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RECENT DEVELOPMENTS IN PHOSPHATE FERTILIZER TECHNOLOGY

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Advances in phosphate fertilizer technology have resulted in the development of several new products in recent years. While these products have higher fertilizer grades or superior handling characteristics, they generally have not been superior to the superphosphates with regard to crop response per unit of applied P.

Use of ammonium phosphates, both monoammonium phosphate and diammonium phosphate, as well as ammoniated superphosphates has increased rapidly since 1950. Commercial production of ammonium polyphosphates is perhaps the most important technological development of the past decade. This has resulted in large-scale use of fluid fertilizers in the United States. In 1972 about 17% of the mixed fertilizers was applied as solutions or suspensions. Other new products are essentially granulated mixtures of several existing fertilizer compounds. These are urea-ammonium phosphate, ammonium phosphate sulfate, and ammonium phosphate nitrate. A decrease in use of normal and concentrated superphosphates has accompanied the increase in use of ammonium phosphates in many countries. Some of the most common commercial phosphate fertilizers are listed in Table 1

New Phosphate Fertilizers

Ammonium polyphosphate is the only really new fertilizer which is being produced on a commercial scale. The term polyphosphate is used to denote materials containing phosphates which are more condensed than orthophosphates. Condensation occurs when water is driven off and two molecules of orthophosphate combine to form pyrophosphate (Fig. 1). Longer chain polyphosphates are formed by further condensation. Polyphosphate fertilizers are produced from superphosphoric acid which was developed at TVA. Much of the research and development work on the polyphosphates has been done in the TVA laboratories and pilot plants. Recent development of the pipe reactor process has resulted in increased polyphosphate contents of fluid fertilizers as well as cheaper investment costs.

Ammonium polyphosphate fertilizers contain 40 to 80% of their P as polyphosphates, depending on the polyphosphate content of the superphosphoric acid base solution; the remainder is orthophosphate (5). The principal polyphosphate fertilizer is 10-34-0, a solution, but suspension fertilizers of higher grades are also produced. TVA has produced a granular ammonium polyphosphate, 15-62-0, which is mainly used for manufacture of fluid fertilizers. The higher analyses result in lower shipping costs as compared with fluid fertilizers. Potassium polyphosphates with grades as high as 0-50-40 are now being made commercially in the U.S. (1).

Results of many greenhouse and field experiments have shown little or no consistent agronomic advantage of polyphosphate fertilizers over ammonium orthophosphates when rates and placement are similar. A summary of results from six TVA greenhouse experiments is shown in Table 2.

In five experiments the polyphosphates were superior to orthophosphates, while the reverse was found in the sixth experiment. The reasons for these small differences in agronomic effectiveness are not known.

Polyphosphates hydrolyze to orthophosphates in soils, the rate of hydrolysis being higher in soils with high biological activity. Results of laboratory experiments have shown that as much as half of the polyphosphate applied to soils hydrolyzed within two weeks. Hydrolysis is the reverse reaction of the equation shown in Fig. 1. Because about half of the P in polyphosphate fertilizers is initially in the orthophosphate form and because of the rather rapid hydrolysis of polyphosphates in soils, it is not surprising that availability of P to plants is similar with both ortho- and polyphosphate fertilizers.

Polyphosphates have the ability to maintain much higher concentrations of Zn, Fe, Mn, and other metallic ions in solution (sequestration) than do orthophosphates. The higher solubility of Zn and Fe makes polyphosphates more effective carriers of these micronutrients. Claims have been made that polyphosphates may also sequester micronutrients in the soil, thereby making them more available to plants. However, research data show that the level of micronutrients in the soil solution is not affected for more than one day after polyphosphate applications. Therefore this sequestering action is not of much practical importance in soils.

Granular urea-superphosphate mixtures can be produced in conventional granulation plants to yield products which have satisfactory storage and handling characteristics (2). Urea reacts with superphosphate to form a urea-monocalcium phosphate adduct which is detrimental to the physical condition of the fertilizer. Formation of this adduct can be

avoided by limiting the formulation to less than 25% urea, adding diammonium phosphate to neutralize the free acidity in the superphosphate, adding ammonium sulfate, and controlling heat and moisture inputs in the process. Hydrolysis of urea from excessive heat results in a decrease in water solubility of the P. Typical fertilizer grades which can be formulated in this process are 15-15-15 and 10-20-10 (6).

Agronomic effectiveness of N or P in the above mixtures is equivalent to that of each component applied alone. Under some conditions crop response to P in the mixture may be lower if the level of water-soluble P has been appreciably decreased in the manufacturing process.

Rock phosphate has been used to supply P for crops for 150 years. Plant availability of P varies with the deposit and fineness of grinding of the rocks as well as soil properties and the crop species. Some rock phosphates are quite effective on acid soils. Citrate solubility of P in rock phosphates is closely related to the degree of substitution of carbonates and other ions in the apatite structure (4). Plant availability of P in rock phosphates is also correlated with citrate solubility (8). Dry matter production and P uptake by rice increased with increasing citrate solubility of P in phosphate rocks obtained from various locations (Table 3). Thus, the geographic origin and chemical characteristics of rock phosphate are very important in determining its agronomic value.

Rock phosphates acidulated with less than the stoichiometric amount of acid in the manufacturing process have been suggested for use in some areas. If effective for crops, this would result in lower production costs. Research results have shown that these granular products are not as effective as fully acidulated superphosphate, except on very

acid soils (7). Under these conditions the unacidulated products would also be effective. Therefore, partially acidulated rock phosphates have not proved to be competitive with other products.

Urea-phosphate rock mixtures are being considered as a relatively cheap product which can be applied to acid soils in granular form (6). Urea is the granulating medium for finely ground phosphate rock. Dissolution of urea allows disintegration of the granules to expose more surface area of the phosphate rock after soil application. Agronomic effectiveness of P in this product depends on the distribution in the soil as well as reactivity of the phosphate rock. Obviously this product may not be as effective as finely ground phosphate rock mixed alone with soil. Yet, the superior storage and handling characteristics of the granular product may make granular urea-phosphate rock a satisfactory fertilizer for use in the tropics, especially for rice. Application of a granular product is much more convenient than finely ground phosphate rock.

Ultra-high-analysis compounds are being studied as potential fertilizers by TVA. The highest fertilizer grade of diammonium phosphate is now 18-46-0. The limiting grade for ammonium phosphate is 14-73-0, which would be produced by condensation of linear polyphosphates or by conversion to cyclic metaphosphates. Beyond this limit, radically different types of compounds such as those with covalent P-N-P bonds with little or no oxygen would be required. The N in these compounds would be present as amides and imides rather than the ammonium form. Many of these compounds have been tested under greenhouse conditions (10). The most promising compounds are phosphonitrilic hexaamide monohydrate, $P_3N_3(NH_2)_6 \cdot H_2O$, which

has a grade of 50-85-0 and phosphoryl triamide (44-75-0). It should be emphasized that these compounds are only in the developmental stage. Large-scale manufacturing processes of these compounds have not been developed so economics of their use cannot be estimated. Because of their higher analyses, they offer promise as fertilizers for the future.

Water Solubility in Phosphate Fertilizers

A maximum of about 25-30% of the P applied to soils is recovered by the first crop, even under ideal conditions. The remainder is "fixed" in forms in the soil which are slowly available to succeeding crops.

The relationship between crop response and the level of water-soluble P in fertilizers depends on several factors. Water-soluble phosphates react rapidly with soil constituents to form less-soluble compounds. Aluminum and iron phosphates form in acid soils, while calcium phosphates usually form in neutral to calcareous soils.

Reactions of fertilizers in soils have been studied extensively by TVA and others (3). Many reaction products have been identified and several properties of these products have been determined. The level of water-soluble P in these compounds varies somewhat, although it is generally quite low. Crop response to two water-soluble phosphate fertilizers applied to the same soil may not be the same, depending on the nature of their reaction products.

Water-soluble phosphates diffuse much farther in soil than water-insoluble phosphates; therefore, a greater volume of soil is affected by water-soluble phosphates. This increases the probability of plant root interception of soil affected by fertilizer phosphate. Early crop response is usually greater from water-soluble phosphates when root distribution is

limited. This is very important with short-season crops, such as vegetables, when they are planted on phosphorus-deficient soils.

Phosphates of low water solubility dissolve faster when more surface area comes into contact with the soil. Broadcast applications of these materials are usually more effective than banding. Finely ground materials low in water-soluble P are more effective than granular products for the same reason. In contrast, band application of water-soluble phosphate fertilizers decreases the surface area and reduces the amount of fixation in acid soil.

Because of the wide variation in soils and crop species planted in Colombia, crop response to various phosphate fertilizers can be greatly affected by their level of water-soluble P. Placement of these fertilizers also may greatly change their relative effectiveness under varying soil conditions and for various crops.

Evaluation of Fertilizers

A discussion of new fertilizers should also include methods for evaluation of such products. Because soil-fertilizer reactions are so varied, new fertilizers should be compared with those presently used before recommendations are made.

Fertilizer evaluations are either for research or demonstration purposes. Replicated treatments in a proper experimental design are required to obtain research data. Two requirements needed to obtain research data on phosphate fertilizers are (a) more than one nonzero P rate should be applied and (b) all nutrients other than P must be applied to the soil in nonlimiting amounts. Principles and methods of fertilizer evaluation

are well described in a TVA bulletin by Terman and Engelstad (9). Crop yields and nutrient uptake are criteria generally used to evaluate fertilizers. Agronomic effectiveness of phosphate fertilizers was recently reviewed by Terman (7).

Demonstrations are used to introduce new fertilizers to farmers or to the fertilizer industry. Treatments may not be replicated in demonstrations. The new fertilizers should be compared with commonly used fertilizers at the same P rate (or rates) and with the same type of placement. If new application methods are being demonstrated, the old methods should be included for a direct comparison. Fertilizer demonstrations which are not carefully conducted are of little or no value. They may even be detrimental in introducing a new product or practice.

Summary

While several new phosphate fertilizers have been developed in recent years, none of these products is clearly superior to the superphosphates in terms of agronomic response. Their main advantages lie in better handling characteristics, higher analyses, more convenience, and more choices of products. Some of these newer products have not been evaluated under tropical conditions and comparisons with the superphosphates should be made.

Efforts to improve physical properties of fertilizers have resulted in granular products which are free flowing and easier to apply. The bulk shipment of solid fertilizers and subsequent blending to obtain desired mixed grades is increasing. Fluid fertilizers are also well

adapted to handling and field application by mechanized, labor-saving methods.

Development of high-analysis fertilizers has resulted in decreased transportation costs per unit of plant food. These high-analysis materials have a very low sulfur content and in some instances additional sulfur may be required for optimum crop production. Granular mixtures of urea and certain P sources result in higher N-P grades. Effectiveness of N and P in urea-ammonium ortho- or polyphosphate mixtures is similar to that when the components are applied separately. Mixtures containing urea and superphosphates usually have undesirable physical properties unless formulations are carefully controlled.

Production of polyphosphate fertilizers based on superphosphoric acid is probably the most important development in phosphate fertilizer technology in recent years. Fluid ammonium polyphosphate fertilizers, both solutions and suspensions, are now used in many areas. These products are quite versatile and many mixed grades can be produced. Micronutrients and various herbicides or pesticides may be mixed with fluid fertilizers and applied to soil.

Rock phosphates, varying widely in citrate solubility and geographic origin, have been tested as P sources in acid soils in a number of tropical countries. Results show that effectiveness of P in rock phosphates for plants was directly related to their citrate solubility, which is in turn closely correlated with the chemical nature of their apatitic mineral structure. However, the most effective rock phosphates were not quite equal to superphosphate in terms of yield response.

Ultra-high-analysis fertilizers containing up to 55% N and 40% P (92% P_2O_5) are under laboratory and greenhouse investigation. Covalent

P-N bonds and P-N-P linkages in certain compounds result in nutrient contents more than twice those now in commercial use. Several of these compounds have been shown to be effective sources of N and P. However, economic production of these products has not yet been developed.

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Table 1. Compounds present in P, NP, and PK commercial and experimental fertilizers (9).

Fertilizer material	Representative grades % N-P_2O_5-K_2O	Water solubility of P, (%)	Major compounds present
P Sources			
Phosphoric acid:			
Wet-process	0-55-0	100	H_3PO_4
Furnace grade	0-55-0	100	H_3PO_4
Super acid	0-79-0	100	H_3PO_4, polyphosphoric acids
Superphosphate:			
Ordinary (H_2SO_4)	0-20-0	85	$Ca(H_2PO_4)_2 \cdot H_2O$, $CaSO_4 \cdot 2H_2O$
Triple (WP H_3PO_4)	0-45-0	87	$Ca(H_2PO_4)_2 \cdot H_2O$
High-anal. (super acid)	0-54-0	90	$Ca(H_2PO_4)_2$
Dicalcium phosphate:			
HCl process	0-40-0	4	$CaHPO_4 \cdot 2H_2O$, $CaHPO_4$
Electric furnace H_3PO_4	0-48-0	3	$CaHPO_4$, $CaHPO_4 \cdot 2H_2O$
Calcium metaphosphate	0-62-0	5	Vitreous Ca polyphosphate, $Ca_2P_2O_7$

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Table 1 (continued).

Fused tricalcium phosphate	0-28-0	< 2	Alpha and Beta $Ca_3(PO_4)_2$
Rhenania phosphate	0-33-0	< 2	Ca silico-phosphates
Serpentine phosphate glass	0-22-0	< 2	Ca Mg silico-phosphates
Basic slag	0-9-0	< 2	Ca silico-carnotite
Colloidal "clay" phosphate	0-22-0	< 1	Apatite, Al phosphates
Florida phosphate ore	0-32-0	< 1	Carbonato apatite
NP and PK Sources			
Ammoniated ordinary superphosphate	4-14-0	35	$NH_4H_2PO_4$, $CaHPO_4$, reprecipitated apatite, $CaSO_4 \cdot 2H_2O$
Ammoniated concentrated superphosphate	5-47-0	50	$NH_4H_2PO_4$, $CaHPO_4$, $(NH_4)_2HPO_4$, reprecipitated apatite
	9-48-0	50	
Ammonium phosphate nitrate	30-10-0	100	$NH_4H_2PO_4$, NH_4NO_3, $(NH_4)_2HPO_4$
	25-25-0	100	
	28-14-0	100	
Ammonium phosphate sulfate	11-48-0	> 90	$NH_4H_2PO_4$, $(NH_4)_2SO_4$
	13-39-0	> 90	
	16-20-0	> 90	
	16-48-0	90	$NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$

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Table 1 (continued).

Diammonium phosphate	21-53-0	100	$(NH_4)_2HPO_4$
	18-46-0	> 95	
Ammonium polyphosphate	15-60-0	100	$NH_4H_2PO_4$, $(NH_4)_3HP_2O_7$, longer chain polyphosphates
Urea ammonium phosphate	34-17-0	100	$CO(NH_2)_2$, $(NH_4)_2HPO_4$
	29-29-0	100	
	25-35-0	100	
Urea ammonium polyphosphate	36-18-0	100	$CO(NH_2)_2$, $(NH_4)_3HP_2O_7$, $NH_4H_2PO_4$
	30-30-0	100	
	22-44-0	100	
Nitric phosphate	20-20-0	40	$CaHPO_4$, $NH_4H_2PO_4$, $Ca(NO_3)_2$, reprecipitated apatite
Potassium polyphosphate	0-50-40	5	K polyphosphates

Table 2. Apparent recovery of phosphorus from granular phosphate fertilizers by corn grown in greenhouse pots (7).

Experiment No.	Soil pH	Apparent P recovery, %*		
		CSP	MAP	APP
1	6.0	21	21	24
2	6.2	20	23	24
3	6.3	17	21	24
4	6.5	28	29	30
5	7.0	19	25	18
6	8.0	16	20	21
Mean	-	20	23	23

*Slopes from least-squares calculations relating P uptake to multiple rates of P applications. CSP = concentrated superphosphate, MAP = monoammonium phosphate, and APP = ammonium polyphosphate.

Table 3. Response of flooded rice to phosphorus in rock phosphates varying in citrate solubility (8).

P source*	Citrate-soluble P, % of total P	Yield of dry matter,† g/pot	P uptake, mg/pot
CSP	100	64	69
North Carolina PR	24	62	51
Gafsa PR	21	64	53
Florida PR	15	50	38
Morocco PR	11	48	34
Togo PR	9	45	34
Quebec PR	6	38	32
Check	-	36	28

*Concentrated superphosphate (CSP) was granular, all phosphate rocks (PR) were -200 mesh; P application rate was 40 ppm.

†Yield of rice grain plus straw.

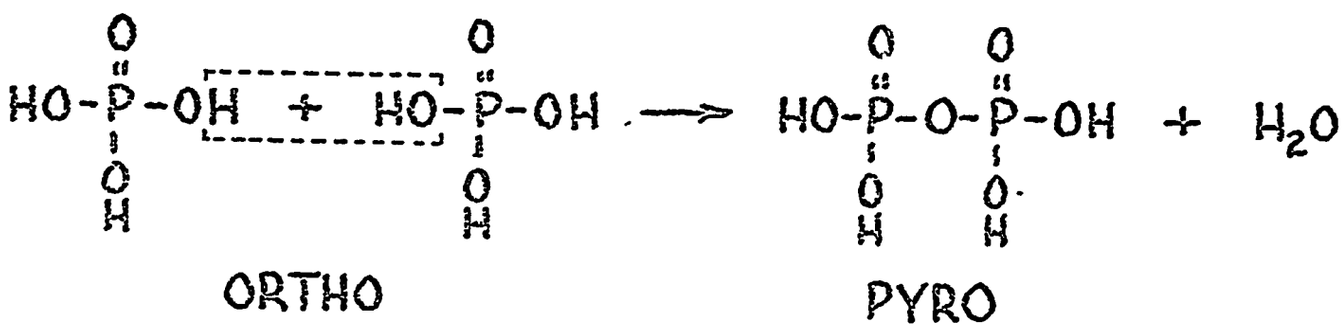

Fig. 1. Condensation of orthophosphoric acid to pyrophosphoric acid.