil fertility and high soil fertility plus ground limestone. UF-85 applied at a rate of 50 gallons per acre also significantly reduced the scab under conditions of low and high soil fertility. These results indicate that UF-85 is effective for controlking scab under soil and weather conditions conducive to severe disease development.

Literature Cited

- Darby, J. F., Florida Univ. Agr. Expt. Sta. Research Rept., July 1956.
- (2) Fink, H. C., *Plant Disease Reptr.* 40, 190-2 (1956).
 (3) Hooker, W. J., *Ibid.*, 38, 187-92
- 3) Hooker, W. J., *Ibid.*, **38,** 18/–92 (1954).
- (4) Houghland, G. V. C., Cash, L. C., *Ibid.*, **38**, 777-80 (1954).
- (5) Walker, J. C., Larson, R. H., Albert, A. R., *Am. Potato J.* 15, 246-52 (1938).

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QUICK CURING OF SUPERPHOSPHATE

Effect of Ball Mill Grinding on Acidulation of Phosphate Rock

R. R. ROUNSLEY¹ and D. R. BOYLAN Chemical Engineering Department, Iowa State College, Ames, Iowa

An investigation was undertaken to determine the effect of grinding during the acidulation of phosphate rock. Bench-scale work was carried out in a 1-quart, laboratory ball mill made of stainless steel, which was equipped with a heating chamber so that the material could also be dried in the mill. A normal superphosphate product suitable for commercial use was obtained within an hour after the addition of the first acid. Successful pilot plant operation showed that the bench-scale results could be duplicated on a larger scale and on a continuous or semicontinuous basis. An economic comparison of the process with an equivalent standard normal superphosphate process indicated that this quick-curing process was competitive, if not favored.

I N THE USUAL MANUFACTURE of normal superphosphate, the required amounts of sulfuric acid and phosphate rock are mixed and allowed to "set up" in some kind of closure. The resulting porous solid is mechanically disintegrated and transferred to piles for curing while the chemical reactions are allowed to go to completion. During this curing period of from 4 to 6 weeks, the free acid and free moisture contents are reduced and the available phosphorus content is increased.

¹ Present address, Mead Corp. Chillicothe, Ohio.

Processes in which the curing period is reduced or eliminated entirely are referred to as quick-curing processes. Their advantages (3, 5) include: product can be shipped directly from process, thus reducing bulk storage space required and working capital tied up in inventory; opportunities for producing a granular product are greater; operating conditions can be chosen with more flexibility for attaining maximum conversion; and production rates can be adjusted to meet an almost instantaneous demand because the final product can be produced in a matter of hours.

Previous Work

A close approach to a quick-curing process was first achieved in this country when the Davison Chemical Corp. (19) granulated fresh superphosphate in a rotary drum and dried it in a rotary dryer. Bridger and Kapusta (5) developed a quick-curing process at Iowa State College in 1952 in which 50 to 65% sulfuric acid was used and a product, ready for immediate shipping was produced.

In 1953, a process was announced in Japan (15) in which the reaction between sulfuric acid and rock was promoted by

Table I. Screen Analysis of Florida Pebble Phosphate Rock

Screen Mesh	Weight % of Sample
+ 65	7.1
-65+100	15.1
-100 + 150	7.5
-150 + 200	27.2
-200	43.1

passing an alternating electric current through the mixture for $2^{1/2}$ hours. An exceptionally high acidulation ratio was used to achieve the quick-curing effect.

In January 1957, the Tennessee Valley Authority announced a process (6) for a quick-curing normal superphosphate. In this process ultrafinely ground rock was acidulated with an excess of dilute acid. The acidulated material was subsequently dried.

Although the use of excess acid in the last two processes makes the economics somewhat questionable, the advantage of overacidulated material in ammoniated and mixed goods may justify the expense.

Process Variables

Several factors are known to affect the reaction between sulfuric acid and phosphate rock. Perhaps the most important is acid concentration. The initial reaction rate increases as more dilute acid is employed. Under the usual acidulation conditions, 70% sulfuric acid appears to give the best results (17). Use of higher acid concentrations results in poor mixing, while the calcium sulfate formed as a by-product tends to coat the particles (11). On the other hand, use of too dilute acid results in a product with a high moisture content and poor physical characteristics. The reaction is slow or incomplete because of resulting low temperature.

Acid temperature is also of some importance. Temperatures of 35° to 65° C.

(Dry B	osphate Rock (7) asis)
Component	%
CaO	47.8
MgO	0.4
F	4.6
P_2O_5	33.4
B.P.L. ^a	72.8
$SO_3{}^b$	0.2
Fe_2O_3	1.05
Al_2O_3	1.35
SiO_2	9.07
Moisture	0.51

equivalent per cent of $Ca_3(PO_4)_2$. ^b Not determined.

are generally used (12). With lower acid temperature, the reaction is sluggish. With higher acid temperature, the mixture of acid and rock thickens too rapidly (18).

The particle size of the rock has a marked effect (8, 13, 17). Grinding before acidulation is beneficial; however, the effect of particle size is small in the size range of 20 to 95% through 100 mesh. Extremely fine grinding results in greatly increased rate of reaction (17).

The calcium sulfate formed during acidulation is thought to coat the rock particles and to prevent further reaction. Grinding during the acidulation should prevent such coating and provide a clean surface on the rock particles for the reaction to proceed. No evidence of this ever having been done appears in the literature, and the present work was undertaken to determine the effect of grinding during acidulation.

Laboratory Procedure

Materials and Methods. The phosphate rock used in these studies was Florida pebble obtained from the Davison Chemical Corp. plant at Perry, Iowa. Although the rock was transported and stored in covered 55-gallon

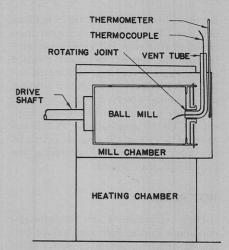


Figure 1. Cross section of ball mill and heating unit

steel drums, sufficient moisture was present or adsorbed to cause agglomeration. The rock was passed through a gyratory crusher and rolls to break up the lumps. Little, if any, actual grinding took place. Screen analyses are given in Table I.

Free moisture and free acid analyses of the product were carried out according to the procedure of the Association of Official Agricultural Chemists (2). The colorimetric procedure of Bridger, Boylan, and Markey (4) was used in the determination of phosphorus pentoxide. A typical chemical analysis of the rock used is given in Table II.

Bench-scale tests were made in a 1-quart, stainless steel, laboratory ball mill. The mill contained 4.5 pounds of 0.75-inch diameter stainless steel balls. A cover was used with a vent tube in a rotating joint to permit refluxing of the vapor or drying at atmospheric pressure. The ball mill was enclosed in a chamber which could be heated indirectly as shown in Figure 1. This heating shell was constructed of 18-gage galvanized iron and provision was made to measure

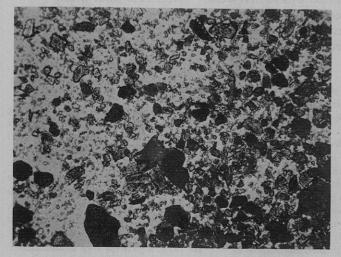


Figure 2. Photomicrograph of raw phosphate rock, $100\times$ magnification

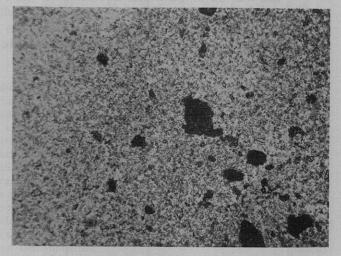


Figure 3. Photomicrograph of freshly acidulated phosphate rock, $100 \times$ magnification

the temperature of the gas within the mill chamber.

The mill was equipped with two condensers; a vertical condenser to reflux any escaping vapors when drying was not desired and an inclined condenser to condense the vapors coming from the mill during the drying operation. Measurement of the amount of condensate gave a good indication of the progress of drying.

In the test procedure, the desired quantities of 72% sulfuric acid and rock were first mixed in a beaker, the mixture was emptied into the mill, and the last traces of rock and acid were washed from the beaker into the mill with the required amount of dilution water.

After the mill was assembled, grinding was started, and the reflux condenser was attached. Heated grinding was accomplished by maintaining the mill chamber temperature between 110° and 115°C. Actual product temperature at this point was about 103°C, measured by means of a thermocouple inserted through the vent tube into the mill.

When grinding action with reflux had continued for the desired length of time, drying was started. The reflux condenser was removed, the inclined condenser connected and the heat input increased to maintain the required mill chamber temperature. As in earlier runs, a white crystalline precipitate formed in the condenser at a product-free moisture content of about 3 or 4%. This occurred after a drying time of 30 to 60 minutes. The precipitate formation was used as a criterion for stopping the drying operation in many of the runs.

At the end of the drying step, the product was removed from the mill and either immediately analyzed, diluted with water, or extracted with acid to stop the reaction.

Laboratory Results. Quick-cured normal superphosphate was made in the laboratory ball mill using batches of 50 to 100 grams of rock. The variables studied were grinding temperature, grinding time, drying temperature, acidulation ratio, and acid concentration. The results of these studies are given in Table III. The data indicate, in general, that there is little effect of acid concentration below 60% or of drying temperatures between 125° and 150° C., as determined by the appearance of the white precipitate in the condenser tube.

A microscopic examination of the rock before and after acidulation showed that the primary effect of acidulation is the production of a large amount of fines. Figures 2 and 3 are photomicrographs showing this. The sample of superphosphate for Figure 3 was taken after about 1 minute of mixing in a beaker and was washed to remove the soluble products. The fines shown do not contribute heavily to the total weight.

Table III.	Results of Quick-Curing Normal Superphosphate in a Laboratory
	Ball Mill

Dall Mill										
		Acid		Drying		Pr	oduct A	nalysis, '	%	
Run No.	Acidul. Ratio	Сопсл., %	Prelim. Grind	Temp., °C.	Total P ₂ O ₅	C.I. P ₂ O ₅	Avail. P ₂ O ₅	Conv.	Free moist.	Free acid
54-6 61 62 63 64 65 69 70 71 72 73 74	$\begin{array}{c} 1.45\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.80\\ 1.58\end{array}$	39.1 39.1 39.1 39.1 39.1 39.1 39.1 39.1	Hot Cold Cold Cold Cold Cold Cold Hot Hot Cold Hot Hot	$125 \\ 150 \\ 125 \\ 125 \\ 150 \\ 125 \\ 135 \\ 135 \\ 125 $	$\begin{array}{c} 22.0\\ 20.3\\ 19.8\\ 20.4\\ 21.5\\ 21.2\\ 20.3\\ 20.6\\ 20.9\\ 21.8\\ 21.6\\ 22.1\\ \end{array}$	4.2 0.9 0.6 0.8 1.3 1.0 0.8 0.8 0.7 0.7 1.1 2.6	$\begin{array}{c} 17.9\\ 19.3\\ 19.1\\ 19.6\\ 20.1\\ 20.2\\ 19.5\\ 19.8\\ 20.2\\ 21.1\\ 20.5\\ 19.5\\ 19.5\\ \end{array}$	$\begin{array}{c} 81.0\\ 95.4\\ 97.0\\ 96.0\\ 94.5\\ 95.5\\ 95.9\\ 96.1\\ 96.6\\ 96.9\\ 94.9\\ 88.1\\ \end{array}$	2.43 2.97 4.55 3.39 3.61 3.25 3.78 3.98 4.66 2.60 4.90 2.66	$\begin{array}{c} 1.80\\ 1.53\\ 1.91\\ 2.71\\ 1.14\\ 0.87\\ 0.60\\ 2.34\\ 3.42\\ 0.74\\ 2.08\end{array}$
75 76 77 78 79 80-I 81 82	$\begin{array}{c} 1 .80 \\ 1 .80 \\ 1 .80 \\ 1 .80 \\ 1 .80 \\ 1 .80 \\ 1 .80 \\ 1 .80 \\ 1 .58 \end{array}$	39.1 39.1 55.5 72.2 39.1 39.1 39.1 39.1 37.4	Hot Hot Cold Cold Hot Hot Cold Hot	150 125 125 135 135 150 135 125	20.3 20.7 22.5 22.6 20.7 20.8 20.7 21.6	$\begin{array}{c} 1 . 0 \\ 0 . 6 \\ 1 . 2 \\ 4 . 3 \\ 0 . 8 \\ 0 . 7 \\ 1 . 0 \\ 2 . 1 \end{array}$	$\begin{array}{c} 19.3\\ 20.1\\ 21.3\\ 18.3\\ 19.9\\ 20.1\\ 19.7\\ 19.5 \end{array}$	95.0 97.1 94.6 80.9 96.0 96.6 95.2 90.3	3.53 3.43 3.46 2.56 2.78 3.07 3.40 3.17	$\begin{array}{c} 2.36\\ 0.56\\ 1.81\\ 2.62\\ 2.55\\ 1.88\\ 1.21\\ 0.13 \end{array}$
87 89 90 91	1.80 1.80 1.80 1.80	39 . 1 55 . 5 39 . 1 55 . 5	Cold None Cold None	165 125 135 135	20.4 20.3 21.7 25.5	0.6 0.5 0.9 1.5	19.8 19.8 20.8 24.0	97.1 97.5 95.8 94.2	3.46 5.81 2.73 4.06	0.94 1.79 2.51 3.24
92-I 92-II 93 94 96-II 97 104 115 120	1.80 1.80 1.80 1.80 1.80 1.80 1.80 1.80	39.1 39.1 61.1 39.1 39.1 39.1 39.1 39.1 39.1 55.5	c Cold Cold Cold Cold Cold Cold 45 min. None	ь 135 185 125 125 200 125 5 135	$\begin{array}{c} 14.2\\ 21.0\\ 20.6\\ 21.7\\ 21.4\\ 19.9\\ 20.4\\ 13.9\\ 21.0\\ \end{array}$	$\begin{array}{c} 3.6 \\ 1.1 \\ 0.5 \\ 1.1 \\ 0.7 \\ 0.6 \\ 0.5 \\ 1.2 \\ 0.6 \end{array}$	$\begin{array}{c} 10.6\\ 19.9\\ 20.1\\ 20.7\\ 20.7\\ 19.3\\ 19.9\\ 12.7\\ 20.4 \end{array}$	74 6 94.7 97.6 95.2 96.7 97.0 97.5 86.3 97.2	2.58 4.69 3.28 3.18 4.32 3.31 1.94	$\begin{array}{c} 9.05\\ 3.04\\ 1.67\\ 2.54\\ 1.50\\ 2.14\\ 1.54\\ 1.54\\ 1.59\end{array}$
121-I 121-II 121-III 122-I 122-II 132-4 150	1.80 1.80 1.80 1.80 1.80 1.80 1.80 1.02	39.1 39.1 39.1 39.1 39.1 72.0 50.0	15 min. 30 min. 60 min. None 5 min. Cold Cold	ь ь ь 125 125	13.4 19.2 13.9 18.8 13.0 20.7 25.2	2.8 2.6 2.0 7.8 2.0 1.8 10.7	11.6 16.6 11.9 11.0 11.0 19.0 14.5	86.5 86.5 85.6 58.5 84.6 91.6 57.5	1.85 2.63	 1.32

Material mixed in Mixmaster rather than mill.

^b Analysis of wet material ground cold, no drying used.

⁹ Material from 92-I placed in mill for drying.

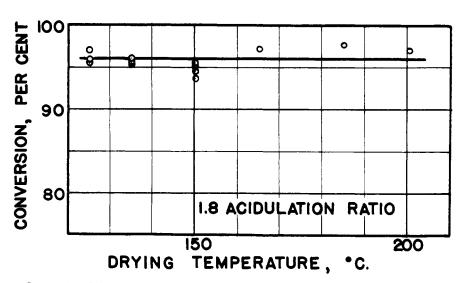


Figure 4. Effect of drying temperature on conversion preground at 30° C.

The effect of mill chamber drying temperature on the conversion of normal superphosphate is shown in Figures 4 and 5. Acidulated samples were preground either hot or cold for 45 minutes before starting the drying operation. According to these data, the mill drying temperature had little or no effect on the final conversion of the product, and there was no significant difference between pregrinding the sample with or without heating.

Actual measurements of the product temperature were made when a mill chamber drying temperature of 185° C. was used. Although the product temperature measurements were made about 5 minutes after the free moisture had dropped to 3%, as indicated by the precipitate formation in the condenser, the product temperature was still below 147° C. After 5 more minutes, the product temperature increased another 10° C. This indicated that conditions approximating constant rate drying existed as long as the free moisture content of the product was above 3%.

Drying proceeded rapidly in the ball mill even at temperatures as low as 125° C. in the mill chamber. Recently, Hatch and Regen (10) investigated drying under similar conditions with equally rapid drying rates.

No consistent correlation between final free acid and free moisture content was indicated and little variation was found in their actual values. Free moisture content varied between 2.5 and 4.9% while the free acid content ranged from 0.5 to 3.5%. These values compare favorably with common commercial superphosphate (20).

Decrease in the acidulation ratio below the recommended 1.8 caused a rapid drop in the conversion of the product as shown in Figure 6. This same effect was reported by Bridger and Kapusta (5).

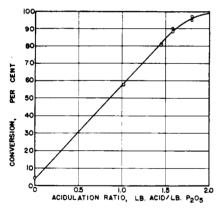


Figure 6. Effect of acidulation ratio on conversion

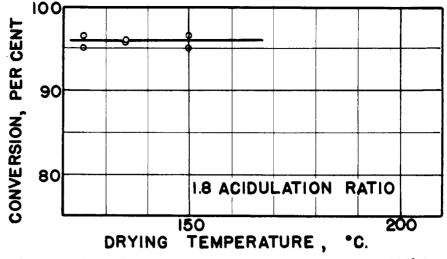


Figure 5. Effect of drying temperature on conversion, preground at 103° C.

Figure 7 shows that the effect of acid concentration used in the acidulation was small as long as the acid strength was below 60%. Above this concentration conversion dropped off rapidly. The data of Bridger and Kapusta for Roto-Louvre quick curing show the same effect, indicating that the initial free moisture content is significant. At these high acid concentrations, the balls did not move freely in the mixture.

The results of runs 89, 91, and 120 in Table III indicate that high conversion (about 95%) could be obtained if the drying were started immediately, without preliminary grinding. To check this, samples were taken "wet" from the mill during the grinding period and analyzed. Figure 8 shows the effect of grinding time on the availability, which indicates that long grinding is unnecessary. However, conversions higher than 86%were not obtained.

The drying step does, therefore, seem to increase the conversion. Apparently the effect of moisture loss is overcome by the increased reaction rate. This has also been noted by Meyers (14) who showed that concentrating a dilute phosphoric acid and rock mixture in a rotary dryer promoted the reaction.

To determine whether the high conversions obtained in the ball mill were the result of grinding or of good mixing or drying technique, acidulations were made using a Sunbeam Mixmaster Model 9 and the laboratory ball mill as a control. Analyses were made immediately after 10 minutes mixing, after 45 minutes in the Mixmaster and after 45 minutes in the ball mill. The results are given in Table IV. The ball mill is superior. Furthermore, this represents an improvement in conversion over the laboratory ball mill data of Bridger and Kapusta (5) in which the basis was drying technique alone.

The results of the bench-scale work showed that a quick-curing process was possible using a laboratory ball mill. To demonstrate the process on a larger scale, a pilot plant for producing 50 to 100 pounds per hour was constructed. The pilot plant was expected to assist in solving the related problems in materials handling, grinding, and heat transfer.

Pilot Plant Work

A flow sheet for the pilot plant is given in Figure 9. The pilot plant was essentially a heated tube mill, lined with 16-gage stainless steel, with provision for feeding acid and rock and removing product continuously. Flint balls were used. The acid was introduced into the mill from a rotameter; the rock was fed with a vibrating feeder. The acid and

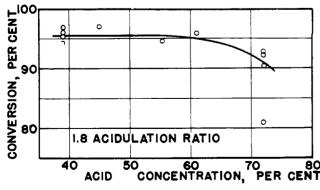


Figure 7. Effect of acid concentration on conversion

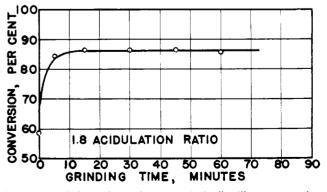


Figure 8. Effect of grinding time in ball mill on conversion

Table IV. Comparison of Conversion with and without Grinding

Run	Sample	Free Acid, %	Conv., %
84-I	Freshly mixed rock (10 min.)		65.0
92-I	45 minutes in Mix- master	9.05	74.6
76-I	45 minutes in ball mill (cold)	7.60	82.5

rock were mixed, ground, and dried in the mill where the action of the balls and the addition of heat promoted the reaction. The product was discharged from the opposite end of the mill in a powdered or granular form.

The mill was heated indirectly, a portion of the hot air being recycled. Exhaust vapors from the mill, containing various gases produced by side reactions, were removed at the feed end of the mill, scrubbed to remove the fluorides, and separated in a cyclone to remove water droplets. The scrubbed gas was discharged from the building (Figure 10).

The acid used in the pilot plant was diluted and cooled in batches of about 35 pounds to a concentration of 50%. The rock used was the same as that used in the laboratory work. The diluted, cooled acid was then pumped to a storage tank where it was fed into the mill by gravity.

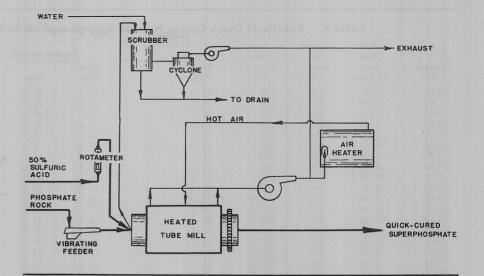
Although the rock feeder was calibrated, its calibration changed with the humidity of the air. This change in calibration affected the acidulation ratio. To evaluate the acidulation ratio properly, an analysis for sulfate was made on the product. As the only significant source of sulfate was the sulfuric acid and the rock was the only source of phosphate, the initial acidulation ratio could be evaluated.

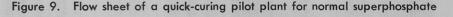
Pilot Plant Results. Because the first four runs with the pilot plant were made for the purpose of evaluating operating technique and eliminating mechanical trouble, little data were collected for these runs. The data for the preliminary and steady-state runs are given in Table V.

The conversion of all samples taken during operation of the pilot plant is plotted in Figure 11 as a function of the acidulation ratio. The solid line represents the data from the bench-scale work taken from Figure 6. The data of Figure 11 clearly show that the results from the pilot plant are equivalent to those of the bench-scale ball mill.

The most important aspect of the pilot plant work, not shown in the data, was that the normal superphosphate could be handled adequately on a continuous basis.

At a product moisture content of approximately 5%, a granular product was obtained. At lower moisture content, the product was fine powder.





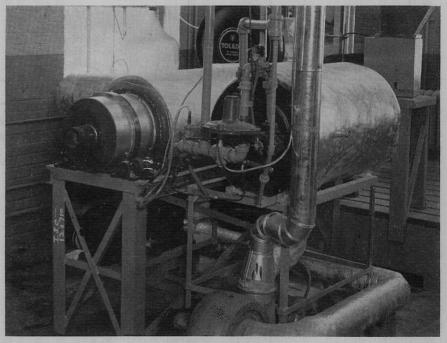


Figure 10. View of discharge end of tube mill

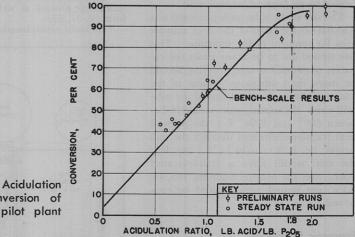


Figure 11. Acidulation ratio and conversion of product from pilot plant runs

Evaluation of the Process

Proposed Process. A proposed layout for a 480-ton-per-day, quick-cured, normal superphosphate plant is shown in Figure 12. In the proposed layout, the rock and acid would be brought in by

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Table V.	Results of Quick-Curing) Normal Superphosphate ir	Pilot Plant Tube Mill
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	Rock Feed	Outlet Air	Inlet Air			Pro	duct Analysis,	%			
Sample No.	Rate, Lb./Min.	Temp., °F.	Temp., °F.	Total P ₂ O ₅	C.I. P ₂ O ₅	Avail. P2O5	Conv.	Moist	Free acid	SO3	Acidul. Ratio
1-01	0.50	350	620	19.4	2.3	17.1	88.2	11.0	5,0	27.6	1.71
1-02	0.50	350	620	18.5	0.7	17.8	96.2	8.2	8.5	32.6	2,13
2-01	0.30	400	770	20.7	0.0	20.7	100.0	1.66		36.1	2.13
2-02	0.30	400	768	22.4	0.8	21.6	96.5	0.37	2.46	38.1	1.95
4-01	0.50	450	825	25.2	10.4	14.8	58.7	2.72	1.76	21.3	1.00
4-02	0.50	450	800	24.0	6.6	17.4	72.5	3.74	1.07	23.3	1.06
4-03	0.50	450	800	25.1	10.9	14.2	56.7	2.94	1.20	20.2	0.95
4-04	0.50	450	800	23.8	7.0	16.8	70.6	3.60	0.91	23,2	1.17
4-05	0.50	450	800	23.1	4.1	19.0	82.2	4.09	1.13	25.1	1.31
5-01	0.35	450	850+	22.3	4.7	17.6	79.0	4.03	2.07	26.0	1.41
5-02	0.30	450	850-	22.0	2.0	18,0	90.0	4.78	2.25	29.9	1.80
5-03	0.30	450	850+	20.8	3.3	17.5	84.2	3.70	3.43	29.4	1.71
5-04	0.30	450	850+	20.3	1.7	18.6	91.6	4.76	2.02	29.8	1.78
5-05	0.20	450	850+	21.5	2.7	18.8	87.5	3.86	3.31	29.5	1,66
5-06	0.20	450	850+	21.1	0.9	20,2	95.8	6.98	1.89	29.2	1,67
5-07	0.20	450	850+	25.1	9.0	16.1	64.2	3.79	0.47	21,0	1,00
5-08	0.20	450	850+	27.2	14.2	13.0	47.8	2.67	0.76	18.3	0.80
5-09	0.20	450	850+	27.0	15.1	11.9	48.0	2.66	0.36	16.0	0.70
5-10	0.20	450	850+	27.7	16.5	11.2	40.5	2.42	0.28	14.2	0.60
5-11	0.20	450	850+	26.8	15.2	11.6	43.3	1.88	0.25	12.7	0.55
5-12	0.20	450	850+	25.3	9.2	16.1	63.6	2.13	0.32	22.2	1.05
5-13	0.20	450	850+	28.9	16.3	12.6	43.6	1.41	0.06	16.8	0.69
5-14	0.20	450	950+	27.4	15.4	12.0	43.8	1.76	0.00	16.8	0.72
5-15	0.20	450	850+	27.5	15.0	12.5	45.5	0.62	0.00	15.4	0.66
5-16	0.20	450	850+	27.3	13.1	14.2	52.0	0.46	0.00	21.0	0.92
5-17	0.20	450	850 +	26.4	10.8	15.6	59.1	2.07	0.50	22.5	1.02
5-18	0.20	450	850+	25.2	11.8	13.4	53.2	5.80	0.26	17.4	0.82

railroad cars. The rock would be conveyed to a storage pile of 2 weeks' capacity and the acid pumped to a tank holding 10 days' supply. The rock would be moved by conveyor from the storage pile to overhead hoppers which would discharge into each of the five tube mills. The acid and water for dilution would be pumped to the mills and automatically metered in proportion to the rock. As a ball or tube mill is capable of handling the grinding of phosphate rock (16, 18), no preliminary rock grinding equipment has been proposed.

The product from the mills would be moved by belt conveyor to storage or bagging.

An exhaust system for the mills would also be provided with a scrubber to remove the fluorides. The mills would be heated by oil burners for each unit.

The size of the tube mills proposed was selected on the basis of the heat transfer area for removal of the moisture. This size turned out to be many times the capacity of the mill so that grinding should be more than adequate. Some of the assumptions used in the sizing of the tube mill were: the heating gases would be between 600° and 1200° F.; the over-all heat transfer coefficient through the mill would be 8 B.t.u./(hr.) (°F.) (sq. ft.); the mill would have a stainless steel liner; and the heat of reaction, 105,000 B.t.u. per pound mole, would be conserved.

Economic Evaluation

An estimate of the total fixed capital cost for a conventional normal superphosphate plant and for the proposed

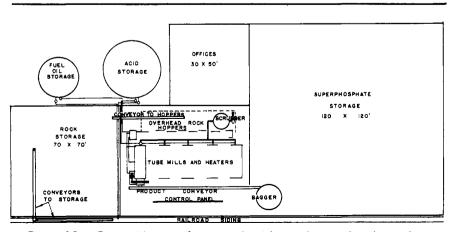
Table VI. Fixed Capital Cost Estimates for a Batch and the Proposed Quick-Curing Superphosphate Plants

(Basis: product, normal superphosphate, 20% available P2O5; capacity, 120,000 short tons per year; location. Ames, Iowa; and period, December 1956 costs)

	Installet Cos	st, Dollars ^a
ltem	B stch	Quick-cure
Land and railroad siding	18,500	18,500
Process building	91,500	87,900
Materials handling and storage facilities	400,000	233,100
Major grinding equipment	60,000	243,700
Acid mixing and dilution equipment dens	65,000	
Heating equipment		15,100
Instrumentation and controls		20,500
Bagging equipment	50.000^{b}	50,000
Contingencies, 20%	137,000	133,800
Total installed equipment	\$ 822,000	\$ 802,600
Insurance and taxes, 2%	16,400	16,100
Contractor profit, 10%	83,800	81,900
Construction overhead, 15°	138,300	135,100
Total fixed capital investment	\$1,060,500	\$1,035,700

" Equipment costs for the batch process are taken from (9). Comparable costs for the quick-cure process, as well as the burden items for both processes, have been estimated from (1, 21, 22).

^b Includes superphosphate grinding equipment.



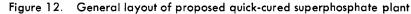


Table VII. Production Cost Estimates for a Batch and the Proposed Quick-Cured Normal Superphosphate Plants

(Basis: 1 ton of normal superphosphate, 20% available P2O5, 20 tons per hour, and 250 days per year; location, Ames, Iowa; acid source, St. Louis, Mo.; and rock source, Mulberry, Fla.)

		Batch		Quick-Cure		
ltem	Unit Cost	Quantity/ton	Cost/ton	Quantity/ton	Cost/ton	
Raw materials						
Acid	\$35.15/T	0.371 T	\$13.04	0.371 T	\$13.04	
Rock	15.0904/T	0.594 T	9.45	0.594 T	9.45	
Water	0.04/T	0.341 T	0.01	0.341 T	0.01	
			\$22.50		\$22.50	
Labor			011.50		444.50	
Unskilled	1.60/hr.	0.150 man-hr.	0.24	0.100 man-hr.	0.16	
Semiskilled	2.10/hr.	0.150 man-hr.	0.32	0.100 man-hr.	0.21	
Skilled	2.50/hr.	0.100 man-hr.	0.25	0.050 man-hr.	0.12	
Supervision	3.00/hr.	0.0167 man-hr.	0.05	0.0167 man-hr.	0.05	
Reserve	20% of above		0.16		0.11	
			\$ 1.02		\$ 0.65	
Services			0		÷ 0.05	
Power	0.02/kwhr.	20.83 kwhr.	0.42	16.67 kwhr.	0.33	
Heat	0.000467/100 B.t.u .		0.00	577,000 B.t.u.	0.27	
Water	0.03/1000 gal.	208 gal.	0.01	833 gal.	0.03	
Maintenance		0		0		
Including labor	20%/vr. of fixed capital		0.44		0.43	
Packaging	0.15/bag		3.60		3. 6 0	
Indirect costs						
Depreciation	10%/yr. of fixed capital		0.88		0.86	
Taxes and insurance	3%/yr. of fixed capital		0.27		0.26	
Overhead	50% of labor		0.51		0.33	
Total production cost			\$29.65		\$29.26	

quick-curing plant is presented in Table VI. Although the total cost for the two processes are about the same, individual items in the cost estimate vary greatly. As the batch normal superphosphate plant requires storage facilities for curing for 30 days, the handling and storage equipment for the plant is the biggest item. For the quick-curing process the grinding equipment, which includes the stainless steel-lined tube mills, is the biggest item. Although \$50,000 is listed for both processes for bagging equipment, the author who compiled the costs for the batch process (9) included superphosphate grinding equipment in this figure.

The manufacturing costs for the two processes are compiled in Table VII. Because the proposed quick-curing process is well adapted to automatic control, considerable saving in labor is affected. Part of the saving, however, is cancelled by the cost of heat in the quick-curing process.

The working capital, net profit, and return on investment are compared in Table VIII for the batch and quickcuring plant. The principal advantage for the quick-curing process is the reduction of working capital. The batch process requires curing of the product for 30 days with a resulting large inventory; the quick-curing process requires no curing.

According to these estimates, the quick-curing process may be economically favorable in comparison with the normal superphosphate process.

Literature Cited

- (1) Aries, R. S., Newton, R. D., "Chemical Engineering Cost Estimation," Mc-Graw-Hill, New York, 1955.
- (2) Assoc. Offic. Agr. Chemists, Wash-

Table VIII. Comparison of Estimated Return on Investment for a Batch and the Proposed Quick-Cured Superphosphate Plants

(Basis: product, normal superphosphate and 20% available P_2O_5 ; capacity, 20 tons per hour, 250 days per year; and location, Ames, Iowa)

		Batch	Quick-Cure		
ltem	Cost, \$/ton	Amount, \$	Cost, \$/ton	Amount, \$	
Annual sales ^a Manufacturing cost Gross profit Administration and selling cost at 3%	32.34	3,880,800 3,558,000 322,800	32.34	3,880,800 3,511,200 369,600	
of annual sales Net profit, before taxes Taxes, 50% Net profit, after taxes		116,400206,400103,200103,200		$116,400 \\ 253,200 \\ 126,600 \\ 126,600$	
Working capital Raw materials inventory Acid, 10 days Rock, 2 weeks In process inventory Product inventory Production for 30 days Credit, 30 days Total working capital	35.15 15.09 29.65 29.65 29.65 32.34	$\begin{array}{r} 62,500\\ 60,300\\ 427,000^{b}\\ 199,200\\ 427,000\\ 465,500\\ \hline 1,641,500\end{array}$	35.15 15.09 29.26 29.26 29.26 32.34	62,500 60,300 1,500 199,000 421,000 465,500 1,209,800	
Fixed capital Total fixed + working capital Return on investment, %		$\frac{1,060,500}{2,702,000}$		$\frac{1,035,700}{2,245,500}$	

^a Based on current dealer's price in Des Moines. Iowa. ^b Based on 30 days' storage.

ington, D. C., "Official Methods of Analysis," 7th ed., pp. 6-28, 1950.

- (3) Bridger, G. L., Tenn. Valley Authority, Chem. Eng. Rept. No. 5, 1949.
- (4) Bridger, G. L., Boylan, D. R., Markey, J. W., Anal. Chem. 25, 336-8 (1953)
- (5) Bridger, G. L., Kapusta, E. J., Ind. Eng. Chem. 44, 1540 (1952).
- (6) Chem. Eng. News 35, No. 4, 60 (1957).
- (7) Drobot, W., Ph.D. thesis, Iowa State College, Ames, Iowa, 1950. (8) Gray, A. N., "Phosphate and Super-

phosphate," 2nd ed., pp. 126-7, E. T. Herron and Co., London, 1944.

- (9) Hardy, W. L., Snell, F. D., Ind. Eng. Chem. 48, No. 11, 41A (1956).
- (10) Hatch, L. P., Regen, W. H., *Chem. Eng.* **63**, No. 3, 120 (1956). (11) Kobe, K. A., "Inorganic Process
- Industries," p. 314, Macmillan, New York, 1948.
- (12) Marshall, H. L., Hendricks, S. B., Hill, W. L., Ind. Eng. Chem. 32, 1631 (1940).
- (13) Marshall, H. L., Rader, L. F., Jacob, K. D., *Ibid.*, **25**, 1253 (1933).

- (14) Meyers, H. H., U. S. Patent 1,475,959 (Dec. 14, 1923).
- (15) Moriga, Hantaro, *et al.* (to Sumitomo Chemical Industries Co.), Japan. Patent **915**('53), (March 5, 1953).
- (16) Niemitz, G., Reedy, R. W., Chem. Eng. 63, No. 12, 132 (1956).
- (17) Nunn, R. J., Dee, T. P., J. Sci. Food Agr. 5, 257 (1954).
- (18) Parrish, P., Ogilvie, A., "Calcium Superphosphate and Compound Fer-

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tilizers," pp. 73-6, 101-4, Hutchinson's Publ., London, 1939.

- (19) Sauchelli, V., "Manual on Fertilizer Manufacture," 2nd ed., p. 86-7, Davison Chemical Corp., Baltimore, Md., 1954.
- (20) Siems, H. B., "Chemistry and Manufacture of Superphosphates and Phosphoric Acid" (K. D. Jacob, ed.), pp. 167-91, Academic Press, New York, 1953.
- (21) Tyler, C., "Chemical Engineering Economics," 3rd ed., McGraw-Hill, New York, 1948.
- (22) Zimmerman, D. T., Lavine, I.,
 "Chemical Engineering Costs," Industrial Research Service, Dover, N. H., 1950.

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Simplified Approach to Calculations for Formulating High-Analysis, Mixed Fertilizers

J. G. MacARTHUR and J. W. JONES

Research Center, Spencer Chemical Co., Merriam, Kan.

With the advent of high-analysis fertilizers, formulation has become increasingly difficult. This is particularly true in granulation processes where water affects the analysis or when several raw materials are required to supply one plant food. As there have been few data published on fertilizer formulation, a knowledge of the accurate and simplified method of formulating high-analysis fertilizers presented herein will be useful to manufacturers.

 $\mathbf{F}_{\text{culated on a ton basis.}}$ Once the raw materials to be used for a given grade are defined, the units of each plant food per ton (or per cent plant food) are simply divided by the decimal fraction of the plant food in the raw material to obtain the pounds of raw material necessary to supply that plant food. When the plant foods have been supplied. and the total weight of finished product does not equal 2000 pounds, an inexpensive and usually inert filler is added. Should the weight of the desired materials supplying the plant food exceed 1 tonwhich usually occurs in mixtures of the superphosphates-a second formula using the raw materials that can satisfy the formula requirements must be calculated.

In most instances, the maximum amount of normal superphosphate in the formula is desired; however, when this grade requires a mixture of normal and triple superphosphates, the quantity of each is calculated using two equations and two unknowns—a comparatively simple manipulation.

The addition or removal of water from that formula during manufacture will change its analysis. Steam arising from a batch mixer during ammoniation indicates water is being removed but, normally, not enough is removed to affect the analysis. Water added to ammoniator, to enhance granulation, is usually a quantity sufficient to lower the analysis of the mixture in the granulator. Through trial and error methods, a large number of plants have arrived at a

formula that "works" for their planti.e., the product is made with the desired raw materials and the analysis is on grade. Although valid, this method can be time-consuming and costly. The use of electronic computers is beyond the economic limits of most fertilizer manufacturers (1). When it is predicted or known that an appreciable amount of water will be removed by the process and more than two raw materials will react with the free ammonia, the common methods of formulating become increasingly difficult. Too often the result of this situation is a large tonnage of off-analysis fertilizer or a dependency on others for formulas. The authors feel that the method presented in this paper is the simplest approach to highanalysis formulation with the tools available to the average fertilizer manufacturer.

Method of Calculation

Assuming that the moisture content of a product can either be defined or estimated, a grade may be calculated to a bone-dry basis. As in the majority of cases involving potash grades, the potash is supplied by only one sourcenamely, muriate of potash-the fertilizer grade can be considered as a zero potash grade for the purpose of calculation. The basis for this method is the consideration of each neutralizing reaction independently. By breaking down the method of calculating formulas into two basic steps—allowing room for moisture and potash and considering each neutralization as an independent reaction-a series of comparatively simple manipulations can produce the desired formula.

Raw Materials Analysis. The raw materials used to demonstrate this

Table I. Raw Material Analysis

	Material	Analysis, %	<i>H</i> ₂O, %	Bone-Dry Analysis, %
.1	Ammoniating solution	37.0 N	16.6	44.4 N
	5	16.6 NH_{3}		19.9 NH ₃
		66.8 NH₄NO ₃		$80.1 \text{ NH}_{4} \text{NO}_{3}$
B	Anhydrous ammonia	82.0 N		82.0 N
C	Ammonium sulfate	20.0 N		20.0 N
D	Diammonium phosphate	21.0 N		21.0 N
	1 1	53.0 P_2O_5		53.0 P_2O_5
E	75% Phosphoric acid	54.3 P_2O_5	25.0	$72.4 P_2O_5$
F	Normal superphosphate	$20.0 P_2 O_5$	7.0	21.6 P_2O_5
G	Triple superphosphate	$46.0 P_2 O_5$	5.0	$48.4 P_2O_5$
Η	Calcium metaphosphate	61.0 P_2O_5		$61.0 P_2O_5$
Ι	Potassium chloride	$60.0 K_2 O$		$60.0 \text{ K}_2\text{O}$
a	Alphabetical letters identify	material.		