

## Composition and Dissolution of Ammoniated Superphosphate Fertilizers without Potash

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The dissolution of a very lightly ammoniated ordinary superphosphate is similar to that of a mixture of monocalcium and monoammonium phosphates, and the fertilizer produces solutions of monoammonium phosphate and ammonium sulfate in which the ratio of sulfate to phosphate increases with increased ammoniation. When the fertilizer contains ammonium nitrate, the first solution released is highly concentrated in this salt, and dissolution of ammonium phosphate and ammonium sulfate is suppressed by a common-ion effect. The composition of the solutions released can be used to calculate the quantities of the salts identified in the original fertilizer by x-ray diffraction.

RESEARCH on the precipitation of water-soluble phosphate in the soil has shown that the nature of the precipitates is greatly influenced by the composition of the solution that leaves the fertilizer granule (3). Thus, dissolution of monocalcium phosphate, the major component of superphosphate, produces a very acid, highly concentrated phosphate solution that will dissolve significant amounts of iron and aluminum from the soil; these metals are reprecipitated as iron and aluminum phosphates (4). This study was made to determine the effect of ammoniation on the composition of the solution released by ammoniated superphosphate.

### Materials and Methods

Analyses of the six fertilizers are shown in Table I. Fertilizers 247 to 250 were prepared by ammoniating the same ordinary superphosphate with ammoniacal ammonium nitrate solution. Fertilizer 251 was a mixture of ammonium nitrate and concentrated superphosphate, and fertilizer 253 was prepared by ammoniation of the same concentrated superphosphate. Results of greenhouse experiments with these materials were reported by Terman *et al.* (6).

Ten-gram samples of each fertilizer, crushed to -35 mesh, were each placed on a fine fritted-glass filter crucible, 40 mm. in diameter, and covered with a No. 934-AH glass fiber filter paper. Distilled water was dripped onto the covering filter paper at the rate of 1 ml. per hour, and the eluate was collected in tubes mounted on the wheel of a fraction collector that changed tubes every hour. To prevent evaporation of the solutions, the filter crucible was mounted inside a glass vessel continuously ventilated with moist air, and precautions were taken to prevent evaporation from the fraction-collector tubes. The water flow was regulated by displacing water through the side arm of a glass tube by a brass rod which was lowered by a pulley driven by a clock motor.

The water rate of 1 ml. per hour was the highest at which a sample of monocalcium phosphate dissolved to give the theoretical amount of metastable triple-point solution in the system lime-phosphoric acid-water (4). The experimental conditions do not exactly reproduce the conditions in the soil, where the water moves into the granule as a vapor and the solution is drawn off by the matric suction of the soil, but the results are in good agreement with direct observations of fertilizer pellets in the soil (2) and may be used to interpret the behavior of fertilizers in the soil.

The compounds present in the original fertilizers and the leached residues were identified and their relative amounts determined by petrographic examination and x-ray diffraction analysis (7).

### Results and Discussion

The concentrations of ammonium, nitrate, calcium, sulfate, and phosphate ions in the hourly eluates from each fertilizer are shown in Figure 1. The initial solutions released from all the fertilizers contained high concentrations of ammonium nitrate which decreased rapidly. The concentrations of am-

monium and nitrate ions were not equivalent. In fertilizers 247 and 251 the first solution contained an excess of nitrate, but during the dissolution the phosphate concentration rose and the ammonium was then in excess of the nitrate. This pattern of behavior is like that observed in the dissolution of mixtures of monocalcium phosphate and potassium chloride (3), where the deficiency of potassium was due to formation of  $\text{Ca}_2\text{KH}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$ . The behavior of fertilizers 247 and 251 may be interpreted in terms of the formation of the corresponding ammonium salt (5), with the concomitant production of free nitric acid which lowered the pH. The complex salt forms during the dissolution process—x-ray examination indicated that it was not present in the original fertilizers.

The dissolution of fertilizer 253 illustrates the effect of ammoniation on concentrated superphosphate and can be interpreted entirely in terms of the dissolution of a mixture of ammonium nitrate and monoammonium phosphate. The dissolution of the monoammonium phosphate was suppressed at first by the common-ion effect in the very con-

Table I. Composition of Ammoniated Superphosphate Fertilizers

No.	Grade	Composition, %						Fraction, % of P Soluble in		
		N		P	S	Ca	SiO <sub>2</sub>	Water	Ammonium Citrate	
Total	NH <sub>4</sub>	Neutral	Alkaline							
247	7-7-0 (7-16-0)	7.6	4.0	7.4	8.3	16.3	2.9	67	95	93
248	10-6.1-0 (10-14-0)	9.5	5.9	7.3	8.4	16.4	2.6	44	88	64
249	9-6.1-0 (9-14-0)	9.0	7.0	7.8	9.9	17.7	2.5	22	79	42
250	9-6.5-0 (9-15-0)	8.7	7.4	7.9	9.9	17.9	2.6	11	81	41
251	15-10.4-0 (15-24-0)	15.5	7.7	10.8	0.2	7.6	4.9	75	98	96
253	14-12.2-0 (14-28-0)	14.1	8.8	13.1	0.4	9.2	6.0	47	95	78

centrated ammonium nitrate solution, so that the phosphate was released as the nitrate.

The dissolutions of fertilizers 248, 249, and 250 show the effect of increasing ammoniation of ordinary superphosphate. With these materials, the ammonium was always in excess of the nitrate by an amount equivalent to the sum of phosphate and sulfate which were released in the later stages of dissolution after the nitrate was removed.

The proportions of phosphate and sulfate released were greatly affected by the degree of ammoniation of the fertilizer. The behavior of fertilizer 250 approached that to be expected of a

mixture of ammonium sulfate and ammonium nitrate, with all the phosphate remaining in the fertilizer residue as basic calcium phosphates. Except with fertilizers 247 and 251, which were very acid, the solutions appeared to be buffered by the ammonium phosphate in the pH range 3.5 to 4.5, and the pH tended to rise slightly with increased ammoniation.

### Composition of Fertilizers

The compositions of the solutions released during the dissolution may be used to determine quantitatively some

of the compounds present in the original fertilizer that were identified petrographically or by x-ray. The data in Figure 1 are not, however, satisfactory for this purpose. Although the water was added to the fertilizer at a constant rate, the volumes of eluate collected at hourly intervals were not uniform, because some solution was trapped by the fertilizer in the early stages of leaching and subsequently released as the solid dissolved. To avoid this difficulty, a second set of dissolutions was made in which each fertilizer was leached with water at 1 ml. per hour for 24 hours, and the total eluate was analyzed. The results are shown in Table II.

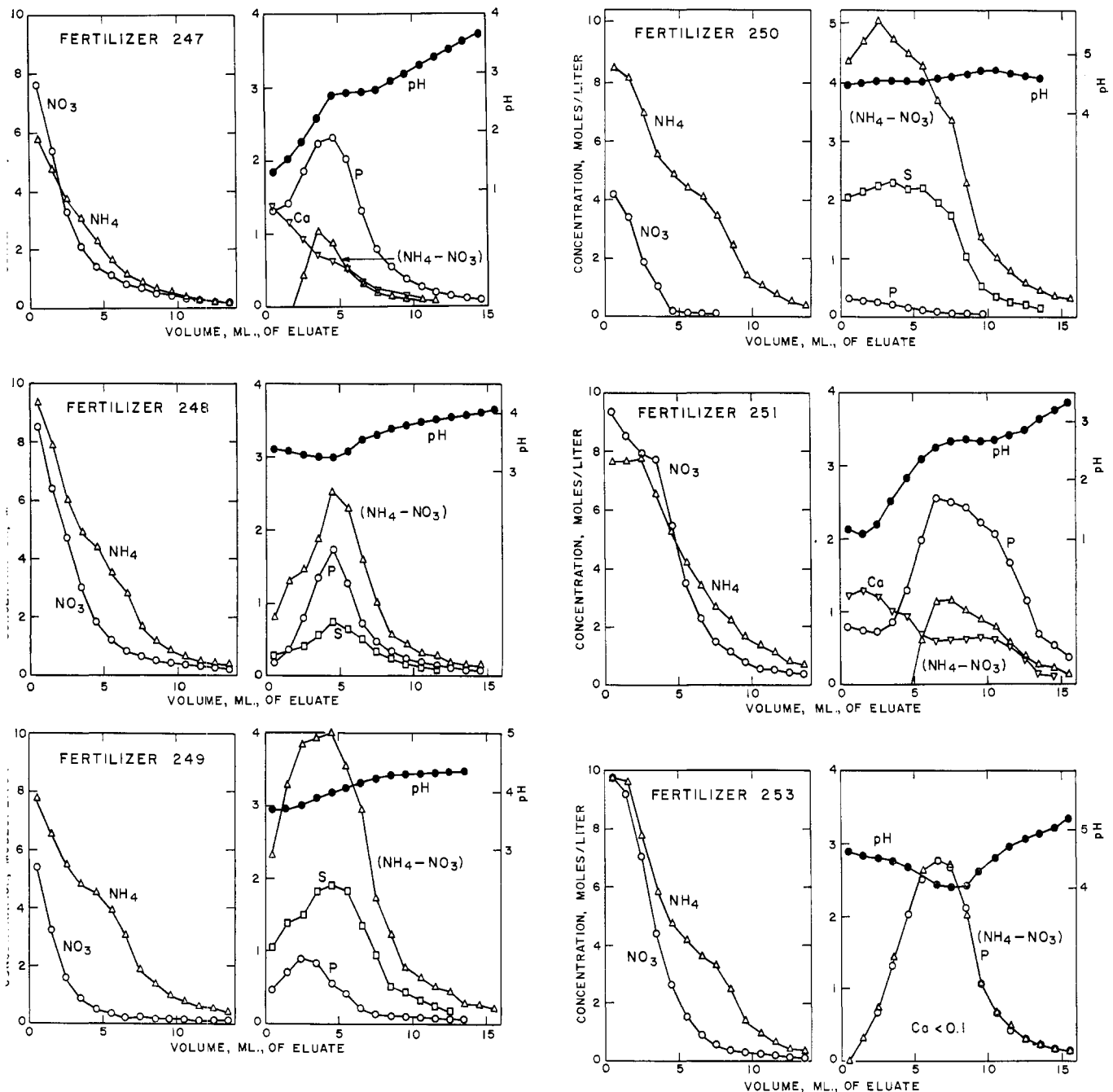


Figure 1. Dissolution of fertilizers

Ten-gram samples leached with 1 ml. of water per hour; receivers changed every hour

The salts identified in each fertilizer by x-ray diffraction are listed in Table III. The residues contained only gypsum and basic calcium phosphates as significant phases. In fertilizers 248, 249, and 250 the amounts of ammonium nitrate are given directly by the nitrate removed (Table II), and the remaining ammonium must therefore be combined with phosphate and sulfate. The amount of monoammonium phosphate corresponds to the phosphate released, and the ammonium sulfate is obtained by difference. In fertilizers 248 and 249, this ammonium sulfate is present entirely as ammonium syngenite,  $\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , and the remaining anhydrite can be estimated directly. Fertilizer 250 contains no free calcium sulfate, and the proportions of syngenite and free  $(\text{NH}_4)_2\text{SO}_4$  must be estimated from the soluble and total sulfate contents.

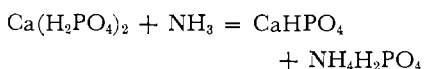
In fertilizer 247, which contains monocalcium phosphate, the excess of ammonium over nitrate represents monoammonium phosphate. The formation of  $\text{Ca}_2(\text{NH}_4)\text{H}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$  during the dissolution can be ignored, since this salt is unstable and hydrolyzes to dicalcium phosphate in the later stages of the dissolution.

Fertilizers 248, 249, 250, and 253 contain two forms of calcium phosphate. The amounts of each can be calculated on the assumption that they are dicalcium phosphate,  $\text{CaHPO}_4$ , and apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ . The mole fraction of dicalcium phosphate,  $D$ , in its mixture with apatite is calculated from the equation

$$D = (5R - 3)/(4R - 2)$$

in which  $R$  is the mole ratio of phosphorus to calcium in the water-insoluble portion of the fertilizer after allowance for any calcium present as sulfate. In fertilizer 251, which contains little or no apatite, a similar calculation can be made to apportion the phosphate between mono- and dicalcium phosphates.

When more than two calcium phosphates are present, as in fertilizer 247, the amounts of each cannot be calculated without further assumptions. If the dicalcium phosphate present was formed in the early stages of ammoniation by the reaction



the fertilizer must contain equivalent amounts of dicalcium and monoammonium phosphates. The remaining calcium and phosphate can then be apportioned between monocalcium phosphate and apatite.

The results of the calculations are shown in Table IV. On a percentage basis, the sums of the components are 86 to 94% of the total weight of the fertilizers. The remainder must consist

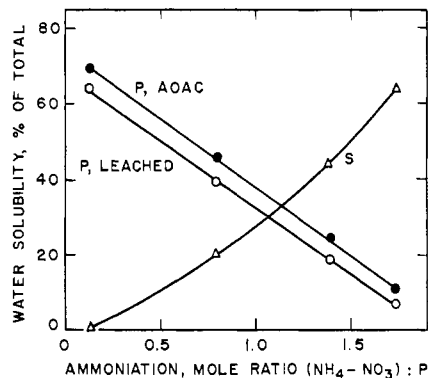


Figure 2. Effect of ammoniation on water solubility of phosphorus and sulfur in ordinary superphosphate

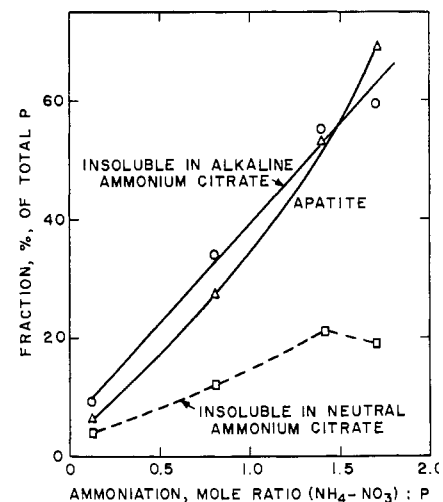


Figure 3. Effect of ammoniation on phosphorus in ordinary superphosphate

Table II. Compositions of Original Fertilizers and Amounts of Components Removed by Leaching

No.		Millimoles/10 Grams of Fertilizer					Degree of Ammoniation <sup>a</sup>
		NH <sub>4</sub>	NO <sub>3</sub>	P	Ca	S	
247	Total	28.5	25.7	22.6	40.7	26.1	0.12
	Removed	26.8	25.0	14.5	6.9	0.8	
248	Total	42.1	24.3	22.6	41.0	27.3	0.79
	Removed	39.3	25.0	8.9	1.0	5.5	
249	Total	47.7	13.7	24.2	44.3	30.7	1.40
	Removed	46.4	14.2	4.7	0.6	14.8	
250	Total	52.9	10.0	24.8	44.8	30.8	1.72
	Removed	50.0	10.0	1.8	0.6	19.7	
251	Total	55.0	56.0	33.9	19.0	0.8	0.00
	Removed	54.0	54.0	22.6	10.6	0.5	
253	Total	62.5	38.2	40.3	23.0	1.1	0.60
	Removed	62.5	37.5	18.5	2.5	1.0	

<sup>a</sup> Mole ratio  $(\text{NH}_4 - \text{NO}_3) : \text{P}$ .

Table III. Compounds Identified in Fertilizers by X-Ray Examination

Compound	Fertilizer <sup>a</sup>					
	247	248	249	250	251	253
NH <sub>4</sub> NO <sub>3</sub>	+	++	+	+	++	++
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	+	++	+	0	0	++
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0	0	0	++	0	0
CaSO <sub>4</sub>	++	++	+	0	0	0
Ca(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O	0	++	++	++	0	0
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	+	0	0	0	++	0
CaHPO <sub>4</sub>	+	+	0	0	+	+
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	+	+	+	+	0	+

<sup>a</sup> ++ = major phase, + = minor phase, 0 = absent.

of alumina, iron oxide, silica, water, fluorine, and conditioner, of which no account was taken, and some allowance must be made for experimental error, which may be more than 5% of each component.

#### Effects of Ammoniation

The effects of ammoniation are shown by the data in Table IV and Figure 2. The amount of phosphate dissolved

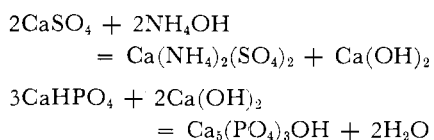
correlates well with the AOAC water-soluble phosphate—as a first approximation the water-soluble phosphate may be regarded as the monoammonium phosphate present. The water-soluble sulfate, however, is not directly correlated with the free ammonium sulfate because of the formation of syngenite,  $\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , which dissolves incongruently in water with precipitation of gypsum.

**Table IV. Calculated Compositions of Ammoniated Superphosphates**

No.	Composition, Millimoles/10 Grams of Fertilizer								
	$\text{NH}_4\text{NO}_3$	$\text{NH}_4\text{H}_2\text{PO}_4$	$(\text{NH}_4)_2\text{SO}_4$	$\text{CaSO}_4$	$\text{Ca}(\text{NH}_4)_2(\text{SO}_4)_2$	$\text{H}_2\text{O}$	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$\text{CaHPO}_4$	$\text{Ca}_3(\text{PO}_4)_2\text{OH}$
247	25	3.5	0	26	0	0	6.5	3.5	1.0
248	25	9	0	19	4	0	7.5	2.1	
249	14	5	0	2	15	0	6.6	4.5	
250	10	2	10	0	10	0	5.8	5.8	
251	54	0	0	1	0	16.4	1.0	0.0	
253	39	19	1	0	0	0	20 <sup>a</sup>	0.6 <sup>a</sup>	

<sup>a</sup> Without allowance for  $\text{Ca}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ .

The conversion of anhydrite to syngenite and ammonium sulfate during the ammoniation results in the formation of apatite. Although the reactions are complex, they may be represented as



The solubility product of calcium sulfate,  $a_{\text{Ca}} \cdot a_{\text{SO}_4}$ , shows that the decomposition of gypsum or anhydrite is independent of pH. The solubility product of apatite,  $a_{\text{Ca}}^5 \cdot a_{\text{H}_2\text{PO}_4}^3 / a_{\text{H}^+}^7$ , indicates that the limiting calcium ion concentration above which it will form decreases rapidly with rising pH. Thus, although calcium sulfate and monoammonium phosphate may be a stable salt pair at low degrees of

ammoniation, there is a critical level of ammoniation above which calcium sulfate acts as a continuous source of calcium for the formation of the more basic phosphate.

The effect of ammoniation on the composition of the water-insoluble phosphates in ammoniated ordinary superphosphate is shown in Figure 3. There is good correlation between the amount of phosphate calculated to be present as apatite and the fraction that is insoluble in alkaline ammonium citrate solution, and either quantity can be used as an index of the degree of ammoniation of ammoniated ordinary superphosphate. The fraction of phosphate soluble in neutral ammonium citrate is much less significant. The discrepancies between solubilities in neutral and alkaline citrate solutions indicate that 60 to 70% of the

apatitic material is soluble in the neutral reagent.

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**FERTILIZER NUTRIENT RELEASE**

**Composition and Dissolution of Ammoniated Superphosphate Fertilizers Containing Potash**

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Potassium chloride added to superphosphate has little effect on the form of the phosphate when the mixture is ammoniated, but reacts with ammonium nitrate to form potassium nitrate and ammonium chloride. Ammoniation of mixtures of ordinary superphosphate and potassium chloride forms potassium syngenite,  $\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , and at high degrees of ammoniation as much as half the potassium is converted to this water-insoluble salt. When diammonium phosphate is the ammoniating agent, insoluble sulfates such as syngenite are dissolved. Ammoniation of concentrated superphosphates containing added potassium chloride yields monopotassium phosphate. Dissolution of potassium-containing ammoniated superphosphates releases solutions of ammonium and potassium phosphates with pH's in the range 2.5 to 4.5; the pH rises as the degree of ammoniation of the superphosphate is increased.

THE composition and dissolution of a series of ammoniated superphosphate fertilizers containing no potassium salts have been described (2). Similar studies were made of fertilizers prepared by ammoniating mixtures of superphosphate and potassium chloride.

The compositions of the fertilizers are shown in Table I. Fertilizers 302, 303,

199, and 304 were experimental TVA materials, field-tested as sources of phosphorus by Wright, Lancaster, and Anthony (3). Fertilizers F15 and T6 were domestic commercial products, and EA and EB were European commercial products.

The experimental procedure was the same as in the previous study (2). The

results of the fractional 1-hour elution experiments are presented in Figure 1; no fractional elutions were made of the European fertilizers. The amounts of the component elements removed in a single 24-hour elution are shown in Table II.

Comparison of the data in Figure 1 with those for comparable potassium-