FERTILIZER CALCULATIONS

The Calculation of Formulations
for Granular Fertilizers

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The formulation of granular fertilizers is discussed with particular emphasis on the methods of calculating moisture, heat, and ammoniation requirements. The method is based on first defining the requirements for granulation and then selecting the raw materials to meet these requirements. The chemistry of ammoniation has been expanded to include a basis for calculating the ammonia retention of various mixtures of normal superphosphate, triple superphosphate, phosphoric acid, and diammonium phosphate. A comparison is shown between calculated results and actual plant tests.

THE PROBLEM of calculating formulations to be used in the manufacture of granular fertilizers is complex. The formulator is restricted to combinations of raw materials which give a product containing the required concentration of nutrients. Within this limitation, he must find combinations of raw materials which will granulate well in the plant. The granules produced must be in the proper size range, and simultaneously the required production level must be maintained. In addition, loss of nitrogen and reversion of available phosphate must be minimized. After considering all of the possible combinations, the formulator then must pick the combination which gives the lowest possible raw material costs.

The behavior toward granulation is the most difficult requirement to predict. The three main factors which control the formation of granules are moisture, heat, and soluble salt content. The problem is thus one of assigning numbers to these quantities which can be related to the optimum conditions for granulation. This paper aims to point out these relationships, to show how the conditions required for optimum granulation can be estimated, and to provide data for estimating the ammonia retention of complex phosphate mixtures in which phosphoric acid and diammonium phosphate are used along with superphosphates.

If the behavior of different formulations could be predicted with complete accuracy, there would be no need for running plant tests. Obviously, present knowledge of granulation is too incomplete to make these highly accurate predictions at the present time. However, even moderately accurate predictions can

help the manufacturer reduce the loss of plant time and materials in attempting to make impossible formulations work, provide a sound basis for changes in the formulation to achieve the desired performance, assist in the selection of raw materials, and make cost comparisons possible between different formulations on a basis of approximately equivalent plant performance.

Requirements of a Formulation

There are many factors which influence the agglomeration of fertilizers, such as the size and porosity of the raw material particles, the equipment used, and the operating conditions. These factors are not considered in the present discussion because they cannot be controlled by specifying the pounds of raw materials to be used.

There are seven major requirements (Table I) which are controlled by the formulation of a complete (NPK) fertilizer. Consequently, seven raw materials will be required. Water and filler are considered as raw materials when used in a formulation. A raw material may be eliminated each time a requirement is removed, as in the omission of potassium chloride from a grade or not requiring a specified ammoniation level for the phosphates. At other times, the amount of a given raw material may be so small that for practical purposes it can be eliminated. However, the latter circumstance must be regarded as a special case and not the general rule. Table I gives the most common methods (not a complete list) of the ways of adjusting formulations to meet these requirements. The seven requirements are expressed mathematically

Table I. Common Raw Materials Generally Used to Meet Requirements of Granulation

Requirement	Raw Materials Adjusted
Units of N	Nitrogen solution, basic source[a]
Units of P_2O_5	Normal superphosphate, basic source[a]
Units of K_2O	Potassium chloride, basic source[a]
Total weight, dried	Add filler, low analysis. Replace normal with triple superphosphate, high analysis.
Ammoniation balance	Replace solution with anhydrous ammonia, to use extra ammonia retention. Add sulfuric acid, increase ammonia retention.
Water balance	Add water to increase moisture. Increase recycle or replace solution with ammonium sulfate to decrease moisture.
Heat balance	Add sulfuric acid, increase heat. Increase recycle or replace sulfuric acid and anhydrous ammonia or solution with ammonium sulfate, reduce heat.

[a] By "basic source" is meant that as much as possible of these raw materials are generally used and that other raw materials replace the basic source for some specific reason.

as functions of the variables involved in Table II.

Nutrient and Material Balances. The first four requirements are concerned only with achieving the proper analysis of the finished product. These requirements present no real problem in calculations. The ammoniation, water, and heat balances require further consideration, because they are less easily calculated and are directly related to the actual granulation process.

Ammoniation Balance. The term "degree of ammoniation" will be used here to express per cent of maximum ammonia retention by phosphates and acid which are utilized to the absorbed, uncombined ammonia added as anhydrous ammonia and as "free" ammonia in a nitrogen solution. The maximum (practical) ammonia retention for normal and triple superphosphates (3, 9) is generally assumed to be 6 and 4 pounds per unit of phosphorus pentoxide, respectively, although there is by no means complete agreement among the various investigators. There are few or no experimental data on the ammonia retention of phosphoric acid in phosphate mixtures (6). Interactions occur with the gypsum present in normal superphosphate, as discussed in a later section on the chemistry of ammoniation. As a result of interactions, the ammonia retention of mixtures of phosphoric acid with superphosphate cannot be accurately calculated by adding up the ammonia retention of the different phosphates. Figure 1 translates this chemistry into a usable form for calculating the ammonia retention of mixed phosphates. Formulations based on this chart have been run successfully in a number of different plant tests; however, additional testing is being carried out under more thoroughly controlled conditions.

The total ammonia retention of the formulation may be calculated as follows. The units of phosphorus pentoxide added as normal superphosphate divided by the total units of phosphorus pentoxide in the formulation give the per cent of phosphorus pentoxide added as normal superphosphate and which may be readily determined. Similarly, the per cent of the phosphorus pentoxide added as triple superphosphate and as phosphoric acid may be determined. By locating a point on the three-component diagram (Figure 1), the average ammonia retention of the mixture in pounds of ammonia per unit of phosphorus pentoxide in the mixture can be read from the contour lines of constant ammonia retention. Thus, by multiplying the average ammonia retention per unit of phosphorus pentoxide by the total units of phosphorus pentoxide in the formulation, the total ammonia retention of the phosphate mixture is obtained (Equation R-5). The ammonia retention of sulfuric acid is based on the conversion of the sulfuric

Table II. Equations Expressing Requirements

Units of N $= (a_1A + b_1B + c_1C + d_1D)/2000$ R-1

Units of P_2O_5 $= (d_2D + e_2E + f_2F + g_2G)/2000$ R-2

Units of K_2O $= h_3H/2000$ R-3

Total weight (dried) $= 2000$ lb. $= A + B + C + D + E + F + G + H + I + J + 20(M_p - M_f)$ R-4a

M_p = moisture in product as $\%$ H_2O

M_f = moisture in feed as $\%$ H_2O $= (b_6B + e_6E + f_6F + g_6G + i_6I + j_6J)/(A + B + C + D + E + F + G + H + I + J)$ R-4b

Per cent of maximum practical ammoniation utilized $= (a_4A + b_4B + d_4D)/[f(d_2D, e_2E, f_2F, g_2G) + i_8I]$ R-5

$f(d_2D, e_2E, f_2F, g_2G) = $ (av. lb. NH_3 per unit of P_2O_5) $\times (d_2D + e_2E + f_2F + g_2G)/20$ (total units of P_2O_5)

(from Figure 1)

Recycle required $= R = $ lb. of recycle per lb. of feed $= (M_f - M_g)/(M_g - M_r)$ R-6

M_f = moisture in feed, see Equation R-4b

M_r = moisture in recycle as $\%$ H_2O

M_g = moisture required for granulation $= f(b_5B)$ see Figure 2

Heat required $= H_0(1 + xR) = e_7E + f_7F + g_7G + i_7I$ R-7

$H_0 \approx 3500$ cal./100 g. $\left.\right\}$ see "Heat Balance"

$x \approx 0.6$

Symbols

Material	Lb./ Ton	Per cent						Heat
		N	P_2O_5	K_2O	Free NH_3	NH_4NO_3	H_2O	
Ammonia, anhydrous	A	a_1			a_4			
Nitrogen solutions	B	b_1			b_4	b_5	b_6	
Ammonium sulfate	C	c_1						
Diammonium phosphate	D	d_1	d_2		d_4			
Phosphoric acid	E		e_2				e_6	e_7
Normal superphosphate	F		b_2				f_6	f_7
Triple superphosphate	G		g_2				g_6	g_7
Potassium carbonate	H			h_3				
Sulfuric acid	I						i_6	i_7
Water	J						j_6	

i_8 = lb. of ammonia absorbed per pound of sulfuric acid.
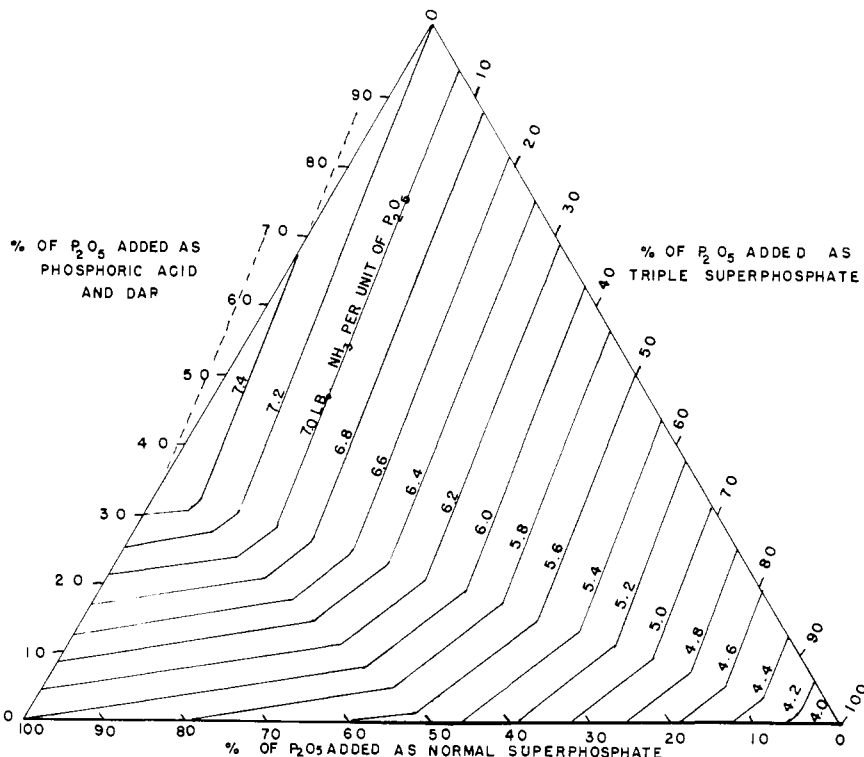
Figure 1. Maximum practical ammonia-holding capacity of mixed phosphates

acid to ammonium sulfate. The weight of 66° Bé. acid divided by 3.1, or the weight of 60° Bé. acid divided by 3.72, gives the pounds of ammonia which can be held. The sum of the ammonia retention of the total phosphates added to that of the sulfuric acid gives total ammonia retention. The per cent of maximum ammoniation is the per cent of total ammonia retention neutralized by the total uncombined ammonia.
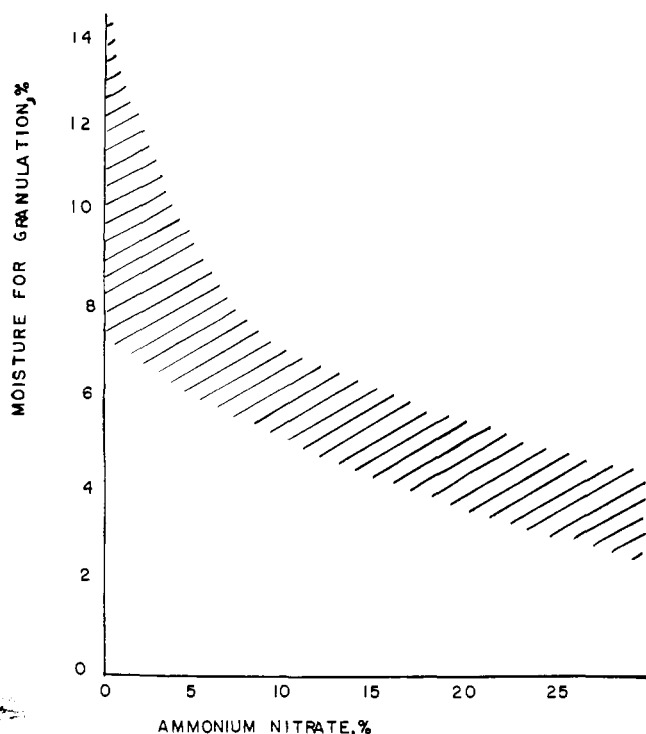
Water Balance. The moisture re-

Figure 2. Moisture requirements for granulation

quirements for optimum granulation will depend upon the temperature of granulation and the amounts of the various soluble salts which are present (2, 5, 7, 11, 13), and to some extent, upon the equipment which is used in the plant. The solubility of ammonium nitrate is considerably greater than that of other salts used in fertilizers with the exception of urea. Consequently, as a first approximation, it may be assumed that the ammonium nitrate concentration will be the governing factor with respect to the amount of water required for granulation. Furthermore, if it is assumed that the granulation will be taking place around 200° F., it is possible to establish a general relationship between the moisture requirements for granulation and the amount of ammonium nitrate present in the formulation. At higher temperatures, the greater solubility of the salts decreases the amount of water required. However, this effect is partially compensated for by the increased evaporation of water in the ammoniator.

The moisture content in the granulator will depend upon the relative amounts and moisture contents of both the feed materials and the recycle added to the ammoniator-granulator system. Because recycle is used as a means of reworking of fines (including those produced from milling oversized particles), the amount of recycle will depend upon how closely the product is sized. As a result, the formulator must have some knowledge of what level of recycle to expect for the particular product being prepared and the capabilities of the plant to

handle different amounts of recycle. Because the formulation used will automatically balance out at a characteristic recycle ratio in the plant, it is up to the formulator to adjust the formulation to give approximately the desired recycle ratio.

The calculation of water balance may be considered, by assuming that a new formulation has been obtained and that it is to be checked for water balance. From the amount of nitrogen solution used and the per cent of ammonium nitrate present, the per cent of nitrate in the final product may be calculated as ammonium nitrate, although part of the nitrate will be present as other salts. By using the calculated per cent of ammonium nitrate, the approximate moisture requirements for granulation may be obtained from Figure 2. This moisture content is that expected in the ammoniator after the feed and recycle have been blended together. To estimate how much recycle will be required, it is necessary to know how much water will be introduced with the raw materials and how dry the recycle will be. By use of Equation R-6, the recycle may be calculated.

If, for example, it is assumed that a recycle of 0.5 pound per pound of product is generally required (from experience) to give the desired plant operation and maximum plant production and a recycle of 3.5 is calculated, it is fairly certain that the formulation will be too wet, unless higher recycles than 0.5 are used. If the recycle calculated is negative, the formulation will probably require water which can easily be

added as required. However, in this case, it may be cheaper to reformulate and use more nitrogen solution. In general, one would like to have at least three similar formulations, before making an actual plant test, which differed in the amounts of raw materials to give recycle ratios of 0, 0.5, and 1.0. The chances would then be very good that one of these would give close to the desired performance in the plant and little time would be wasted in the final selection of the formulation.

Moisture, of course, is only one aspect of the formulation problem and, for the moment, it has been assumed that other requirements, such as heat, have been fulfilled.

The data presented in Figure 2, at best, can predict moisture requirements for granulation to within 1%. Larger deviations will be encountered frequently, because of the failure to consider the effects of the other soluble salts, temperature variations, type of equipment used, and solution time for the various salts. However, the results are in rough agreement with the studies of Hardesty and coworkers (5) who have studied the effects of various salt concentrations on moisture requirements for granulation. In spite of these limitations, the use of moisture relationships is extremely useful in discarding formulations which are completely out of line with respect to the proper moisture balance. The greatest deviations from the curve (Figure 2) occur at low ammonium nitrate concentrations. Under these conditions, the effects of other soluble salts are of greater importance, because they are not obscured by the more soluble ammonium nitrate. Fortunately, formulations employing low concentrations of nitrogen generally require additional water. Under these conditions, the amount of water can be determined in the plant test and need not be predicted with accuracy in computing the formulation.

Little or no information is available on the effects of urea on moisture requirements for granulation. Because the solubility of urea is similar to ammonium nitrate, it may be expected that the effect on granulation will be similar. On this basis, formulations employing urea can be calculated by assuming that its effect on granulation will be approximately equivalent to that of the same weight of ammonium nitrate. Because urea and ammonium nitrate form a eutectic of very high solubility, moisture requirements for granulation of mixed urea–ammonium nitrate formulations would be expected to be much less than the value predicted on the preceding basis (3). No plant studies have been made yet which would allow moisture requirement correlation. However, limited pilot plant and plant experience with mixed urea–ammonium nitrate solutions indicates that more

water is required when urea replaces part of the nitrate, all other conditions being equal.

Heat Balance. The major aim in calculating a heat balance for the formulation is to ensure that the materials are brought to a suitable temperature range for good granulation. The heat produced must raise the temperature to the granulation temperature. In addition, a certain amount of heat will be lost, the amount depending upon the size and type of equipment employed. The evaporation of water in the ammoniator acts as a temperature modifier because, if excessive heat is produced, the amount of cooling achieved by evaporation of water will be greater.

A method has been developed by which a comparison can be made between the amount of heat which is required and the amount of chemical heat produced by reactions in the ammoniator. The units in which the heat balance is expressed are unimportant as long as a consistent system is employed. The calculations are based on small calories per hundred grams of fertilizer. By multiplying these numbers by 1.8, the British thermal units per 100 pounds of fertilizer are obtained, or by multiplying by 36, the British thermal units per ton may be calculated. The specific heat of the fertilizer mixes can be calculated by totaling the individual specific heat of each raw material. However, a check on formulations for a 5–20–20, 10–20–10, and 12–12–12 grade indicated that the variation in specific heat from grade to grade in most cases does not justify the time spent in making these calculations. For practical purposes, it may be assumed that the fertilizer materials have a specific heat of approximately 0.35. A typical value for the heat required to bring the raw materials being fed to the plant at 60° F. up to the granulating temperature would be 3500 calories. Of these, approximately 2700 calories are consumed in heating the feed from 60° to 200° F. and the remaining 800 calories are lost in water evaporation and by heat transfer through the equipment. With raw materials at 0° F., an additional 1200 calories might be required, whereas at 100° F., the heat requirements might be 800 calories less. Heat will be absorbed also in heating the recycle from the temperature at which it is fed into the system up to the temperature of granulation. The amount of heat absorbed will depend upon the amount and the temperature of the recycle. If the recycle is entering the system at 110° F., the temperature of the recycle must be increased by only 85° F. to bring it to a temperature of 200° F. for granulation, as compared with the temperature of the raw materials which must be increased by 140° F. Consequently, in this case, only 0.6 as much heat will be absorbed in heating 1 pound of recycle than is ab-
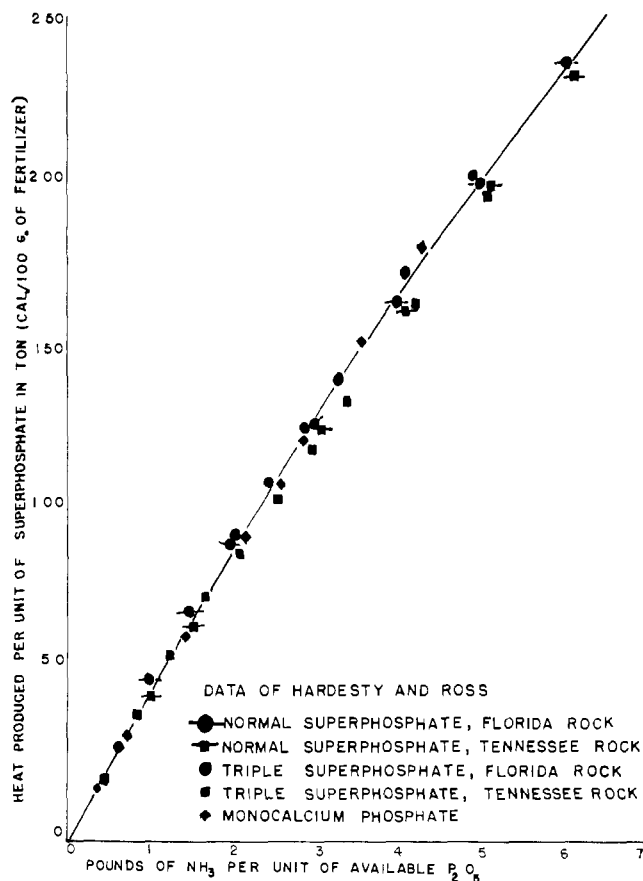

Figure 3. Heat of ammoniation of superphosphates

sorbed in heating 1 pound of feed. The over-all heat requirements can thus be estimated by an equation of the type

$$H = H_0(1 + xR)$$

in which

$H_0 \approx 3500$; R = pounds of recycle per pound of product

The value of x is determined by the recycle temperature and can be calculated by the equation

$$x = \frac{T_g - T_r}{T_g - T_f} \approx 0.6$$

in which

T_g = temperature in the granulator
T_r = temperature of the recycle
T_f = temperature of the raw materials

Steam is sometimes used as a source of heat in granulation, although the more common practice is to depend exclusively upon chemical heat. When using steam as a heat source, 1 pound of 100% quality steam per ton of fertilizer is equivalent to 27 calories per 100 grams of fertilizer. The over-all heat balance may then be used to estimate the steam requirements.

The chemical heat is produced almost exclusively by reactions of the free ammonia present in the nitrogen solutions or of the anhydrous ammonia with the phosphates or other acidic materials in

the formulation. Because the amount of heat produced per pound of ammonia absorbed depends to a much larger extent upon the material reacting with the ammonia than upon whether the ammonia is added in the form of a nitrogen solution or anhydrous ammonia, it is logical to calculate the amount of heat produced on the basis of the different types of ammonia-absorbing material rather than on the form in which the ammonia is introduced. The heat produced when anhydrous ammonia is absorbed by various types of superphosphates has been determined in the laboratory by Hardesty and Ross (4). These experimental results have been replotted (Figure 3) in terms of the heat produced per unit of phosphorus pentoxide when different levels of ammoniation are employed. When presented in this way, the results show that the heat produced in absorbing a given amount of ammonia by one unit of phosphorus pentoxide is essentially the same for both normal superphosphate and triple superphosphate whether manufactured from Tennessee or Florida rock. Although the amount of heat per unit of phosphorus pentoxide is independent of the type of superphosphate used, the amount of heat is influenced to a large extent by the amount of ammonia absorbed. Thus, normal superphosphate ammoniated to
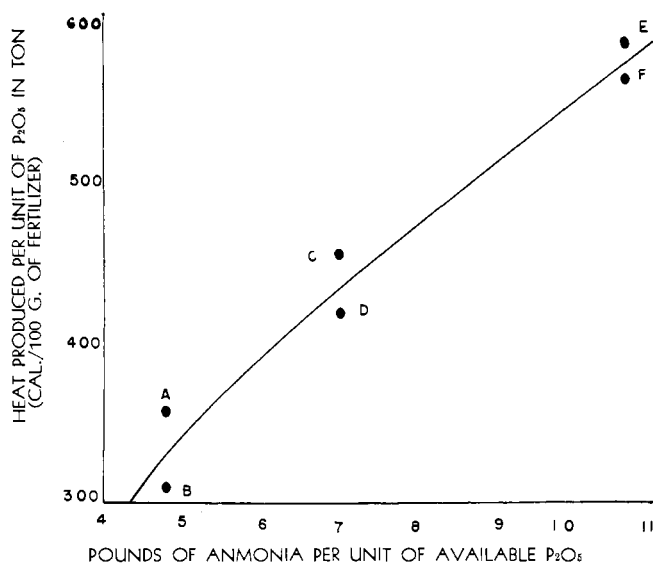
Figure 4. Heat of ammoniation of 75% phosphoric acid

6 pounds of ammonia per unit of phosphorus pentoxide will produce 233 calories, whereas triple superphosphate ammoniated to 4 pounds of ammonia per unit of phosphorus pentoxide will produce 160 calories (Figure 3). Because the concentration of phosphorus pentoxide in the fertilizer is the same whether expressed in units per ton or grams per hundred grams of fertilizer, the total heat produced by ammoniation of the superphosphate may be estimated by multiplying the units of normal superphosphate in the grade by 233 and the units of triple superphosphate by 160 or whatever numbers correspond to the degree of ammoniation used in the formulation.

The amount of heat produced by the ammoniation of phosphoric acid has been calculated from the heats of formation (12) of the raw materials and products formed (see Chemistry of Ammoniation). The amount of heat produced depends to some extent on whether the ammonium salts are produced as solids or as solutions and how much gypsum (from normal superphosphate) is present to increase ammonia retention. However, these effects (Figure 4) are of less importance than the amount of ammonia absorbed. Thus, the heat produced per unit of phosphorus pentoxide when phosphoric acid reacts with ammonia depends primarily on the amount of ammonia absorbed. The heat produced may be estimated to within 10% by assuming that 500 calories are produced per unit of phosphoric acid in formulations which are fully ammoniated.

One pound of 66° Bé. sulfuric acid in the formulation liberates 24.6 calories on ammoniation of 100 grams of fertilizer, whereas 1 pound of 60° Bé. acid releases 18.4 calories per 100 grams of fertilizer. By summing the various sources of chemical heat, the total may

then be compared with the estimated requirements based on operating conditions, amount, and temperature of the recycle employed. If the heat balances calculated in these two ways agree within 1000 calories, satisfactory granulation temperatures can generally be expected.

Calculating New Formulations

The discussion so far has been concerned with the analysis of existing formulations to find out what factors render them good or poor, and the evaluation of untried formulations. There is no easy way of preparing a new formulation based on a given set of raw materials. Because correcting for one of the requirements may upset some of the other requirements previously established, a completely satisfactory formulation generally requires a series of approximations. One may start out using only nitrogen solution, normal superphosphate, potassium chloride, and a filler or triple superphosphate. A check of the ammoniation balance will show whether sulfuric acid is required or whether anhydrous ammonia may be used. After suitable adjustment has been made for the ammoniation balance, a check of the moisture balance will determine whether some of the nitrogen solution must be replaced by ammonium sulfate, or if additional water will be required.

After establishing the proper water balance, the heat balance is next checked to determine whether additional acid must be added, or if acid must be removed and replaced by an equivalent amount of ammonium sulfate. In the meantime, these changes have upset the material balance, necessitating readjustment of the amount of filler or triple superphosphate to end up with the proper weight which, in turn, changes

the ammoniation balance which must then be recalculated, etc. Eventually, however, a consistent set of results should be obtained.

In order to find the optimum formulation for good granulation, one may calculate a series of such formulations based on different recycle rates. If one calculates a formulation to be used with a relatively high recycle rate, and then uses less, overgranulation will result because of too much heat and moisture. On the other hand, if one calculates a formulation to be used with very little recycle, and then uses more recycle, insufficient granulation will result because the mixture is too cold and too dry. Somewhere in between these extremes must lie an optimum formulation. This optimum formulation is best found in the plant by testing a series of formulations calculated to use different recycle rates.

If one is primarily interested in formulations for the study of the economics of selecting different raw materials, one then need be certain only that the formulation is sufficiently close to the optimum and that the final test in the plant will not result in significant changes in the raw material cost. The method of formulation which has been described should be sufficiently accurate for good cost comparisons. By this method, it may be determined which nitrogen solution would be most economical in use, whether the use of phosphoric acid or diammonium phosphate can lead to over-all cost savings, and at which recycle rate the plant should operate to give the best balance between raw material cost and production capacity.

This method of calculating formulations is not a simple one. Considerable man-hours can be spent in solving the various formulation problems which arise daily. For this reason, the Monsanto Chemical Co. has spent considerable time and effort in developing a program by which an electronic computer can carry out these computations rapidly. Thus, in a matter of seconds, a formulation can be completely solved (10).

Formulating with Phosphoric Acid and Diammonium Phosphate

The problems of formulating with phosphoric acid are essentially the same as those with triple superphosphate. Formulations may be calculated in which either part or all of the triple superphosphate is replaced with phosphoric acid. In making these calculations, it is necessary to take into consideration the higher concentration of phosphorus pentoxide in the phosphoric acid, the greater ammonia retention, the higher water content, and the greater amount of heat produced on ammoniation of phosphoric acid as compared with triple superphosphate.

In contrast to phosphoric acid, diammonium phosphate provides an equally high nutrient raw material which contains no water and produces essentially no heat in the formulation. The ammonia present in diammonium phosphate is held much less tightly than that present in ammonium sulfate. Failure to recognize this fact can result in improper formulation causing ammonia losses. This problem, however, may be easily corrected by providing sufficient extra ammonia retention to hold that part of the ammonia which otherwise would be lost from the diammonium phosphate. A simple method for determining a correct degree of ammoniation in formulations employing diammonium phosphate is to calculate the diammonium phosphate as if it were a mixture of anhydrous ammonia and 100% phosphoric acid. On this basis, the combined units of phosphorus pentoxide from diammonium phosphate (and phosphoric acid, if any) are regarded as coming from phosphoric acid. The ammonia in the diammonium phosphate is added to the total free ammonia (anhydrous ammonia and the free ammonia in the nitrogen solution).

Diammonium phosphate, as purchased, contains approximately 10.4 pounds of ammonia per unit of phosphorus pentoxide which corresponds to 0.256 pound of ammonia per pound of diammonium phosphate used.

Chemistry of Ammoniation of Phosphates

The conditions for ammoniation in a granulation plant are generally held within limits: 4 to 10% moisture, 160° to 240° F., and a contact period of a few minutes. Consequently, the chemistry is concerned primarily with what happens under these conditions. The resulting mixture is rather complex and the question of how the various elements are chemically combined requires more information than is obtained by analysis of the elements present. Starting with the work of Bassett (1), numerous investigators have studied the problem. Keenen (8) made certain conclusions on the basis of the chemical composition of the water-soluble and citrate-soluble fractions. White, Hardesty, and Ross (14) based their results primarily on the amount of ammonia lost on heating air-dried samples previously ammoniated with different amounts of ammonia. Other investigations have been based on the amount of water-soluble and citrate-insoluble phosphorus pentoxide present (9, 15). While the reactions occurring with individual phosphates have been studied extensively, little consideration has been given to complex mixtures. To be able to predict the behavior of phosphoric acid and diammonium phosphate as raw materials, required more

quantitative knowledge of the chemistry of the ammoniation of mixtures of different phosphate raw materials.

The same chemistry must explain the ammoniation of both normal and triple superphosphate. The only major difference in the reactions must result from the large amount of gypsum present in the normal superphosphate. Unless essentially complete conversion of gypsum to ammonium sulfate and dicalcium phosphate is assumed, the higher ammonia retention of normal superphosphat (on a phosphorus pentoxide unit basis) cannot be readily explained. The chemical reactions (1 to 6) are consistent with the observed water-soluble phosphorus pentoxide content of ammoniated triple superphosphate, but do not account for the presence of 20 to 35% of water-soluble phosphorus pentoxide in normal superphosphate ammoniated to 6 pounds of ammonia per unit of phosphorus pentoxide. The water extraction might cause the ammonium sulfate formed in situ to solubilize some of the phosphate

$$(NH_4)_2SO_4 + CaHPO_4 \rightarrow (NH_4)_2HPO_4 + CaSO_4$$
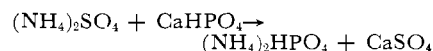
In any event, the proposed chemistry has been able to provide a basis for formulations with phosphoric acid and diammonium phosphate which has been successful in plant tests.

The basic chemistry has been placed on a semiquantitative basis by calculating the degree to which the various reactions go to completion. The calculations were made in such a manner that the basic chemistry was brought into agreement with the accepted practices on ammoniation rates. The ammoniation rate of phosphoric acid was next calculated by assuming that the same basic chemistry applies, and that the individual reactions occur to the same extent. Finally, firsthand experience was obtained on a series of plant demonstrations at the Ark-Mo Plant Food Co. and other plants to ensure that theory and practice were in general agreement.

The study of the basic chemistry relating to ammoniation practice assuming optimum conditions of temperature and moisture gives the following results.

Reaction	Completed, %	
$Ca(H_2PO_4)_2 + NH_3 \rightarrow$ $CaHPO_4 + NH_4H_2PO_4$	100	(1)
$NH_4H_2PO_4 + CaSO_4 + NH_3 \rightarrow$ $CaHPO_4 + (NH_4)_2SO_4$	100	(2)
$H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$	100	(3)
$NH_4H_2PO_4 + NH_3 \rightleftharpoons$ $(NH_4)_2HPO_4$	50	(4)
$3CaHPO_4 + NH_3 \rightleftharpoons$ $Ca_3(PO_4)_2 + NH_4H_2PO_4$	33	(5)
$2CaHPO_4 + CaSO_4 + 2NH_3 \rightleftharpoons$ $Ca_3(PO_4)_2 + (NH_4)_2SO_4$	25	(6)

Equations 5 and 6 are similar in that both

involve the conversion of dicalcium phosphate to a more basic form, which has been represented as tricalcium phosphate. Thirty-three and 25% reaction, respectively, for these equations results in the same final mole ratio of tricalcium to monocalcium phosphate of 1 to 6.

The differences in ammonia retention (pounds of ammonia absorbed per unit of phosphorus pentoxide) of mixtures of phosphates can be explained in terms of Equations 1 to 6, and the quantity of gypsum added by use of normal superphosphate. The gypsum reacts with phosphoric acid or triple superphosphate to increase the ammonia capacity. Because of this interaction, the ammonia retention of mixtures of phosphate sources is not simply the sum of the capacities of the individual components.

The amount of gypsum formed by acidulation of pure phosphate rock may be represented by the equation:

$$Ca_{10}(PO_4)_6F_2 + 7H_2SO_4 \rightarrow 3Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF \quad (7)$$
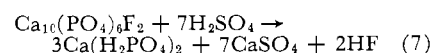
Commercial phosphate rock generally contains a higher proportion of calcium, as well as other impurities, and fluorine is incompletely removed during acidulation. In actual practice, approximately 7.5 moles of gypsum are produced for every 3 moles of monocalcium phosphate. On the other hand, triple superphosphate resulting from acidulation with phosphoric acid may be pictured as an impure monocalcium phosphate with essentially no gypsum present.

One mole of monocalcium phosphate contains one mole of phosphorus pentoxide and as the first step in ammoniation absorbs one mole of ammonia (Equation 1). Expressed in fertilizer terminology, this reaction corresponds to an ammoniation rate of 2.4 pounds of ammonia per unit of phosphorus pentoxide in forming dicalcium phosphate and monoammonium phosphate. However, the gypsum present in normal superphosphate can react further with ammonia and monoammonium phosphate to produce more dicalcium phosphate and ammonium sulfate (Equation 2), absorbing an additional 2.4 pounds of ammonia per unit of phosphorus pentoxide or a total of 4.8 pounds. Further ammoniation to a maximum total of 6.0 pounds requires that a still more basic phosphate be formed (Equation 6) which is represented as tricalcium phosphate, although it might be a form of hydroxyl apatite. Thus, about one fourth of the dicalcium phosphate can be converted to an equivalent amount of tricalcium phosphate with reasonably efficient absorption of an additional 1.2 pounds of ammonia and without serious reversion to citrate-insoluble phosphorus pentoxide.

The initial step in the ammoniation of triple superphosphate also follows Equation 1. The ratio of tricalcium to di-
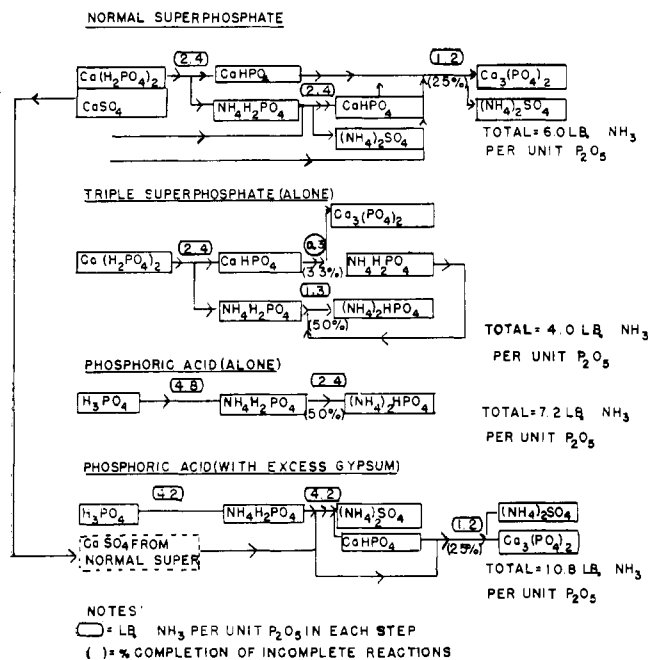
Figure 5. Outline of ammoniation reactions

NOTES:
⬭ = LB. NH₃ PER UNIT P₂O₅ IN EACH STEP
( ) = % COMPLETION OF INCOMPLETE REACTIONS

calcium phosphate will be about the same as for normal superphosphate, if the triple superphosphate particles are sufficiently soft and porous to permit penetration of ammonia which reacts according to Equation 5. However, because only 1 mole of monocalcium phosphate is produced (Equation 1) and the reaction is only one third complete, only an additional 0.3 pound of ammonia can be absorbed. Consequently, the additional ammonia absorption which can be realized must result from the conversion of monoammonium phosphate to diammonium phosphate (Equation 4) which, in going halfway to completion, absorbs about 1.3 pounds of ammonia ($^1/_9$ mole of monoammonium phosphate is produced according to Equation 5, in addition to the 1 mole produced according to Equation 1). Thus, the total ammonia absorption is 4.0 pounds of ammonia per unit of phosphorus pentoxide. With phosphoric acid alone, ammoniation results first in the formation of monoammonium phosphate on absorption of 4.8 pounds of ammonia per unit of phosphorus pentoxide (Equation 3) 50% of which is then converted to diammonium phosphate with absorption of an additional 2.4 pounds of ammonia (Equation 4) for a total of 7.2 pounds of ammonia per unit of phosphorus pentoxide.

When phosphoric acid is used in conjunction with normal superphosphate, which is the usual case, the excess gypsum present in the normal superphosphate acts to increase further the ammonia retention of the phosphoric acid. Assuming adequate gypsum present, the monoammonium phosphate produced, Equation 3, can react with gypsum as in Equation 2 to absorb 4.8 pounds more of

ammonia (2.4 pounds per $^1/_2$ unit of acid) and the resulting dicalcium phosphate can react, according to Equation 6, to absorb an additional 1.2 pounds for a total of 10.8 pounds per unit of phosphorus pentoxide as phosphoric acid.

Theoretically, the gypsum in normal superphosphate also can increase the ammonia retention of triple superphosphate to equal that of the normal superphosphate itself. However, because the diammonium phosphate formed in the triple superphosphate, particles first must diffuse out of the triple superphosphate and then diffuse into the normal superphosphate particles to reach the gypsum—complete reaction does not take place. For lack of more complete information concerning this reaction, it is assumed that the reaction goes only about halfway. In other words, the maximum rate for triple superphosphate with excess normal superphosphate present is assumed to be 5 pounds of ammonia per unit instead of the theoretical 6 pounds per unit. In contrast to triple superphosphate, the phosphoric acid being applied in liquid form and producing only soluble salts on ammoniation can react more completely with the gypsum in the normal superphosphate to increase its ammoniation capacity.

The foregoing chemical reactions have been outlined in schematic form (Figure 5). The contribution of each reaction to the total absorption of ammonia is given.

Finally, to complete the information on ammoniation rates, it is necessary to determine the amount of excess gypsum present in normal superphosphate which is available for increasing the ammonia capacity of phosphoric acid or triple superphosphate. In actual practice,

about 7.5 moles of gypsum are formed with each 3 moles of monocalcium phosphate (rather than the theoretical 7.0 moles according to Equation 1) or 2.5 moles of gypsum per mole of phosphorus pentoxide. It appears that about half of the gypsum ($1^1/_4$ moles) is used up in ammoniating the normal superphosphate and the other half is available for reaction with phosphoric acid or triple superphosphate. The excess gypsum from one unit of normal superphosphate is sufficient to give the maximum ammoniation rate per one half unit of phosphoric acid or one unit of triple superphosphate. As already mentioned, the phosphoric acid is capable of reacting with gypsum, because it is added in liquid form and is initially converted to soluble ammonium salts which can penetrate the normal superphosphate. Consequently, in calculating the maximum practical ammoniation rates, it is assumed that:

Normal superphosphate always has an ammonia capacity of 6 pounds per unit of phosphorus pentoxide.

Phosphoric acid has a capacity of 10.8 pounds per unit in amounts up to one half the units of normal superphosphate present and 7.2 pounds per unit in excess of this amount.

Triple superphosphate has a capacity of 5 pounds per unit in amounts up to equal the units of normal superphosphate present and 4 pounds per unit in excess of this amount.

In addition, sulfuric acid will react completely with ammonia to form ammonium sulfate

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$$

In order to provide a convenient method for the determination of the ammonia capacity of a mixture of phosphates in a formulation, a triangular diagram (Figure 1) has been prepared which represents all possible combinations of phosphoric acid, normal superphosphate, and triple superphosphate. This chart provides compactly the summation of all the theoretical considerations which have been presented. To use the chart, it is necessary to calculate the per cent of the total units of phosphorus pentoxide added in each of the three forms. The percentages thus calculated locate a single point which (by interpolation between lines) gives the average ammonia capacity for the phosphate mixture in pounds of ammonia per unit of phosphorus pentoxide. Thus, by multiplying the average ammonia capacity by the total units of available phosphorus pentoxide the total capacity for ammonia is obtained.

The diagram (Figure 1) is divided into three areas (the ammoniation-rate lines being parallel in each area). The lower left area represents compositions having enough gypsum from normal superphosphate for the maximum ammoniation of

Table III. Formulations, in Pounds, Used in Plant Tests

Formulation Number and Grade

Material	1 12-12-12 Wet	Dry	2 10-20-10 Wet	Dry	3 8-24-8 Wet	Dry	4 16-20-0 Wet	Dry	5 5-20-20 Wet	Dry	6 10-20-0 Wet	Dry	7 11-48-0 Wet	Dry	8 5-20-20 Wet	Dry	9 12-12-12 Wet	Dry
Ammonia, anhydrous	25	25	78	78	110	110	49	49	73	73	...	...	...	...	...	...	...	...
Nitrogen solution	432[a]	360	367[a]	306	189[a]	158	540[a]	450	108[a]	90	455[b]	428	228[b]	214	94[c]	94	335[b]	315
Ammonium sulfate	300	300	...	...	...	...	400	400	...	...	...	...	...	...	77	77	278	277
Diammonium phosphate	...	...	...	...	...	...	...	...	...	...	...	...	610	610	...	...	225	214
Phosphoric acid	160	125	361	270	331	248	368	276	405	304	...	...	405	304	...	...	...	...
Normal superphosphate	756	694	1020	969	1030	979	700	665	850	808	1170	1077	...	...	353	325	710	652
Triple superphosphate	...	...	...	...	204	194	130	124	17	16	386	363	880	835	725	700	...	...
Potassium chloride	400	400	333	333	267	267	...	...	667	667	...	...	...	...	667	667	410	408
Sulfuric acid	43	40[d]	...	...	...	...	...	...	...	...	...	...	...	...	144[e]	111	165	128
Total weight	2116	1944	2159	1956	2131	1956	2187	1964	2120	1958	2011	1868	2123	1963	2060	1974	2123	1994

Nitrogen Solution Composition

NH_3, %	NH_4NO_3, %	H_2O, %
[a] 16.6	66.8	16.6
[b] 25.0	69.6	6.0
[c] 23.8	69.8	6.4

[d] 66° Bé. sulfuric acid. [e] 60° Bé. sulfuric acid.

Note: Dry weight = wet or "as is" weight minus weight of water in component.

Table IV. Moisture Balance

Formulation No.	NH_4NO_3, % = b_5 B/2000	Moisture in Recycle, % = M_R	Moisture in Feed, % = M_F, Eq. R-4b	Moisture for Granulation, % = M_G from Figure 2 High	Av.	Low	Recycle Calculated, Lb. Recycle/Lb. Product, $R = (M_F - M_G)/(M_G - M_R)$ Low	Av.	High	Recycle Found, Lb. Recycle/Lb. Product
1	14.4	2.5	8.6	6.3	5.4	4.5	0.6	1.1	2.0	1.45
2	12.2	2.5	11.0	6.6	5.8	4.9	1.1	1.6	2.5	1.50
3	6.3	1.8	15.4	8.6	7.4	6.3	1.0	1.4	2.0	0.94
4	18.0	2.7	11.0	5.8	4.8	3.8	1.7	3.0	6.6	2.48
5	3.6	2.3	11.8	10.3	8.5	6.7	0.2	0.6	1.3	1.20
6	15.7	2.0[a]	6.8	6.1	5.1	4.2	0.2	0.5	1.2	0.20
7	15.7	2.0[a]	8.9	6.1	5.1	4.2	0.2	0.5	1.2	0.25-0.50[a]
8	2.6	2.0	11.3	11.2	9.4	7.2	0.1	0.4	0.8	0.75
9	11.3	2.5	6.5	7.6	6.3	5.0	0.1	<0.1	<0.1	0.00[b]

[a] Estimated. [b] Fines not removed. Product yield = 95% of 6/20 mesh.

Table V. Ammoniation Balance

Maximum Ammoniation

Formulation No.	Phosphate Units Superphosphate Normal	Triple	Phosphoric Acid	DAP	Lb. NH_3/unit P_2O_5 = Y, Figure 1	Lb. Ammonia/Ton All phosphates = Y (units of P_2O_5)	Sulfuric acid	Total	Free Ammonia Added, Lb. As solution = b_4 B/100	As anhydrous	As DAP = d_4 D/100	Total	Maximum Ammoniation, %
1	7.5	..	4.5	..	7.57	91	14	105	72	25	..	97	92
2	10.2	..	9.8	..	7.50	150	..	150	61	78	..	139	93
3	10.3	4.7	9.0	..	6.84	164	..	164	31	110	..	141	86
4	7.0	3.0	10.0	..	6.94	139	..	139	90	49	..	139	100
5	8.5	0.5	11.0	..	7.38	148	..	148	18	73	..	91	62
6	8.9	11.1	..	..	5.36	107	..	107	114	..	..	114	107
7	..	20.7	11.0	16.3	5.83	280	..	280	57	..	156	213	76
8	3.4	16.6	..	..	4.50	90	38	128	18	94	..	112	88
9	6.9	..	..	6.0	7.55	91	63	154	84	..	58	142	92

Table VI. Heat Balance

Formulation Number	1	2	3	4	5	6	7	8	9
Heat Produced, Cal./100 G. Fertilizer									
Normal superphosphate, units × 233	1750	2380	2400	1630	1980	2590	..	793	1610
Triple superphosphate, units × 160	..	..	750	480	60	1440	3310	2660	..
Phosphoric acid, units × 500	2260	4920	4500	5000	5500	..	5500	..	..
Sulfuric acid, lb. × 24.6 for 66° Bé.	1060	..	..	..	..	..	..		
lb. × 18.4 for 60° Bé.								2650	3040
Total heat added, cal./100 g. fertilizer	5070	7300	7650	7110	7440	4030	8810	6103	4650
Recycle, lb./lb. product	1.45	1.50	0.94	2.48	1.20	0.20	0.5	0.75	0
Ammoniator temperature, °F., T_g	190	193	193	180	200	170	210 est.	195	220
$X, (T_g - T_r)/(T_g - T_f)$	0.6	0.6	0.6	0.6	0.6	0.6	0.8	0.6	0.6
H_0	3500	3500	3500	3500	3500	4200[a]	4200[a]	3500	3500
Est., heat required, cal./100 g. fertilizer	6540	6650	5450	8700	6010	4700	6000	5400	3500

[a] Raw materials were at 33° to 38° F.

both phosphoric acid and triple super-phosphate. 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.

Acknowledgment

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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 formulation 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-