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FERTILIZER FORMULATION

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

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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.

FERTILIZER FORMULAS are usually calculated 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 ton—which 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 plant—i.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 high-analysis 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 source—namely, 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[a]	Analysis, %	H_2O, %	Bone-Dry Analysis, %
A	Ammoniating solution	37.0 N	16.6	44.4 N
		16.6 NH_3	...	19.9 NH_3
		66.8 NH_4NO_3	...	80.1 NH_4NO_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
		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_2O_5	7.0	21.6 P_2O_5
G	Triple superphosphate	46.0 P_2O_5	5.0	48.4 P_2O_5
H	Calcium metaphosphate	61.0 P_2O_5	...	61.0 P_2O_5
I	Potassium chloride	60.0 K_2O	...	60.0 K_2O

[a] Alphabetical letters identify material.

Table II. Analyses of Reaction Products

	Reactants[a]	Bone-Dry Analysis, % N	P_2O_5
J	Ammoniated solution–normal superphosphate	9.5	17.0
K	Ammoniating solution–triple superphosphate	13.3	33.9
L	Ammoniating solution–phosphoric acid	27.5	27.5
M	Ammoniating solution–sulfuric acid	28.2	...
N	Anhydrous ammonia–normal superphosphate	4.2	20.5
O	Anhydrous ammonia–triple superphosphate	6.4	44.6
P	Anhydrous ammonia–phosphoric acid	20.2	54.5
Q	Anhydrous ammonia–sulfuric acid	21.2	...

[a] Alphabetical letters identify material.

method are listed in Table I. A typical analysis, including moisture content, is shown opposite each raw material. The ammoniating solution (amm. soln.) containing 37.0% of total nitrogen, 16.6% of free ammonia, 66.8% of ammonium nitrate, and 16.6% of water, was chosen, as together with anhydrous ammonia, it can provide the same ammonia-to-ammonium nitrate ratio found in any of the ammonia–ammonium nitrate–water-containing solutions offered to the fertilizer industry. The analysis of each raw material, on a completely anhydrous or bone-dry basis, is shown in the right-hand column.

Free ammonia carriers will react with the acids in normal and triple superphosphates or with other acids, and these reactions can be carried to certain well-defined end points. For the purpose of this paper, these neutralizing reactions are carried to the following end points: Sulfuric acid is neutralized to diammonium sulfate, triple superphosphate is ammoniated to 3.5 pounds of ammonia per unit of phosphorus pentoxide or a 3.5 degree of ammoniation, normal superphosphate is ammoniated to 5.0 pounds of ammonia per unit phosphorus pentoxide or a 5.0 degree of ammoniation and phosphoric acid is ammoniated to 9.0 pounds of ammonia per unit phosphorus pentoxide or a 9.0 degree ammoniation. (This will produce a mixture of 88% of diammonium phosphate and 12% of monoammonium phosphate.)

Using the bone-dry analysis shown in Table I, the analyses of the combined raw materials are calculated according to conditions just listed. These combined raw materials, together with their bone-dry analyses, are shown in Table II. In each combination, one raw material supplies all of the nitrogen and the other raw material supplies all of the phosphorus pentoxide. The actual amounts of the two raw materials, for any combination listed, are determined by dividing the per cent of each plant food of the combination by the decimal fraction of the analysis of the raw material supplying that plant food. For example, in the combination of ammoniating solution plus normal superphosphate, the quantity of ammoniating solution required is determined by dividing the 9.5 by the decimal fraction of the per cent of nitrogen in the ammoniating solution, which is 0.37. The 17.0% phosphorus pentoxide is supplied by the normal superphosphate and, dividing the 17.0 by the decimal fraction by the phosphorus pentoxide in normal superphosphate, which is 0.20, the quantity of normal superphosphate is determined. Carrying out these two divisions, the combining ratio of ammoniating solution and normal superphosphate is 25.7 parts of ammoniating solution for every 85.0 parts of normal superphosphate. Table III shows the combining ratios for the remaining combinations. Under the total weight column in Table III, all of the combinations have a total weight greater than 100. This is the result of the method used to determine the combining ratios, wherein the bone-dry analysis of the combination was divided by the wet analysis of the raw materials. The first combination in Table III between normal superphosphate and anhydrous ammonia totals 107.6, indicating 7.6 parts of water for every 100 parts of bone-dry reactants. Similarly, the normal superphosphate–ammoniating solution combination, shown by the second line of Table III, totals 110.7 indicating that 10.7 parts of water are supplied by these raw materials with every 100 parts of bone-dry reactants.

The calculations to this point are preliminary and may be used in any number of formulation calculations. As previously indicated, formulating any desired fertilizer grade may be considered as two independent steps. By suitable combination of the individual neutralizing reactions, any desired plant food ratio may be obtained. For example, a 13–13–13 is to be formulated. The choice of raw materials is to be based on the least expensive formula, with no restriction placed by the equipment or the manufacturing process and commercial drying equipment is assumed to be available to dry the product to 1% moisture.

In the finished 13–13–13, 21.7% of the weight would be potash and 1.0% would be water. To obtain the potash–water free base, 13 is divided by 1–0.227. By this calculation, the base is found to be 16.8–16.8–0.

Selection of Raw Materials. There are several combinations of raw materials that will produce this 16.8–16.8–0. The next step is to determine which combination will produce the cheapest formulation, as this was the only consideration stated above limiting the raw materials. The choice should be made on a delivered-cost basis. Because there is some variation in delivered costs between individual plants, a representative figure has been shown opposite each raw material to provide data for Table IV.

Table III. Combining Ratios

	Ammoniating Solution	Ammonia	Total Wt.	Water, %
Normal superphosphate				
102.5		5.1	107.6	7.4
85.0	25.7		110.7	9.7
Triple superphosphate				
97.0		7.8	104.8	4.6
73.7	35.9		109.6	8.8
Phosphoric acid				
100.4		24.6	125.0	20.0
50.6	74.3		124.9	19.9
Sulfuric acid				
79.6		25.9	105.5	5.2
39.1	76.2		115.3	13.3

Table IV. Raw Material Costs

Material	Analysis	$/Unit
Anhydrous ammonia	82.0% N	1.09
Ammoniating solution	37.0% N	1.40
Normal superphosphate	20.0% P_2O_5	0.70
Triple superphosphate	46.0% P_2O_5	1.25
Phosphoric acid	54.3% P_2O_5	1.65
Muriate of potash	60.0% K_2O	0.60
Ammonium sulfate	20.0% N	2.25
Calcium metaphosphate	61.0% P_2O_5	1.60
Diammonium phosphate	21–53–0	0.063/lb.
Sulfuric acid	66° Be.	0.013/lb.

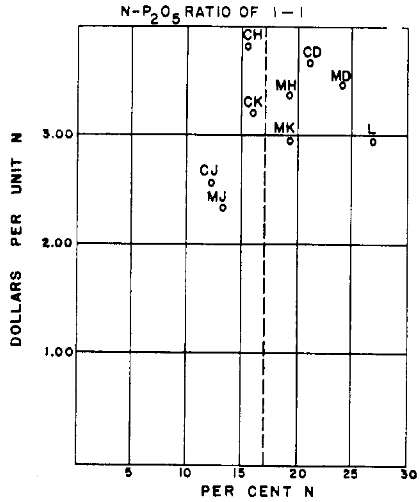

Figure 1. Formulation costs

CH. Ammonium sulfate–calcium metaphosphate
CD. Ammonium sulfate–diammonium phosphate
CK. Ammoniating solution–ammonium sulfate–triple superphosphate
MD. Ammoniating solution–sulfuric acid–diammonium phosphate
MH. Ammoniating solution–sulfuric acid–calcium metaphosphate
L. Ammoniating solution–phosphoric acid
MK. Ammoniating solution–sulfuric acid–triple superphosphate
CJ. Ammoniating solution–ammonium sulfate–normal superphosphate
MJ. Ammoniating solution–sulfuric acid–normal superphosphate

Table V. Combinations for Nitrogen to Phosphorous Pentoxide Ratio of 1 to 1

Combinations	Reactants	N, %	P_2O_5, %
L	62.0% ammoniating solution–38.0% phosphoric acid	27.5	27.5
MD	34.4% ammoniating solution–19.8% sulfuric acid–45.8% DAP[a]	24.8	24.8
CD	62.3% ammoniating sulfate–37.7% DAP	20.4	20.4
MK	44.4% ammoniating solution–15.5% sulfuric acid–40.4% triple superphosphate	19.5	19.5
MH	43.4% ammoniating solution–25.0% sulfuric acid–31.6% calcium metaphosphate	19.3	19.3
CK	14.8% ammoniating solution–50.6% ammoniating sulfate–34.6% triple superphosphate	16.7	16.7
CH	73.3% ammoniating sulfate–24.7% calcium metaphosphate	15.1	15.1
MJ	30.2% ammoniating solution–7.8% sulfuric acid–62.0% normal superphosphate	13.4	13.4
CJ	15.5% ammoniating solution–27.5% ammoniating sulfate–57.0% normal superphosphate	12.4	12.4

[a] Diammonium phosphate.

Table VI. Algebraic Formulation

L Ammoniating solution—phosphoric acid 27.5% N
MJ Ammoniating solution—sulfuric acid–normal superphosphate 13.4% N

Equation 1 $0.275 \times L + 0.134 \times MJ = 16.8$

Lb. of N in $L \times$ lb. of L + Lb. of N in $MJ \times$ lb. of MJ = lb. of N required

$$L + MJ = 100$$
$$MJ = 100 - L$$
$$MJ = 75.9\%;\ L = 24.1\%$$

Formula 16.8–16.8–0

L
$0.241 \times 1486 =$ 358 lb. ammoniating solution
$0.241 \times 1012 =$ 244 lb. phosphoric acid

MJ
$0.759 \times 730 =$ 552 lb. ammoniating solution
$0.759 \times 127 =$ 126 lb. sulfuric acid
$0.759 \times 1350 =$ 1017 lb. normal superphosphate
2297

Table VII. 13–13–13 Formula

Material	16.8–16.8–0 Base	Allowance K_2O	Allowance H_2O	Lb./Ton	Plant Food N	Plant Food P_2O_5	Plant Food K_2O
Ammoniating solution	910 ×	0.782 ×	0.99 =	704	260.5		
Normal super	1017 ×	0.782 ×	0.99 =	787		157.4	
Phosphoric acid	244 ×	0.782 ×	0.99 =	189		102.6	
Sulfuric acid	126 ×	0.782 ×	0.99 =	98			
Muriate of potash				434			260.4
				2212	260.5	260.0	260.4
					13	13	13

As it is customary for the industry to refer to the plant food ratios of grades, the neutralizing reactions may be combined and tabulated according to a nitrogen–phosphorus pentoxide ratio of 1 to 1, as shown in Table V. Utilizing the delivered cost data for the raw materials and the combinations of reactants in Table V, a comparison of the formula costs may be made. Each combination has a different analysis and the formula cost divided by the per cent of nitrogen of each combination provides a common basis for comparison. The plot of these formula costs, in terms of dollars per unit of nitrogen *vs.* the per cent of nitrogen, is shown by Figure 1. Locating 16.8% of nitrogen on the abscissa and drawing a vertical line at this point, shows that the combination represented by the point *MJ* and the point *L* will produce the least expensive formula. The point *MJ* or the combination of points *MJ* and *L* will provide the least expensive formula for any grade having a nitrogen–phosphorus pentoxide ratio of 1 to 1, under the conditions stated. A table using the neutralizing reactions may be constructed for any desired nitrogen–phosphorus pentoxide ratio.

The correct plant food ratio has already been established and the proportions of each combination may be determined through the use of simultaneous equations, using either the per cent of nitrogen or the per cent of phosphorus pentoxide as the basis. For this example, the per cent of nitrogen was chosen, and the calculations are shown in Table VI. By these calculations, the formula for a 16.8–16.8–0 is 24.1% of combination *L* and 75.9% of combination *MJ*. Reducing these to raw materials, *L* will supply 358 pounds of ammoniating solution, 244 pounds of phosphoric acid; and combination *MJ* will supply 552 pounds of ammoniating solution, 126 pounds of sulfuric acid, and 1017 pounds of normal superphosphate. As the 16.8–16.8–0 base constituted only 77.4% of the original 13–13–13, this decimal times the weights of the ingredients in the 16.8–16.8–0, plus the potash, provides the finished formula. In Table VII, the allowances for potash and water are shown separately. The total weight of these raw materials is 2212 pounds (Table VII), which will produce 2000 pounds of a 13–13–13 containing 1% moisture.

An alternate means of determining the combinations of raw materials that will satisfy the grade and reaction requirements is through the use of a graph. A formulation graph may be constructed by defining the ordinate as the per cent of nitrogen and the abscissa as the per cent of phosphorus pentoxide. The analyses of each individual reaction (Table II), as well as the raw materials (Table I), are plotted in Figure 2. All

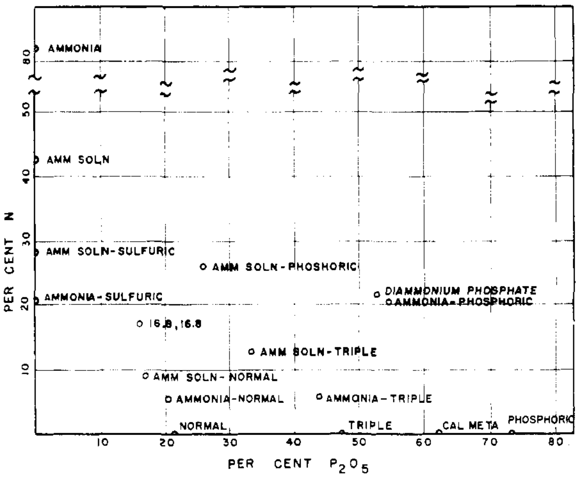

Figure 2. Analysis, on bone-dry basis, of reaction products and of raw materials

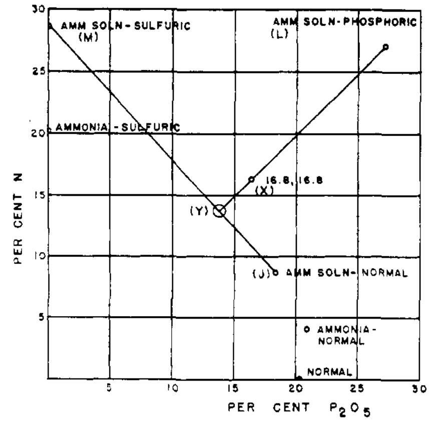

Figure 3. Determination of proportions of the desired raw materials from 16.8–16.8 point, *X*

analyses are on a bone-dry basis. Taking the 13–13–13 as an example, the grade to be formulated is a 16.8–16.8–0. As the initial step, the 16.8–16.8 point is plotted (Figure 3) and the proportions of the desired raw materials are determined in the following manner:

Construct a line between the points epresenting combinations *M* and *J*. Draw a second line from the point representing combination *L* through the point representing the desired composition, to an intersection with the first line. For convenience, designate this intersect point *Y*. Measure the line segment *MY* and divide this length by the total length of the line, *MJ*, times 100, to determine the per cent of combination *J* in the composition represented by point *Y*. Similarly, the length of the line segment *YJ* divided by *MJ*, times 100, equals the per cent of combination *M* in that same composition. With these calculations, point *Y* represents a composition of 78.8% combination *J* and 21.2% combination *M*.

The same method used to determine the composition represented by point *Y*, may be used to determine the composition represented by point *X*. The line segment *XY* divided by the total length of the line *LY*, times 100, is the per cent of combination *L* contained in 16.8, 16.8. This is determined to be 24.1%. The 16.8, 16.8 is composed of 24.1% of combination *L* and 75.9% of composition *Y*. Composition *Y* has already been shown to contain 78.8% of combination *J* and 21.2% of combination *M*. Therefore, 16.8, 16.8 is composed of 24.1% combination *L*, 59.8% combination *J*, and 16.1% combination *M*. These percentage figures may be used to calculate the formula of the 16.8–16.8–0 base, which, with the addition of potash, will produce the 13–13–13. The quantities obtained are identical to those obtained using the algebraic method.

The initial calculations required to prepare the tables and graphs are somewhat lengthy; however, they should be useful over a period of time, as there is little variation in the analysis of the raw materials for a given plant.

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FORAGE CROP CONSTITUENTS

The Isolation and Analysis of Hemicelluloses of Brome Grass

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Hemicelluloses are closely associated with cellulose in plants; in forage grasses they amount to 35% to 40% of the dry matter of the cell walls. When separated from the cellulose, they appear to be mixtures and extremely complex. Their chemical study begins with their separation as a crude mixture and the identification and quantitative determination of the sugars and uronic acids which they contain. Considerable progress has been made in the study of hemicelluloses in wood and in such agricultural by-products as straw and corncobs. In some cases, hemicelluloses, which seem to have molecular identity, have been isolated from the mixtures (*1*, *3*). In forage grasses, however, little work has been done. Binger, Sullivan, and Jensen (*5*) found four sugars—xylose, glucose, arabinose, and galactose—and at least one uronic acid in the

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