

both phosphoric acid and triple superphosphate. The area covering the lower central portion has enough gypsum for all of the phosphoric acid and part of the triple superphosphate. The upper area contains enough gypsum for only part of the phosphoric acid and none for the triple superphosphate to have its maximum ammoniation rate. Thus, it is assumed in making the calculations that because phosphoric acid is in liquid form, it will preferentially react with gypsum. However, the chemistry would be the same in either case.

Plant Tests

The data summarized in Tables III, IV, V, and VI were obtained in five different plants, all of which employed continuous drum-type ammoniators with nominal capacity in excess of 15 tons per hour of product. All but formulation No. 9 were run in plants employing controlled recycle systems. Emphasis has been placed on the more unusual types of

formulation in the selection of examples, because these generally present more of a problem to the formulator.

The data indicate the precision with which predictions can be made when formulating on the systematic basis outlined in the preceding sections.

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Literature Cited

- (1) Bassett, H., *Z. anorg. Chem.* **53**, 49-62 (1907).
- (2) Hardesty, J. O., *Agr. Chem.* **10**, No. 8, 50 (1955).
- (3) Hardesty, J. O., *Chem. Eng. Progr.* **51**, 291-5 (1955).
- (4) Hardesty, J. O., Ross, W. H., *Ind. Eng. Chem.* **29**, 1283-90 (1937).
- (5) Hardesty, J. O., Szabo, A., Cummings, J. G., *J. AGR. FOOD CHEM.* **4**, 60-3 (1956).

- (6) Hein, L. B., Hicks, G. C., Silverberg, J., Seatz, L. F., *Ibid.*, **4**, 318-30 (1956).
- (7) Hignett, T. P., *Agr. Chem.* **11**, No. 3, 34 (1956).
- (8) Keenen, F. G., *Ind. Eng. Chem.* **22**, 1378-82 (1930).
- (9) Kumagai, R., Rapp, H. F., Hardesty, J. O., *J. AGR. FOOD CHEM.* **2**, 25-30 (1954).
- (10) Payne, J. H., Daniels, S. D., *Ibid.*, **4**, 920-8 (1956).
- (11) Rapp, H. F., Hardesty, J. O., *Ibid.*, 426-33 (1957).
- (12) Rossini, F. D., *et al.*, *Natl. Bur. Standards (U. S.), Circ.* **500**.
- (13) Smith, R. C., *Agr. Chem.* **11**, No. 2, 34 (1956).
- (14) White, L. M., Hardesty, J. O., Ross, W. H., *Ind. Eng. Chem.* **27**, 562-7 (1935).
- (15) Yates, L. D., Nielsson, F. T., Hicks, G. C., *Farm. Chem.* **117**, No. 7, 38 (1954).

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FERTILIZER CALCULATIONS

Granular Fertilizer Formulation with the IBM 702 Computer

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A granular fertilizer formulation system is used to evaluate economics and operating characteristics of a series of 1-1-1 ratio granular fertilizers. A method of calculating heat requirements for granulation is illustrated. As an example, the effects of varying amounts of diammonium phosphate and phosphoric acid on 12-12-12, 13-13-13, and 14-14-14 grade granular fertilizer formulations are used. The relationship of the effect of variation in these raw materials upon raw material cost and recycle to yield a workable formulation is shown. By using the manufacturer's raw material costs and specifications, it is possible to evaluate the use of specific raw materials in manufacturing operations.

THE MANUFACTURER of granular mixed fertilizers can benefit from the combination of a practical granular fertilizer formulation system and the speed of an electronic computer. The formulation system described by Payne and Webber (2) is flexible enough to be adapted to any mixed fertilizer granulation process. By adapting a formulation system such as this to an electronic computer program one can rapidly evaluate the effects of variations in operating conditions, equipment, and raw materials on economic and operational aspects of manufacture.

To produce a granular fertilizer formu-

lation with the formulation system mentioned above, it is necessary to solve discontinuous and nonlinear functions. For this reason, a nonlinear computer program is used which is an iterative process comparable to the trial-and-error approach to the solution of a problem. Where it might take hours for a human to solve a problem, it is a matter of seconds with an electronic computer (7).

It is possible to study how certain factors affect granular fertilizer formulations. For example, one can obtain a series of formulations at several recycle levels, using various raw materials and raw material costs. It is possible to

limit the level of use of certain raw materials. The heat balance equation can be adjusted to compensate for heat losses in certain equipment or to compensate for extreme ambient temperature conditions.

The purpose of this paper is to show how the fertilizer manufacturer can use such a formulation system to study thoroughly the effects of many variables through the speed of an electronic computer. In evaluating and using a series of fertilizer formulations one can most profitably study the economic relationships and the heat requirements of these formulations. A study of the depend-

ence of raw material cost upon other factors can be made when it is possible to obtain a large number of formulations. By evaluating the heat requirements of his granulation unit under varying ambient operating conditions, the manufacturer can select a fertilizer formulation which will ensure a good granular product.

The heat requirements for granulation are dependent upon raw material temperatures, ambient temperature, production rate, amount and temperature of recycle, and heat loss from the granulation equipment. The formulation system being used here (2) is based upon the assumption that a fairly constant temperature is maintained in the granulating mass. Control of other factors which affect formulation (moisture and soluble salt content) have been discussed previously (7). The control of heat necessary to maintain the proper granulating temperature will be discussed here.

The heat requirement for proper granulation is given by the equation

$$H = H_0(1 + aR) + k' \quad (1)$$

where

H = heat required for granulation, in calories per 100 grams of product

H_0 = heat required to raise 100 grams of fertilizer material to granulating temperature exclusive of heat losses from granulating equipment

R = recycle, in pounds of recycled material per pound of product

k' = constant for a particular manufacturing unit under certain operating conditions

and $a = \frac{T_g - T_r}{T_g - T_f}$

where T_g = temperature in granulator

T_r = temperature of recycled material

T_f = temperature of raw materials

The previous publication by Payne and Webber (2) expresses this heat requirement by the equation

$$H = (H_0 + k')(1 + aR)$$

where k' under nominal operating conditions is estimated to be 800 calories to account for heat loss through vaporization of water and radiation. If the value for H as produced by the chemical reactions in the manufacturing process is within ± 1000 calories of the value required by the recycle level, it is assumed that this will give the proper amount of heat. Although not rigorously correct, this expression was chosen because it is more convenient and gives a good approximation to the desired value. It has been shown that Equation 1 provides much better flexibility for this formulation method in adapting the system to specific manufacturing sites and operating conditions. Further, it has been found that by

using Equation 1 for calculating heat requirements, the value of H can be determined to a better precision than the 1000 calories previously used.

In adapting the heat equation to his particular plant operation, the manufacturer must consider two things: the temperatures of the raw materials and the ambient temperature at which he is operating, and the value of k' for his equipment. In adapting the heat equation to existing operating temperatures, the values of H_0 and the constant a must be recalculated. This will be illustrated in an example. The value of k' can be estimated by an analysis of formulations which are known to work in the equipment being used. By analyzing these workable formulations for heat requirements at various recycle levels, a value of k' can be calculated and its average value used in selecting subsequent formulations.

To illustrate the use of heat calculations a specific case will be considered in which this method was used to select formulations for a particular manufacturing unit. The case in question involved the start-up of a new granulation unit. As no fertilizer had ever been made with the equipment, there was no way to estimate heat requirements from previously used formulations. A series of formulations was taken from computer calculations in which the heat produced varied over a wide range. The start-up was conducted under extreme weather conditions with subzero temperatures persisting for some time. It was decided to produce a 12-12-12 fertilizer at a rate of about 5 tons per hour in the plant which was rated at a maximum of 20 tons per hour. The plant used a rotary drum ammoniator-granulator and had facilities for controlling recycle.

To be safe, in case excessive fines were produced, the material was recycled at a rate of 1 pound of recycle per pound of product. This would also allow for more flexible control by use of recycle.

In calculating the heat requirement for operation under these conditions the following assumptions were made:

$$\begin{aligned} T_g &= 0^\circ \text{ F.} \\ T_g &= 210^\circ \text{ F.} \\ T_r &= 40^\circ \text{ F.} \end{aligned}$$

The value of T_r was low, but was assumed to be justified because of the low production rate used.

Then, to calculate the value of H_0 as outlined by Payne and Webber (2):

$$\begin{aligned} H_0 &= (210/1.8 \times 0.35 \times 100) + 800 \\ H_0 &= 4900 \end{aligned}$$

This value is determined by multiplying the temperature change of raw materials to the temperature of the granulator in degrees centigrade times the specific heat times the weight of material in grams. This yields the calories required to raise the temperature of 100 grams of raw material to the granulating temperature.

Table I. Heat Requirements for Granulation Unit

$$H = H_0(1 + aR) + k'$$

	Case 1	Case 2
T_g , ° F.	210	210
T_g , ° F.	10	60
T_r , ° F.	80	100
k'	1600	1600
H_0	3900	2900
a	0.65	0.73
R^a	0.5	1.0
H	6800	6600

^a Values of recycle, R , taken from operating data.

To calculate the value a ,

$$a = \frac{210 - 40}{210 - 80}$$

$$a = 0.81$$

Hence,

$$\begin{aligned} H &= 4900(1 + 0.81R) \\ H &= 8800 \end{aligned}$$

When this 8800-calorie formulation was run at the start-up, it was found that too much chemical heat was being produced, giving excessive temperatures in the ammoniator. The next coolest formulation (the one with less chemical heat produced) was then selected. This formulation produced chemical heat at the rate of 6600 calories per 100 grams of product. The recycle necessary to produce a good granular product was about 0.5. Thus, by use of this formulation system and intelligent estimation of operating conditions, a good granular product was produced on the second formulation tried.

When this information is applied to Equation 1, the more rigorous means of expressing heat requirements, this particular manufacturing unit is seen to require a value of k' of about 1600. Table I summarizes two cases of different operating conditions for the above-mentioned 6600-calorie formulation. These are actual operating data. The estimate of T_r of 40° F. for the above example proved to be too low, the actual value being about 80° F.

Both Case 1 and Case 2 used the same formulation, thus requiring a higher recycle under warmer operating conditions (Case 2). It is here indicated, then, that a higher production rate could be obtained by using a formulation with a lower H value for warm weather operation. However, the raw material cost at this lower value of H could possibly be higher, thus offsetting the advantage of higher production capacity. This again depends upon the particular plant site.

Economic Studies

Probably the most valuable application of a formulation-computer program of

Table II. Raw Materials

	Analysis, N-P ₂ O ₅ -K ₂ O	Cost, Delivered, Dollars
Nitrogen solution ^a	41.0-0-0	1.35/unit
(NH ₄) ₂ SO ₄	21-0-0	1.69/unit
Normal super-phosphate ^b	0-20-0	0.95/unit
Triple super-phosphate ^c	0-46-0	1.40/unit
KCl	0-0-60	0.57/unit
H ₂ SO ₄ , 66° Bé.	...	21.20/ton
H ₃ PO ₄ , 75%	0-54.2-0	1.45/unit
Diammonium phosphate	21-53-0	115.00/ton

^a 72.5% NH₄NO₃, 19.0% NH₃, 8.5% H₂O.
^b 8.0% H₂O.
^c 5.0% H₂O.

this type is the study of the factors which influence raw material costs. A hypothetical study will be shown to illustrate how this method can be used and the conclusions which can be drawn from such a study.

An electronic computer is capable of producing a large number of fertilizer formulations in a very short time. The effects of such factors as recycle rate, raw materials, and individual raw material costs upon total raw material costs can be thoroughly studied.

As an example, a series of 1-1-1 ratio fertilizers in the range of analysis from 12-12-12 to 15-15-15 was studied. In this hypothetical case a manufacturer is considering the use of phosphoric acid and/or diammonium phosphate as raw materials in his plant. A series of formulations is requested in which various recycle rates and various levels of use of diammonium phosphate and phosphoric acid are stipulated. By making comparisons of the raw material costs with these variables the manufacturer can decide whether to use these raw materials and how to use them.

In Table II are listed the raw materials, their analyses, and the delivered costs which were used in this study. No attempt was made to select raw material prices which would apply to a specific geographic location—those selected were simply chosen to provide some basis for running a series of formulations which could be used to illustrate a method.

The two factors to be considered in choosing a formulation or raw material are the total raw material cost per ton of product and the production rate which can be attained with the formulation being used. For this reason the interrelationships of raw material cost, recycle level, and amount of raw material being used in the formulation must be evaluated. Figures 1 through 4 are graphical representations of this interdependence of the three factors.

Figure 1 shows a plot of raw material

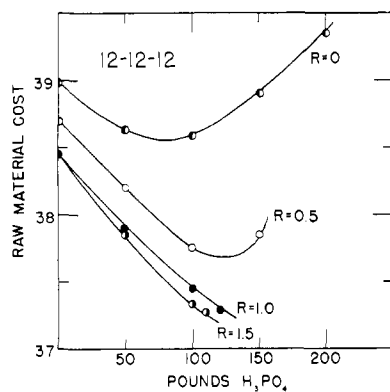


Figure 1. Effect of phosphoric acid on raw material cost at various recycle levels for 12-12-12

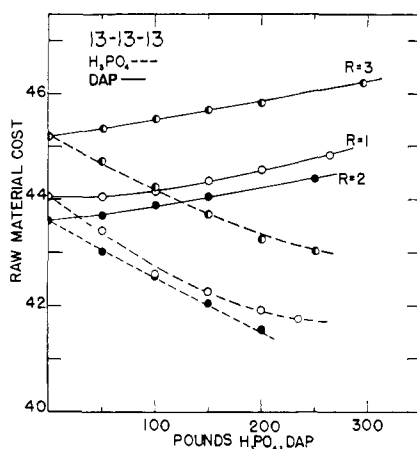


Figure 2. Effects of phosphoric acid and diammonium phosphate on raw material cost at various recycle levels for 13-13-13

cost in dollars per ton of product vs. pounds of 75% phosphoric acid per ton of formulation at different recycle levels. In all cases in this paper, recycle is defined in units of pounds of recycle per pound of product. For making a 12-12-12 at the particular manufacturing site being evaluated, the raw material costs generally decrease as more phosphoric acid is incorporated in the formulation. Further, as higher recycle levels are allowed, raw material costs drop. In the cases of low recycle, the raw material costs rapidly reach a minimum value and then increase as more phosphoric acid is added. The reason for the drop in raw material cost with increasing phosphoric acid is that the more concentrated phosphoric acid allows room in the formulation for the cheaper, less concentrated raw materials. Further, phosphoric acid with its higher ammonia-holding capacity allows the use of more low-cost ammonia. The manufacturer must decide for himself whether the decrease in raw material cost with increasing recycle and the accompanying decrease in production rate is acceptable to him.

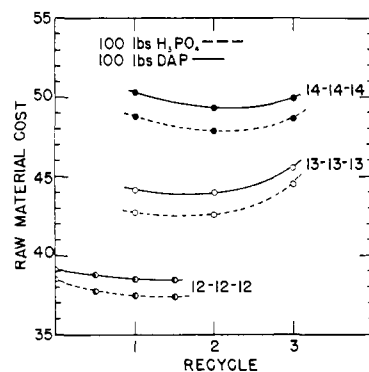


Figure 3. Effect of recycle on raw material cost at 100 pounds of phosphoric acid or diammonium phosphate for various 1-1-1 grades

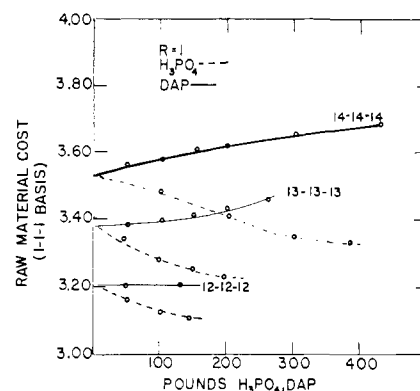


Figure 4. Relative raw material cost as a function of use of phosphoric acid and diammonium phosphate for various 1-1-1 grades at constant recycle level

In Figure 2 the effects of increasing levels of phosphoric acid and diammonium phosphate at different recycle levels are shown. This graph indicates that it is unprofitable to use diammonium phosphate and that the minimum raw material cost is attained under conditions of a recycle value around 2 and at about 200 pounds of phosphoric acid per ton of formulation.

Raw material cost vs. recycle level has been plotted for three different 1-1-1 grades at a constant level of 100 pounds of phosphoric acid and diammonium phosphate in Figure 3. Here it is shown that for all three grades it is cheaper to use phosphoric acid rather than diammonium phosphate, the minimum cost being in the neighborhood of 1 to 2 pounds of recycle per pound of product.

Figure 4 illustrates an interesting comparison of the different grades being studied. Plotted on the ordinate of the graph is the raw material cost of fertilizer formulations reduced to a 1-1-1 basis to equate the costs of raw materials for 12-12-12, 13-13-13, and 14-14-14 grades. These values were obtained by dividing formulation raw material costs

by 12, 13, and 14, depending upon the fertilizer analysis. In the case where no phosphoric acid or diammonium phosphate is used, the unit cost increases as over-all analysis increases. However, in some cases, by changing raw materials, the unit cost of making a higher analysis material becomes less. For instance, at a recycle value of 1, a 14-14-14 grade fertilizer can be produced at a lower unit cost than 13-13-13 where no phosphoric acid is used by including 400 pounds of phosphoric acid in the formulation. In addition, this will produce an increase in production rate and plant nutrient of about 8%. This graph illustrates that another factor to be considered is the cost of changing to higher analysis products in terms of changes in raw materials

and the increased production rate in terms of plant nutrient that can be realized.

The various ways in which a series of formulations can be evaluated from the standpoint of economics of raw material costs gives the manufacturer a sound basis from which to decide on changes in his operations. He will be able to decide upon a formulation and make changes after estimating the effect of changes in production rate with changes in recycle. He can evaluate the advantages of adding new raw materials in terms of increased profits as opposed to the cost of installing new equipment.

It should be emphasized that the foregoing example is a study of a particular location and cannot be used to generalize

the economic effects of diammonium phosphate and phosphoric acid.

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Literature Cited

- (1) Payne, J. H., Daniels, S. D., *J. Agr. Food Chem.* **4**, 925 (1956)
- (2) Payne, J. H., Webber, R. T., *Ibid.*, **8**, 164 (1960).

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FERTILIZER SOLUTIONS ANALYSIS

Determination of Total Nitrogen and Nitrogen Distribution in Fertilizer Solutions

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A fairly rapid yet accurate procedure was developed for the analysis and sampling of nitrogen fertilizer solutions. The Kjeldahl distillation for ammonia content and the use of Devarda alloy treatment, with Kjeldahl distillation, for nitrate content were found satisfactory. For urea content, modifications of the urease hydrolysis technique were made. A convenient and reproducible sampling procedure was tested.

DURING THE FORMULATION of high nitrogen content fertilizer solutions, containing more than one compound as a source of nitrogen, it is necessary to know the concentration of each nitrogen compound in the solution. This information is desirable for estimation of vapor pressure and salting-out properties and for assurance that the total nitrogen content is acceptable.

High nitrogen fertilizer solutions may contain urea, ammonium nitrate, and ammonia in any combination, covering a fairly wide range of total nitrogen content. For characterization of a solution containing all three compounds, three analyses on some combination of either three components or two components and a total is required in general. To devise the most accurate and rapid sampling and analytical technique, a number of methods (1, 2, 5, 10) were considered, evaluated, and investigated.

The determination of total nitrogen by the familiar Kjeldahl technique, as given in the standard methods of the Association of Official Agricultural Chemists including the most recent revisions (1, 6, 7), could not be used, because of the time required and the poor accuracy and precision obtained when prepared mixtures were analyzed. Although excellent results could be obtained, by various modifications of the recommended Kjeldahl procedures for the analyses of the pure components of the mixture alone, the determination of the total nitrogen was discarded as too time-consuming. For consistent results, however, work completed during the course of this study indicated that urea samples might require a fairly dilute digestion and nitrate samples would require almost anhydrous conditions for best recovery (Table I).

For rapid estimation of urea alone, the urease enzymatic hydrolysis method

of Fox and Geldard (3) as modified by Smith, Dock, and Rich (9) appeared very promising if analysis time could be reduced and/or if accuracy could be improved. The latest method (7) using the enzymatic hydrolysis of urea to ammonium carbonate is a variation of the method by Smith, Dock, and Rich but the back-titration employed represents no basic improvement. However, with considerable reliance upon the literature cited, a method satisfactory with regard to both speed and precision was developed.

For the determination of ammonia and the ammonia from the urea, if present, a distillation of the ammonia from the caustic solution into a boric acid solution was adopted. For samples containing only ammonia and urea, a single acid titration of the solution followed by a urease hydrolysis and analysis of the neutralized solution appeared to be excellent.