

Calcium Ammonium and Calcium Potassium Pyrophosphate Systems

EARL H. BROWN, JAMES R. LEHR,
A. WILLIAM FRAZIER, and
JAMES P. SMITH

Division of Chemical Development,
Tennessee Valley Authority,
Wilson Dam, Ala.

Studies were made of the systems lime-ammonia-pyrophosphoric acid-water and lime-potash-pyrophosphoric acid-water at room temperature. All of the solid phases were among the crystalline pyrophosphates described previously. The pyrophosphate fractions of fertilizers prepared from condensed phosphates, such as superphosphoric acid and calcium metaphosphate, probably will consist of salts from this same group. The results of the studies will be useful in explaining the reactions involved in the preparation of these fertilizers and in identifying the components of the fertilizers and of the residues of the fertilizers after contact with soil.

AS THE USE of condensed phosphates, such as calcium metaphosphate and superphosphoric acid (5, 7), in fertilizers increases, larger amounts of pyrophosphates appear in the fertilizers and as products of the reactions of fertilizers with soil (3, 4). In laboratory study of the pyrophosphates, 25 calcium pyrophosphates were identified and described (7), and dimorphic forms of magnesium diammonium pyrophosphate tetrahydrate were identified.

All the 25 calcium pyrophosphates, particularly those containing ammonium or potassium, are stable, nonhygroscopic, crystalline solids, and some contain considerable amounts of phosphorus and nitrogen or potassium (7). Exploratory greenhouse tests showed some of the salts to be effective sources of plant nutrients, and the physical properties of the salts were satisfactory for use as fertilizers. In further investigation of these pyrophosphates, phase-diagram studies were made of portions of the systems lime-ammonia-pyrophosphoric acid-water, lime-potash-pyrophosphoric acid-water, and lime-pyrophosphoric acid-water to define the regions of stability of the different salts, to indicate methods for their preparation, and to identify the salts that might be prepared commercially or that might persist as significant phases in fertilizers produced from condensed phosphates.

The pyrophosphate ion hydrolyzes to orthophosphate in aqueous solution, and no true equilibrium in an aqueous pyrophosphate system can be obtained. The hydrolysis of pyrophosphate is most rapid at both low and high pH's, but at the intermediate pH's that existed in most of the experimental mixtures the rate of hydrolysis is low enough to permit establishment of a fairly steady state or quasi-equilibrium. This steady state persisted

long enough for the observed results to be applied with confidence to interpretation of the reactions of pyrophosphates in fertilizer processing operations and of their behavior in fertilizers when applied to the soil, at least during the first cropping season.

Procedure

The equilibration mixtures were prepared from laboratory preparations of calcium and potassium pyrophosphates (7), reagent-grade ammonium, potassium, and calcium hydroxide, and distilled water. Use of only these reagents limited considerably the regions of the four-component systems that could be investigated, but the reagents supplied soluble pyrophosphate without foreign ions so that steady-state conditions were approached rapidly in a pure system. The regions studied were those of most interest in fertilizer technology.

Proportions of reagents were selected to provide compositions of liquid phases distributed uniformly over the region to be studied. Only mixtures containing at least 80% water were suitable for examination; mixtures containing less than 80% water were semifluid pastes or gels. The mixtures were placed in glass bottles which were stoppered, shaken by hand periodically, and allowed to stand at room temperature (25° to 27° C.).

The pH of each mixture was measured with a Beckman Model H2 pH meter after 15 minutes, 1 and 4 hours, and 1, 4, 7, 14, and 30 days. Small amounts of the solid phases were examined petrographically after 1, 4, 7, and 30 days. The solid phases were examined in greater detail after 30 days, and x-ray diffraction examination was used to confirm identifications of phases present as particles too small for complete optical examination.

The liquid phases were analyzed chromatographically for ortho- and pyrophosphate (2) after 30 days; a few of the liquid phases were analyzed chromatographically again after 150 days to determine the extent of hydrolysis.

In both four-component systems, the greatest changes occurred in the first day. The pH approached its steady state asymptotically as metastable crystal species and unstable gels formed and redissolved. After 1 day, many of the mixtures contained small amounts of residual transient phases in addition to the major solid phase, but steady-state conditions usually were approached within 4 days, and crystallizations were virtually complete within 7 days. Significant changes between 7 and 30 days occurred only in a few mixtures in the potassium system.

Results

$\text{CaO}-(\text{NH}_4)_2\text{O}-\text{H}_2\text{P}_2\text{O}_7-\text{H}_2\text{O}$. The portion of the calcium ammonium pyrophosphate system studied was covered by 56 mixtures of calcium acid pyrophosphate, ammonium hydroxide, and water. Results of examinations of the mixtures after 1, 7, and 30 days are shown in Figure 1. The missing right-hand half of the isosceles triangle in each diagram is occupied by the rest of the field of $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ (AG).

The extension of the field of $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ (AB) above 95% water presents an anomaly, for in this area $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$ was expected to appear. The crystals of $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ formed in mixtures containing more than 95% water were of the usual crystalline form but had epitaxial overgrowths of a dimorphic form of closely related symmetry. The

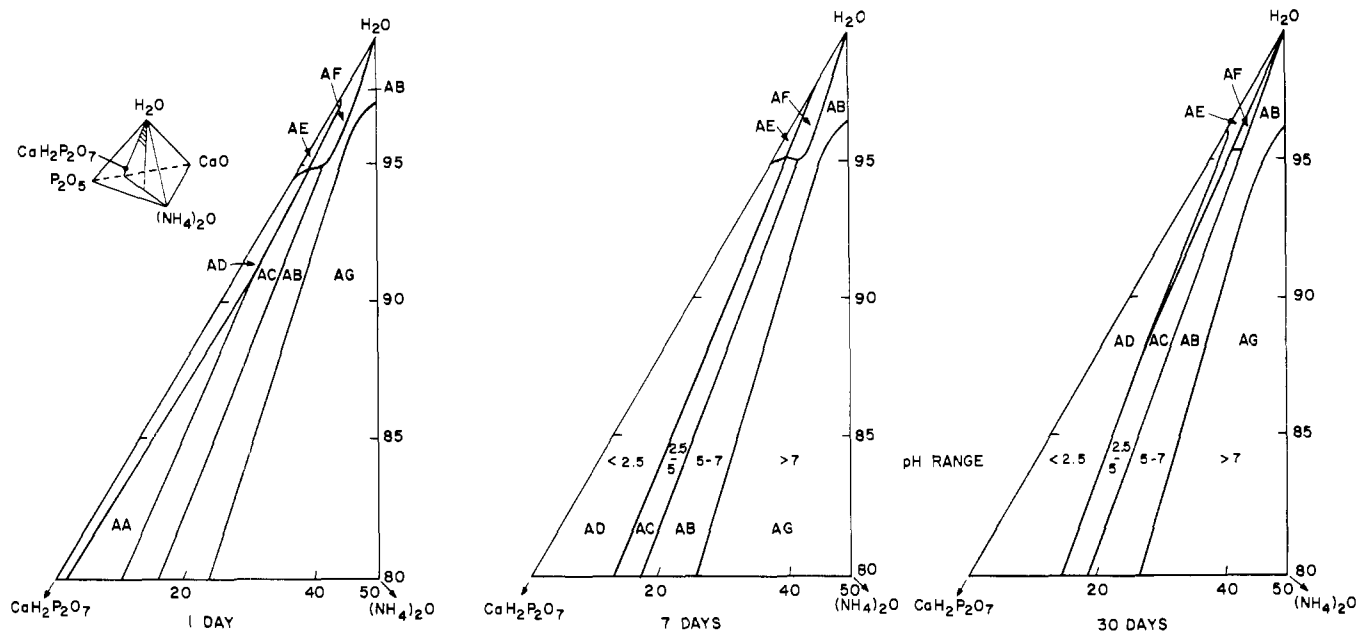


Figure 1. The section $\text{CaH}_2\text{P}_2\text{O}_7\text{--}(\text{NH}_4)_2\text{O--H}_2\text{O}$ of the system $\text{CaO--}(\text{NH}_4)_2\text{O--H}_3\text{P}_2\text{O}_7\text{--H}_2\text{O}$ at room temperature

- AA = $\text{Ca}_2\text{NH}_4\text{H}_3(\text{P}_2\text{O}_7)_3 \cdot 3\text{H}_2\text{O}$
 AB = $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$
 AC = $\text{CaNH}_4\text{HP}_2\text{O}_7$
 AD = $\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$
 AE = $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (triclinic)
 AF = $\text{Ca}_3\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ (orthorhombic)
 AG = $\text{Ca}(\text{NH}_3)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$

Table I. Optical Properties of the Two Forms of $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$

Property	$\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$	Dimorph, Epitaxial Growth
Crystal symmetry	Monoclinic	Monoclinic
Optic sign	Biaxial (-)	Biaxial (+)
N_α	1.520	1.527
N_β	1.528	1.533
N_γ	1.531	1.539
Optic axial plane	(010)	(010)
$2V$	61°	89°
Extinction:	27° in acute	45° in acute
$N_\alpha \wedge c$	β	β
Monoclinic beta	110.5°	110.3°
(012) \wedge (100)	120°	120°
(011) \wedge (100)	138°	138°

two forms can be distinguished only by the small differences in their optical properties—the compositions of both forms, as determined by chemical analysis of crystals containing 0, 50, and 80% of the overgrowth form, are exactly that of $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$. Spectrographic examination showed no difference in chemical composition between the two forms. In keeping with their closely related symmetries, their x-ray diffraction spectra are nearly identical and differ only in slight displacements of a few lines and small changes in intensities.

This unusual mixture of two crystal

forms is an indication of a metastable condition, and it is presumed that $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$ would eventually form in this region. Mixtures containing the two forms of $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$ showed no change, however, in the 150 days they were observed.

$\text{CaO--K}_2\text{O--H}_3\text{P}_2\text{O}_7\text{--H}_2\text{O}$. The portion of the calcium potassium pyrophosphate system studied was covered by 48 mixtures of calcium acid pyrophosphate, tetrapotassium pyrophosphate, potassium hydroxide, and water. Results of examinations of the mixtures after 1, 7, and 30 days are shown in Figure 2.

$\text{CaO--H}_4\text{P}_2\text{O}_7\text{--H}_2\text{O}$. Studies were made of a portion of the ternary calcium pyrophosphate system at room temperature, 50° , 75° , and 100°C .

At room temperature, three solid phases appeared. $\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ was present in all mixtures that contained less than about 95% water; the triclinic dimorph of $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ occupied the region between 95 and 98% water, and the orthorhombic dimorph of $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ occupied the region above 98% water. Between 7 and 30 days, however, the tetrahydrate was replaced gradually by the triclinic dihydrate.

At 50°C ., $\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ was present in all mixtures containing less than 90% water, and triclinic $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ was present in all mixtures containing more than 90% water.

Equilibrations at 75°C . were made for 7 days. In mixtures containing less than 90% water, $\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ was

formed initially, but this was replaced by its monohydrate, $\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot \text{H}_2\text{O}$, within 2 days. Triclinic $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ was present in all mixtures containing more than 90% water.

In equilibrations at 100°C ., any $\text{Ca}_3\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ that was formed initially or added as a starting material was hydrolyzed to $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{CaH}_2\text{P}_2\text{O}_7$ within a few hours. Triclinic $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ persisted as a solid phase in all mixtures, however, probably because of its low solubility.

Discussion

Although the present study was concerned with only mixtures that contained at least 80% water, results of other investigations showed that many of the same salts appeared as stable phases in more concentrated mixtures also. The principal difference resulting from increase in concentration is that the additional salts that appear in the more concentrated mixtures are the more acidic, highly water-soluble compounds of the group of 25 pyrophosphates (7).

In both the ammonium and potassium systems at room temperature, pyrophosphate was the predominant phosphate ion after 30 days, although small but significant amounts of orthophosphate appeared in the solutions in the most concentrated and acidic regions of both systems. The amounts of orthophosphate in the ammonium system appeared to be somewhat larger than those in the corresponding portions of the potassium

system. In neither system, however, was a solid orthophosphate formed.

Of the eight known calcium ammonium pyrophosphates (7), only three— $\text{CaNH}_4\text{HP}_2\text{O}_7$ (AC), $\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$ (AB), and $\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$ (AG)—are stable enough to be considered as fertilizer materials. The other ammonium compound, $\text{Ca}_2\text{NH}_4\text{H}_3(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ (AA), with a region of its own in Figure 1, disappeared within 7 days.

Of the 10 known calcium potassium pyrophosphates (7), nine appear in Figure 2. Of these, however, only five have properties that make them potential fertilizer materials— $\text{Ca}_2\text{KH}_3(\text{P}_2\text{O}_7)_2 \cdot 3\text{H}_2\text{O}$ (KA), $\text{Ca}_3\text{K}_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$ (KC), $\text{CaK}_2\text{P}_2\text{O}_7$ (KG), CaKHP_2O_7 (KH), and $\text{CaK}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ (KM). The other five are either metastable or difficult to prepare commercially. One of the promising compounds, $\text{CaK}_2\text{P}_2\text{O}_7$, has been prepared at TVA by a fusion process, but it has not been reported before as a component of an aqueous system. Its tetrahydrate, $\text{CaK}_2\text{P}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$, is dehydrated rapidly to $\text{CaK}_2\text{P}_2\text{O}_7$ at 250° to 300°C .

Steady state, or quasi-equilibrium, was attained more rapidly in the ammonium than in the potassium system. Most of the changes in the ammonium system took place in the first 7 days, whereas in the potassium system marked changes occurred in mixtures in some regions throughout the 30-day equilibration period. There is, however, considerable similarity in the nature and field boundaries of the solid phases in the two systems—for example, pairs of ammonium and potassium analogs, AA and KA, AB and KL, AC and KH, AG and KG, are formed under similar conditions of concentration and pH.

In the early stages of equilibration, the region of each salt appeared to be a function of composition. After 1 or 2 days, however, the boundaries of the fields tended to become lines of constant pH, an effect that is apparent in the 30-day diagrams in Figures 1 and 2.

Results of the study of the ternary system $\text{CaO}-\text{H}_4\text{P}_2\text{O}_7-\text{H}_2\text{O}$ support the conclusion (7) that of the two pairs of dimorphs of hydrated calcium pyrophosphate, the triclinic dihydrate and the orthorhombic tetrahydrate are the more stable dimorphs. The acid salt $\text{CaH}_2\text{P}_2\text{O}_7$ dissolves incongruently in water and forms either $\text{Ca}_2\text{H}_2(\text{P}_2\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ or its monohydrate, depending on the temperature. The tetrahydrate is quite stable, and in mixtures in which it appeared as the equilibrating phase at room temperature, it persisted for the 150 days the mixtures were observed.

Behavior in Soil. In an exploratory study of the agronomic value of the pyrophosphates, several of the salts were evaluated as sources of phosphorus, nitrogen, and potassium by the short-term

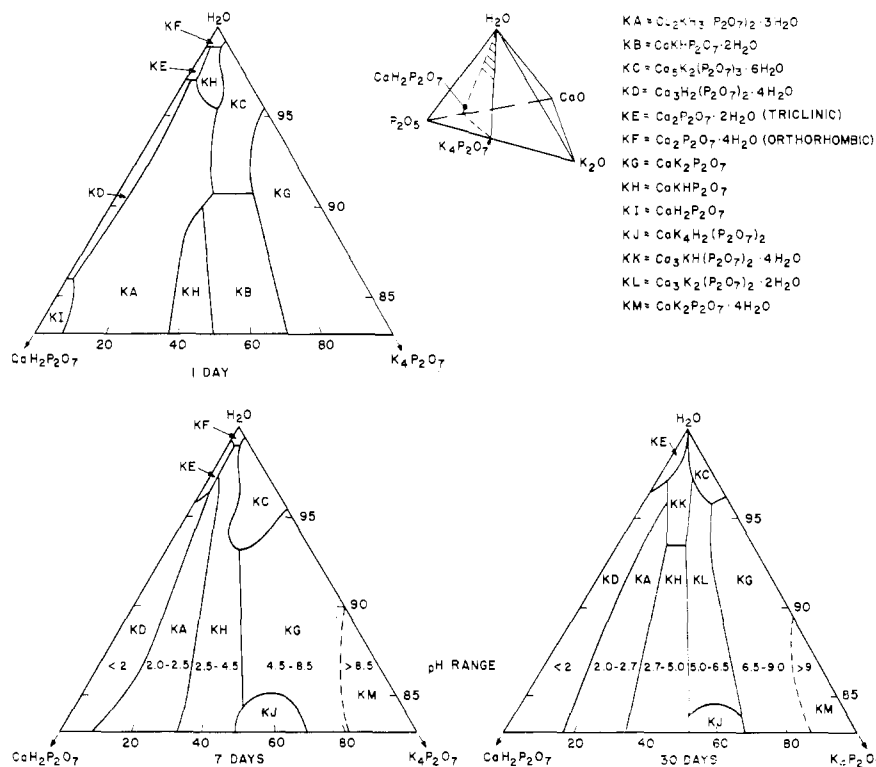


Figure 2. The section $\text{CaH}_2\text{P}_2\text{O}_7-\text{K}_4\text{P}_2\text{O}_7-\text{H}_2\text{O}$ of the system $\text{CaO}-\text{K}_2\text{O}-\text{H}_4\text{P}_2\text{O}_7-\text{H}_2\text{O}$ at room temperature

Table II. Most Promising Fertilizer Materials

Compound	Composition, %		
	N	P (P_2O_5)	K (K_2O)
$\text{Ca}(\text{NH}_4)_2\text{P}_2\text{O}_7 \cdot \text{H}_2\text{O}$	10.4	23.1 (52.9)	...
$\text{CaNH}_4\text{HP}_2\text{O}_7$	6.0	26.6 (60.9)	...
$\text{Ca}_3(\text{NH}_4)_2(\text{P}_2\text{O}_7)_2 \cdot 6\text{H}_2\text{O}$	4.6	20.3 (46.4)	...
$\text{CaK}_2\text{P}_2\text{O}_7$...	21.2 (48.6)	26.7 (32.2)
CaKHP_2O_7	...	24.4 (55.9)	15.4 (18.5)
$\text{Ca}_3\text{K}_2(\text{P}_2\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$...	20.5 (46.9)	8.6 (10.4)

uptake method of Stanford and DeMent (6). This method has value only as a rough screening technique, but the results showed that some of the pyrophosphates may be suitable sources of phosphorus and that some of the ammonium and potassium salts were quite effective sources of nitrogen and potash, respectively.

Results of a conventional greenhouse test of several of the pyrophosphates and of a petrographic study of their alterations in the soil will be published shortly.

The short-term uptake tests ran for 17 days, and 30 days later the fertilizer residues in each pot were examined petrographically. Except for the water-soluble calcium acid pyrophosphate, $\text{CaH}_2\text{P}_2\text{O}_7$, the residues were solution-eroded crystals of the original salts. The pyrophosphates thus supplied nutrients during these short-term tests by simple dissolution. This behavior is in marked contrast to that of calcium orthophosphates which dissolve and reprecipitate

part of the phosphorus in a less available form (4).

Conclusions

The results of the equilibration studies show that the 25 pyrophosphates previously described (7) probably include all the important pyrophosphates that contain calcium and ammonium or potassium. The phase diagrams in Figures 1 and 2 explain the methods of preparation of the different pyrophosphates (7) and suggest alternate methods for some. The results show also that, under the experimental conditions, the hydrolysis of pyrophosphate to orthophosphate is so slow that this hydrolysis is not expected to be significant in either laboratory studies of the compounds or in the preparation of fertilizers containing them.

Of the compounds studied, the six in Table II appear the most promising as fertilizer materials.

Literature Cited

- (1) Brown, E. H., Lehr, J. R., Smith, J. P., Frazier, A. W., *J. Agr. Food Chem.* **11**, 214 (1963).
- (2) Karl-Kroupa, E., *Anal. Chem.* **28**, 1091 (1956).
- (3) Lindsay, W. L., Frazier, A. W., Stephenson, H. F., *Soil Sci. Soc. Am. Proc.* **26**, 446 (1962).
- (4) Lindsay, W. L., Taylor, A. W., *Trans. Intern. Cong. Soil Sci., 7th, Madison, Wis., 1960* **3**, 580 (1961).
- (5) Siegel, M. R., Getsinger, J. G., Mann, H. C., *J. Agr. Food Chem.* **10**, 72 (1962).
- (6) Stanford, G., DeMent, J. D., *Soil Sci. Soc. Am. Proc.* **21**, 612 (1957).
- (7) Young, R. D., Heil, F. G., Phillips, A. B., *J. Agr. Food Chem.* **9**, 4 (1961).

Received for review February 11, 1963.
Accepted April 21, 1963.

FERTILIZER TECHNOLOGY

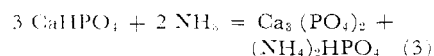
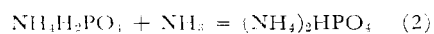
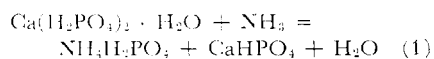
A Study of Ammoniation Reactions in a Fluidized Bed of Superphosphate

LYLE F. ALBRIGHT,
HANS HAUG,¹ and
K. S. ANANTHA RAMAN²
School of Chemical Engineering
Purdue University,
Lafayette, Ind.

Superphosphate fertilizers were ammoniated with anhydrous ammonia in a fluidized-bed reactor over wide ranges of operating variables to obtain products containing up to 9.7% (by weight) ammonia. The results show that the chemical reactions are probably occurring predominantly in the liquid phase present in or on the fertilizer granules. Free moisture contents of the fertilizer of about 0.6 to 15% are preferred; lower contents result in slow ammoniation and higher amounts cause agglomeration. Phosphate reversion was very low and relatively independent of operating conditions.

AMMONIATION of superphosphates is one of the most important operations in the fertilizer industry. Much of its commercial success has resulted from the pioneering work done by the Tennessee Valley Authority, which developed the drum-type ammoniator for industrial application. Ammoniation is a highly complex process, and some of the observations and difficulties arising during operation are not easily explained. At the present time, two of the principal problems are the reversion of phosphates, i.e., the formation of insoluble phosphorus compounds, and the loss of nitrogen during ammoniation and possibly subsequent storage. These difficulties become more severe with increasing degree of ammoniation, i.e., increasing amount of ammonia absorbed per unit mass of superphosphate (7).

The principal reactions occurring during ammoniation of triple superphosphate are as follows (9):



¹ Present address: Engineering Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

² Present address: Rose Polytechnic Institute, Terra Haute, Ind.

Several side reactions may also occur involving impurities such as fluorides, sulfates, plus iron and aluminum salts. The reactions appear to be ionic in character, but little or no discussion has been found in the literature on the mechanism of these reactions.

The rate and extent of the chemical reactions are governed chiefly by tem-

perature, activity of the ammonia, porosity and particle size of the superphosphate, and moisture content. Kumagai *et al.* (7) have studied the effects of these variables on the ammoniation of superphosphate fertilizer in a small, drum-type reactor. Rotating drums are currently used in the great majority of all commercial ammoniating

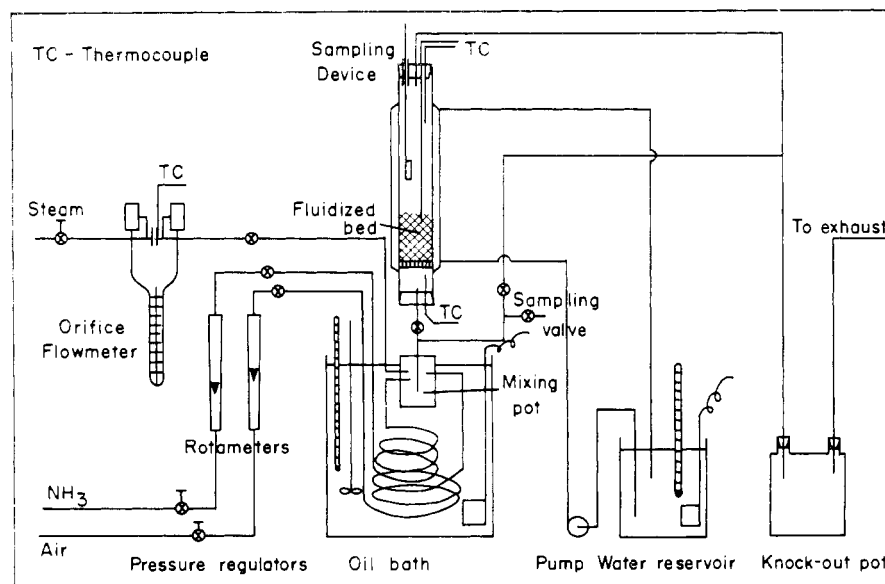


Figure 1. Flowsheet for fluidized-bed ammoniator