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**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

PRODUCTION OF HIGH-POLYPHOSPHATE LIQUID FERTILIZER
BY THE PIPE REACTOR PROCESS

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INTRODUCTION

Liquid fertilizer has been made for a number of years from wet-process superphosphoric acid by neutralizing the acid with ammonia to a pH of about 6 in a liquid fertilizer reactor. The amount of water required to produce the desired grade is also added and the heat of reaction is removed by cooling to prevent hydrolysis of the polyphosphates present in the acid. With the reaction taking place under cooled and aqueous conditions, the polyphosphate content of the liquid fertilizer can be no more than that contained in the acid. The maximum polyphosphate content is usually limited to about 50% of the total P_2O_5 which is the highest degree of conversion that is practical for wet-process acid because of difficulties in producing and handling acids with a higher degree of conversion. The liquids made from wet-process superphosphoric acid with this degree of conversion are marginal because of problems with settling out of ammonium phosphates and precipitation of impurities.

In recent pilot-plant work by TVA a process has been developed for producing a high-polyphosphate liquid fertilizer from wet-process superphosphoric acid which has a polyphosphate content in the range of only 20 to 30% (1). This process is an outgrowth of TVA's work using the direct process for production of polyphosphate from orthophosphoric acid as was the anhydrous melt-granulation process (2, 3).

The process consists of reacting wet-process superphosphoric acid and ammonia vapor in a simple pipe reactor under anhydrous conditions. The heat from the reaction which takes place is sufficient to remove a substantial proportion of the chemically combined water in the orthophosphate to form polyphosphate. The reaction product is in the form of a fluid melt which is converted to a liquid fertilizer (usually 10-34-0 or 11-37-0 grade) by continuous quenching and rapid dissolution in a circulating pool of cooled product liquid fertilizer. The water and additional ammonia required to make the desired product grade are added directly to the pool or to a circulating stream from the pool. The circulating stream is pumped from the pool through a second cooler to storage.

Liquid fertilizers with a polyphosphate content in the range of 80% can be made by the process from an acid feed containing as little as 5% polyphosphate. The advantage of a high level of polyphosphate is that a higher grade liquid product, 11-37-0 instead of 10-34-0, can be made without crystallization of ammonium phosphate. Also, precipitation of the impurities usually found in wet-process acid is delayed for an extended period. Magnesium is the most troublesome of the impurities normally found in wet-process acid. It has been determined that the tripolyphosphate and higher condensed phosphates are the most effective in sequestering the magnesium (4). It is desirable to have a polyphosphate content of about 80% so as to assure there will be sufficient quantities of these forms of polyphosphate to provide the degree of sequestration required. Acids made from the four major U.S. sources of phosphate rock have been used with good results; the sources are central Florida, north Florida, north Carolina, and the western (Idaho region) deposits.

TVA has a patent covering the process (5). Industry has adopted the process quite extensively with good results. It is estimated that approximately 50 plants of this type are now in operation in the U.S. of which at least 5 are of the mobile type. Further use of the process has been delayed because of limited supplies of the wet-process superphosphoric acid. The supply problem is expected to improve in the next 12 to 18 months.

The pipe reactor process has also resulted in a change in wet-process superphosphoric acid technology (6). Most producers have switched from production of the 50% polyphosphate acid to a 25% polyphosphate product. The lower polyphosphate acid is less expensive and easier to produce because of lower temperature requirements and decreased corrosion problems. A single-stage vacuum evaporator can be used instead of the usual two-stage unit. Also, the acid has better storage and handling characteristics primarily because of its lower viscosity.

DESCRIPTION OF THE PILOT PLANT

Except for the pipe reactor, the equipment required is essentially the same as that required for the conventional process for producing liquid fertilizer from superphosphoric acid. The major components in the pilot plant were a pipe reactor for the formation of high-poly ammonium phosphate melt, a reservoir tank for the circulating pool of liquid fertilizer into which the melt was dispersed and dissolved, a circulation pump, and a cooler for removal of the heat of reaction accumulated in the liquid fertilizer. A flow diagram of the pilot plant is shown in Figure 1. A scrubber was also provided for recovery of ammonia when operating under a specific equipment arrangement. The circulation tank was equipped with a coil containing 20 square feet of heat transfer area immersed in the liquid fertilizer. This coil served the purpose of

vaporizing and preheating the liquid ammonia feed. This arrangement also provided for removal of a portion of the heat accumulated in the liquid fertilizer (Figure 1).

All items of equipment were made from Type 316L stainless steel with the exception of the circulation pump which was cast iron and the shell-and-tube heat exchanger which was Type 304 stainless steel.

The flow rates of ammonia and dilution water to the process were controlled by means of manually controlled rotometers and the acid flow by means of a metering pump. The liquid fertilizer grade was monitored by measuring the pH and specific gravity. The liquid fertilizer grade and polyphosphate content were verified by actual chemical analysis.

The pipe reactor was in the form of an inverted "U" and normally consisted of a 1-inch standard pipe 6 feet long in a vertical position followed by a 24-inch run of 1-inch pipe in a horizontal position and a 34- to 40-inch run of 1-inch pipe in a vertical downward position. The pipe reactor was fitted with a standard pipe tee at the feed end for introduction of the feed acid and ammonia. A diagram of the piping arrangement at the feed end of the pipe reactor is shown in Figure 2. The acid entered the reactor through the side entrance of the pipe tee. The ammonia entered through an open-end 1/2-inch sparger which was inserted through the bottom opening of the pipe tee and terminated about 3 inches above the tee. This was a modification of the original tee reactor in which the ammonia sparger terminated at the centerline of the tee and which served the purpose of removing the relatively expensive pipe tee from the reaction zone to avoid possible corrosion or buildup of scale. This modification caused no adverse effect on the reaction. (Figure 2)

The circulation tank was 26 inches in diameter and 40 inches high with a conical bottom and had a loading level of 24 inches. The circulation pipe was a standard 1-1/2-inch pipe. The cooler had 72 square feet of surface area. The liquid fertilizer passed through the cooler on the shell side and the cooling water on the tube side.

PILOT-PLANT OPERATION

In operation of the plant the wet-process superphosphoric acid containing polyphosphate in the range of 5 to 52% was fed to the pipe reactor at a temperature of about 150°F. Most acids of this type, especially those made from uncalcined rock, require a temperature in this range for satisfactory pumping. Liquid anhydrous ammonia fed to the process was vaporized and preheated to about 120°F in the coil located in the circulating pool tank. With this method of vaporization, about 25% of the required heat removal from the liquid fertilizer was accomplished. After vaporization, the ammonia was split into two streams with about 60 to 70% fed to the pipe reactor and the remainder fed to the circulating stream. This split of the ammonia feed was made to obtain

the maximum reaction temperature in the pipe reactor and the maximum polyphosphate content of the melt. Lower temperatures resulted at higher levels of ammonia flow to the pipe reactor, probably because the relatively low temperature of unreacted ammonia actually served as a cooling medium for the reaction.

The steam, unreacted ammonia, and melt at a temperature in the range of 600° to 650°F discharged from the open end of the pipe at a point either above or below the surface of the circulating pool of liquid fertilizer. When discharged above the pool, most of the unreacted ammonia and the steam generated flashed off and was recovered in a scrubber through which a portion of the circulating stream of liquid fertilizer passed. This method of discharging the melt gave the advantage of not introducing the superheated steam into the pool of liquid fertilizer to cause localized areas of overheating that would promote hydrolysis of the polyphosphate if adequate agitation were not provided. When the melt was discharged below the surface of the pool, there were essentially no fumes from the vessel, but it was necessary to ensure adequate agitation. Both methods of discharge gave comparable products and both are used in industry.

Test results

Typical analyses of the acids used from the four major sources of phosphate rock in the U.S. are tabulated below.

Chemical composition, % by wt.

Type of acid	P ₂ O ₅								w. I. solids
	Total	Polyphosphate, % of total P ₂ O ₅	F ₂ O ₃	Al ₂ O ₃	MgO	SO ₃	F		
Central Florida ^a	67.6	19	1.8	1.0	0.5	3.8	0.3	0.1	
North Florida ^a	70.0	35	1.2	1.9	0.5	2.7	0.3	0.2	
North Carolina ^b	69.9	27	0.7	1.1	0.3	3.0	0.3	0.1	
Western ^b	72.9	41	0.7	1.3	0.8	1.4	0.2	0	

^aUncalcined rock

^bCalcined rock

Satisfactory liquid fertilizers with 80% or more of the P₂O₅ in a polyphosphate form were consistently made using acids from all sources. Most of the work was done with acid made from calcined North Carolina rock because it was most readily available. The normal production rate in the pilot plant was 1 short ton of 11-37-0 per hour. However, rates as low as 600 pounds and as high as 1-1/2 short tons per hour were used with good results. Typical operating data with the various feed acids are shown in Table I.

The normal feed acid temperature was 150°F. When acid made from uncalcined rock was used, it was necessary to heat it to 200°F to obtain 80% or more polyphosphate in the melt. An alternative to the higher level of preheat in the acid was to use a pipe reactor 11 feet long instead of 6 feet. The reaction temperature ranged from 575° to 700°F. Typical analysis of the melt was about 9-68-0 with 79 to 96% of the P_2O_5 in a polyphosphate form. Usually a higher degree of conversion was obtained at the higher reaction temperature, but a close correlation between temperature and polyphosphate content could not be established for the various acids. Normal operating pressure in the pipe was about 15 psig when using a clean uncoiled pipe. It was observed that, as the pipe diameter decreased because of scale buildup, the pressure in the pipe increased and a definite drop in polyphosphate content of the melt occurred, even though the temperature remained the same. Some loss of polyphosphate occurred during dissolution of the melt in the liquid fertilizer. Losses were only minor when the temperature of the liquid in the circulating pool did not exceed 180°F, and provisions were made for rapid dispersal and dissolution of the melt in the liquid fertilizer.

Tests were made to determine the effect of major process variables on the polyphosphate content of the products. These variables and the ranges in which they were tested are as follows :

1. Length of pipe reactor (3-16 ft.)
2. Proportion of ammonia fed to the pipe reactor (60-100%).
3. Production rate (600-2400 lb of 11-37-0/hr).
4. Polyphosphate content of the feed acid (5-49% of total P_2O_5).

The first three variables had little effect in the ranges tested except that a pipe reactor 11 feet long was required when using acid made from uncalcined rock and preheated to only 150°F instead of 200°F. The relationship between the polyphosphate content of the feed acid and the liquid fertilizer produced in the pipe reactor is shown in Figure 3. These data are from tests with an acid made from Florida rock that had an initial polyphosphate content of 49%. The acid was diluted successively four times to 5% polyphosphate, and melt was produced after each dilution (Figure 3).

When the polyphosphate content of the feed acid was about 20 to 25% or more, the polyphosphate content of the melt was 90% or more and about 79% when the polyphosphate content was 5%. These tests showed clearly that superphosphoric acid of any concentration was quite suitable for producing a satisfactory liquid fertilizer.

The prime problems encountered in operation of the pilot plant were corrosion of the pipe reactor and buildup of scale on the inner walls of the pipe reactor which was fabricated from Type 316L stainless steel. These problems were most severe in the first 3 feet of the reactor.

The scale was crystalline iron aluminium ammonium pyrophosphate $[(Fe, Al) NH_4 P_2 O_7]$. This material is very hard and insoluble in acids and protected the pipe from corrosion. Scaling was usually sufficient to provide the required protection with all acids used except that made from calcined North Carolina rock. Formation of scale was not entirely beneficial because it continued to build up and restricted the open area in the pipe. Both corrosion and scaling were reduced to a reasonable rate for most acids by use of a water jacket on the first 3 feet of the pipe reactor. Indications were that if the skin temperature of the pipe were kept below 400°F, the formation of scale was retarded. Cooling was also effective in significantly reducing the rate of corrosion. Cooling caused only a slight decrease in the polyphosphate content of the pilot-plant products. Removal of the scale from the pilot-plant pipe was difficult and was usually accomplished after disassembly by heating the pipe with a torch to about 1200°F where the pyrophosphate was converted to a metaphosphate which could then be easily removed from the pipe. Other methods included hammering on the pipe or driving a rod through the pipe to dislodge the scale.

In addition to the above-described pilot-plant work, TVA has recently done limited work with a 2-inch vertically mounted pipe reactor through which the melt flows downward. The pipe had an overall length of 12 feet. It was fitted with a standard pipe tee at the upper end for introduction of acid and ammonia. The bottom end terminated 2 feet below the liquid level in a conventional type of liquid fertilizer reaction tank. Wet-process superphosphoric acid and ammonia were fed to the pipe through the pipe tee as was done in the inverted U-type pipe reactor. The additional ammonia and water required to make the desired grade of liquid fertilizer were added to the reaction tank. An 11-37-0 liquid fertilizer product was made at a rate of 10 to 13 tons per hour which was much higher than would be produced in the inverted U-type reactor of the same size. The high rate of flow was required to keep the pipe loaded to allow the reaction to proceed. Initial results with this design have been good. A liquid fertilizer containing about 75% polyphosphate was produced in the preliminary tests using a wet-process acid containing about 20% polyphosphate. The advantage of this design is that it simplifies the reactor with only the straight run of pipe required, thus lowering the cost of it.

Product Evaluation

The product grade of the liquid fertilizers produced was maintained at 11-37-0 because of the high solubility as a result of the high polyphosphate content. The products made from calcined rock were clear and green in color, and those made from uncalcined rock were black.

Comparative storage tests were made on 11-37-0 made by the pipe reactor process and 10-34-0 made by the conventional (tank ammoniation) process using all four major sources of wet-process acid. Results of these tests are shown in Table II.

The 11-37-0 products made by the pipe-reactor process all contained 80% or more of the P_2O_5 in the polyphosphate form as compared with only 42 to 57% in the 10-34-0 products made by the conventional process. Also, the high-polyphosphate products had 50 to 60% of the P_2O_5 in the tripolyphosphate and more highly condensed forms as compared with 5 to 15% in the relatively low-polyphosphate products. Typical P_2O_5 species distribution in the two types of products is shown in Table III.

Superiority of the high-polyphosphate products was very pronounced at temperatures of 0°, 32°, and 80°F. At 100°F the superiority was less pronounced because of the relatively rapid rate of hydrolysis of the higher condensed polyphosphates at this temperature. The precipitates that formed at 100° and 80°F contained magnesium; those formed in the pipe reactor 11-37-0 products were $MgAl(NH_4)(P_2O_7)_2 \cdot 6H_2O$, whereas in conventional 10-34-0 they were $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$. The precipitates that formed at lower temperatures were ammonium polyphosphate $[(NH_4)_5P_3O_{10} \cdot nH_2O]$ in the pipe reactor 11-37-0 and diammonium phosphate $[(NH_4)_2HPO_4]$ and magnesium ammonium pyrophosphate $[Mg(NH_4)_2P_2O_7 \cdot 4H_2O]$ in 10-34-0 products at 32°F.

It was concluded that the 11-37-0 remained free of magnesium precipitate when the total polyphosphate level was no lower than 55 to 65% and the tripolyphosphate plus higher forms of polyphosphate was no lower than 6 to 13%.

COMMERCIAL PLANTS

Commercial use of the process has progressed to the point that further expansion is limited by the amount of wet-process superphosphoric acid available. Some of the plants now in operation originally used the conventional-type process and were converted to the pipe reactor process, while others are new construction built specifically for the pipe reactor process.

Essentially all of the plants use an inverted U-type pipe reactor as used in the TVA pilot plant. Most plants are operated at a production rate of 20 to 30 tons of product per hour and make a 10-34-0 grade. The quality of the liquid fertilizer is close to that made in the pilot plant with a polyphosphate content in the range of 70 to 80%. The plants that do have difficulties in obtaining the higher level of polyphosphate probably are not following proper methods for dispersing the melt for rapid dissolution, and some hydrolysis of the polyphosphate occurs before it is dissolved. However, most producers find that products containing 70% polyphosphate have storage qualities that are entirely satisfactory and they are not too concerned with increasing the polyphosphate content.

A sketch of a commercial plant is shown in Figure 4. A photograph of a plant with this design is shown in Figure 5. Other commercial plants are similar to this one in most respects. In this particular plant, the initial 4 feet of pipe is a standard 6-inch pipe followed by an additional 19 feet of 4-inch pipe. A 3-foot length of the 6-inch pipe is jacketed and the feed acid is used as the cooling medium in the jacket. With this method of cooling, there is no loss of the heat of reaction. All of the piping is fabricated from 316L stainless steel. The pipe reactor terminates in a horizontal pipe section 3 feet long which is slotted for discharge of the melt and is located below the pool level directly above the point where the recycle liquor is removed for circulation to the cooler. This arrangement assures discharge of the melt into an active area of the pool for rapid dispersion and dissolution. (Figures 4 and 5)

An evaporative packed tower-type cooler located directly above the circulating pool is used. Air is forced upward through the liquor passing down through the packing to accomplish the evaporative cooling. A 4-1/2-foot section packed with 3-1/2-inch pall rings is used for this purpose. Not shown on the sketch is a demister pad located in the tower above the point where the circulating liquor is sprayed onto the packing in the tower. The product made is pumped to storage from the circulating pool through a heat exchanger for the purpose of vaporizing the feed liquid ammonia and cooling the product before storage. Both the acid and the liquid ammonia are fed to the system directly from rail tank cars with no external source of preheat.

The plant has a capacity of 20 to 30 tons of 10-34-0 per hour and produces a product with a polyphosphate content of about 80% from a feed acid containing about 25% polyphosphate. The betterly limits cost of such a plant as shown is reported to be in the range of \$35,000 to \$40,000. This includes equipment, construction, and startup of the plant, but no facilities for storage of raw material or finished product.

While this sketch shows one particular plant layout, other layouts are possible, such as the use of a pipe reactor which is the same size over the entire length or the use of a shell-and-tube heat exchanger instead of an evaporative cooler. In general, a 4-inch pipe reactor is used for production rates less than 20 tons of liquid fertilizer per hour. A 6-inch pipe is used for at least a portion of the pipe reactor for production greater than 20 tons and up to as high as 40 tons per hour.

The prime problem in all commercial plants is scale formation or corrosion of the first few feet of the pipe reactor. Jacketing of this portion of the pipe has been helpful in delaying corrosion and scale formation as was determined in the pilot-plant work. The individual plant operators have learned the technique of scale removal and this causes no great problem in operation of such a plant. Corrosion is more a problem, especially when using acids with a relatively low impurity content because no scale forms to protect the pipe in the area of corrosion. Acids produced from calcined North Carolina rock are of

this type. When such an acid is used, about 400 hours is the maximum service life that can be expected of the pipe. To minimize the amount of pipe that must be replaced, the first 3 feet is in the form of a spool piece which can be readily removed and replaced. When a scale-forming acid (such as that produced from Florida rock) is used, the life of a pipe is greatly extended.

Losses from this type of plant are no major problem. In tests made at a plant similar to the one shown in Figure 4, it was established that 44 pounds of ammonia, 0.03 pound of P_2O_5 , and less than 0.002 pound of fluorine per hour were lost at a production rate of 20 tons of 10-34-0 per hour. This ammonia loss is no doubt due to the stripping action which occurs in a cooler of this type. The liquid fertilizer passing through the tower is subject to such action since it is at a pH in the range of 6.0 to 6.2. In additional tests when the airflow was stopped, no loss of ammonia could be detected. These data indicate that, if a shell-and-tube type of heat exchanger were used instead of an evaporative-type cooler, the loss of ammonia would be essentially eliminated as was the case in the pilot-plant work.

At least five of the approximately fifty commercial plants now in operation are mounted on flatbed trailers so that they may be moved from one location to another. In this type plant, as well as the permanently located plants, the acid and liquid ammonia are fed directly from rail tank cars to the process. Storage tanks for the product produced are located at the site of operation. Services such as water and electric power must also be available at the site of operation.

CONCLUSIONS

The pipe-reactor process has provided industry with a simple system for producing a high-polyphosphate liquid fertilizer with exceptionally good storage properties from wet-process superphosphoric acid having a low degree of conversion to polyphosphate. The storage properties of the liquid fertilizers made by the pipe reactor process from the low-polyphosphate acid are better than those of products made previously from an acid with the maximum practical level of polyphosphate. Equipment requirements for the pipe reactor process are not extensive or complicated, and installation of such a plant is relatively low in cost. The process allows the manufacturer of wet-process superphosphoric acid to produce an acid of lower concentration which is less costly and easier to handle than the more concentrated acids specifically made previously for producing liquid fertilizers. Utilizing the heat of reaction to obtain conversion of the orthophosphate P_2O_5 to polyphosphate decreases the overall energy requirements for the conversion of phosphate rock to a liquid fertilizer. Additional work is required to find ways to further decrease the corrosion and scale problems of the pipe reactor.

REFERENCES

1. Melina, R.S., Lee, R.G., and Scott, W.C., Fert. Solutions 32 (2), 32-45 (March-April 1972).
2. Young, R.D., Scott, W.C., and Melina, R.S., Proc. 18th Annual Meeting Fert. Industry Round Table, 1968, pp 126-35 (1969).
3. Lee, R.G., Melina, R.S., and Young, R.D., Ind. Eng. Chem., Process Des. Develop. 11 (1), 90-4 (January-March 1972).
4. Tennessee Valley Authority, "New Developments in Fertilizer Technology: Eighth Demonstration (October 6-7, 1970)." TVA Bulletin Y-12, Muscle Shoals, Alabama, 1970.
5. Melina, R.S., U.S. Patent 3,775,534 (November 27, 1973).
6. Hopwood, Lorax E., and Herwell, A.O., "Superphosphoric Acid and the Pipe Reactor Process : A Commercial Boon to Liquid Fertilizers". Paper presented at the Annual Meeting of the American Chemical Society, August 28, 1973, Chicago, Illinois.

TABLE I

Typical Operating Data and Results from Pilot-Plant Pipe Reactor

Tests Using Various Sources of Feed Acid

Source	Feed acid			Anhydrous melt				Liquid fertilizer product			
	P ₂ O ₅ , %	Polyphos- phate % of total P ₂ O ₅	Temp, °F	Reaction temp, °F	N, %	P ₂ O ₅ , %	Polyphos- phate % of total P ₂ O ₅	Temp, °F	Total N, %	Total P ₂ O ₅ , %	Polyphos- phate % of total P ₂ O ₅
North Florida ^a	66.3	5	224	575	10.7	63.7	79	-	-	-	-
North Florida ^a	70.9	45	204	590	9.3	66.9	95	152	10.2	37.5	87
Central Florida ^a	71.0	53	215	700	8.8	67.9	91	140	11.0	38.4	87
Central Florida ^b	67.1	27	151	640	12.8	62.0	81	150	11.3	35.6	81
North Carolina ^b	69.8	26	103	615	11.0	64.4	83	150	11.0	37.0	81
Western (Idaho) ^a	71.9	38	200	645	8.9	68.4	86	150	10.2	38.3	84

^a Uncalcined phosphate rock.

^b Calcined phosphate rock.

TABLE II
Effect of High Polyphosphate on Storage Properties
of Liquid Fertilizer Pipe Solutions

Supraphosphoric acid feed used	North Florida		Western U.S.		North Carolina		Central Florida	
Source of rock								
Chemical analysis, %								
Total P_2O_5	75		72.9		70.2		70.5	
Polyphosphate level	57		41		45		53	
Al_2O_3	2.5		1.3		1.0		1.1	
Fe_2O_3	1.4		0.7		1.0		1.6	
MgO	0.8		0.75		0.58		0.58	
SO_4	2.4		1.7		4.4		1.3	
F	0.1		0.2		0.24		0.17	
W.I. solids	0.6		0.0		0.02		4.0	
<hr/>								
Product	Pipe		Tank		Pipe		Tank	
Reactor type	11-37-0	10-34-0	11-37-0	10-34-0	11-37-0	10-34-0	11-37-0	10-34-0
Grade	6.7	6.0	6.8	6.0	6.4	6.0	6.8	6.0
pH								
Percent of total P_2O_5								
As polyphosphate	70	57	82	42	84	47	85	45
As pyrophosphate	52	41	28	34	25	37	27	36
As triphosphate and higher	48	16	54	8	59	10	58	9
MgO content, %	0.41	0.59	0.58	0.35	0.31	0.29	0.30	0.29
Satisfactory storage time, weeks at								
100°F	5	5	9	1	9	11	10	7
80°F	20	6	25	1	22	13	25	14
52°F	>40	11	>40	1	>40	>40	>40	>32
0°F	14	- ^a	15	- ^a	>40	14	24	>32
Major precipitating phase ^b at								
100°F	I	II	I	II	I	I	I	II
80°F	I	II	I	II	I	II	I	II
52°F	-	III, II	-	III, II	-	-	-	-
0°F	IV	-	IV	-	-	V	-	-

^a Not tested.

^b Major precipitating phase indicated as follows: I = $MgAl(NH_4)_8(P_2O_7)_2P_2 \cdot 6H_2O$; II = $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$; III = $(NH_4)_5HPO_4$; IV = $(NH_4)_7P_2O_{10} \cdot nH_2O$; V = $NH_4H_2PO_4$.

TABLE IIITypical Phosphate Species Distribution in Liquid FertilizersMade from Wet-Process Superphosphoric Acid

<u>P₂O₅</u> <u>species</u>	<u>Species distribution, % of total P₂O₅</u>	
	<u>Pipe reactor process</u>	<u>Conventional process</u>
Ortho	21	52
Pyro	31	36
Tri	23	7
Tetra	12	4
Penta	7	-
Higher	6	1

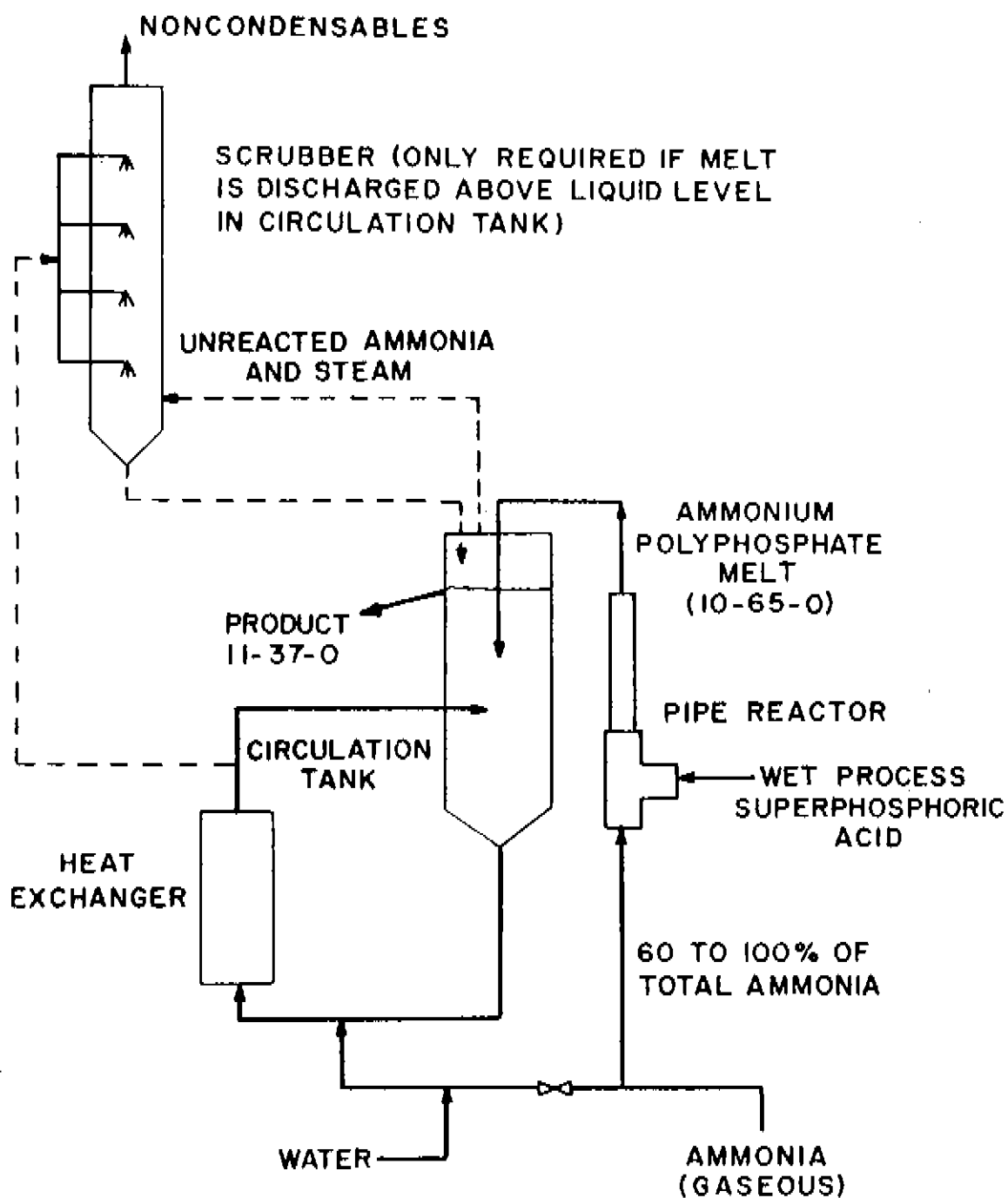


Figure 1: Production of 11-37-0 Liquid Fertilizer of High Polyphosphate Content from Low-Conversion Wet-Process Superphosphoric Acid

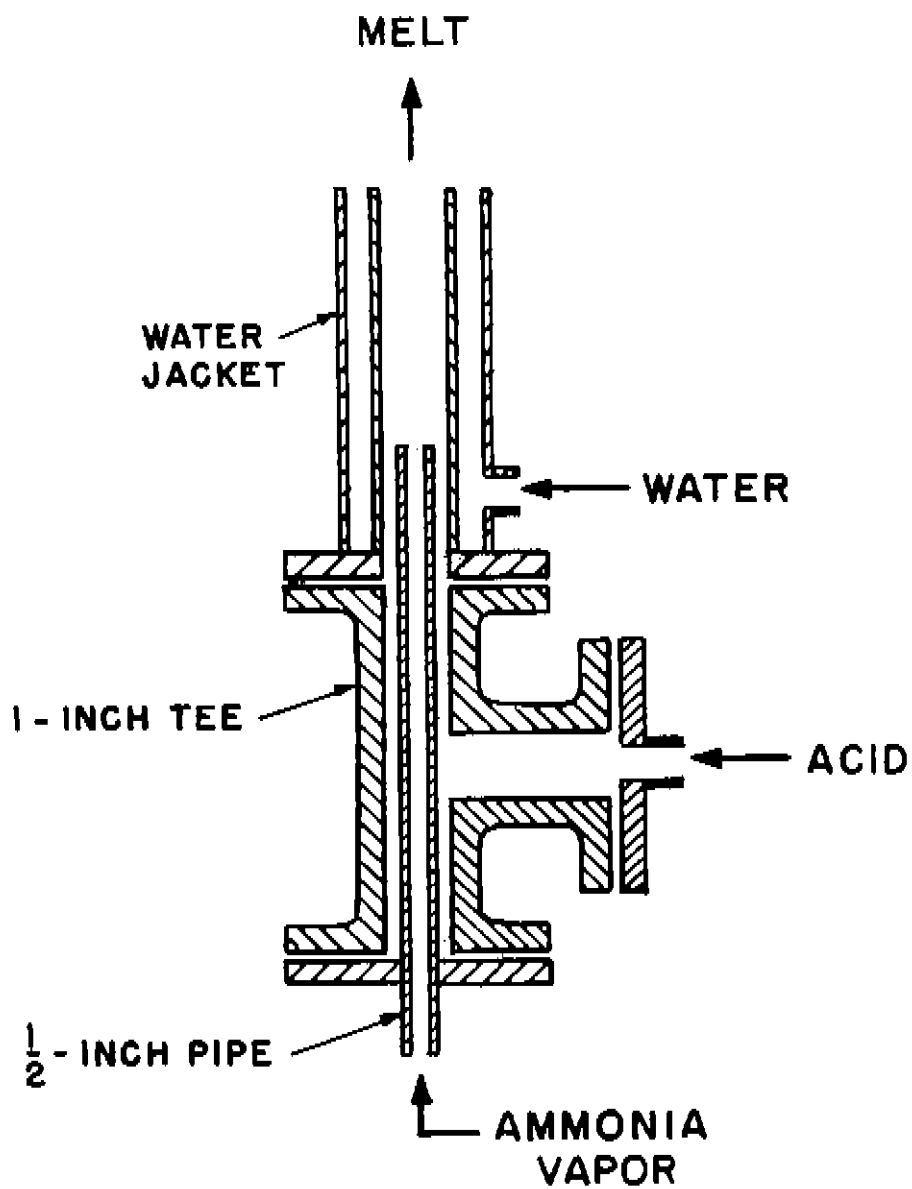


Figure 2: Acid-Ammonia Feed Arrangement for Pipe Reactor

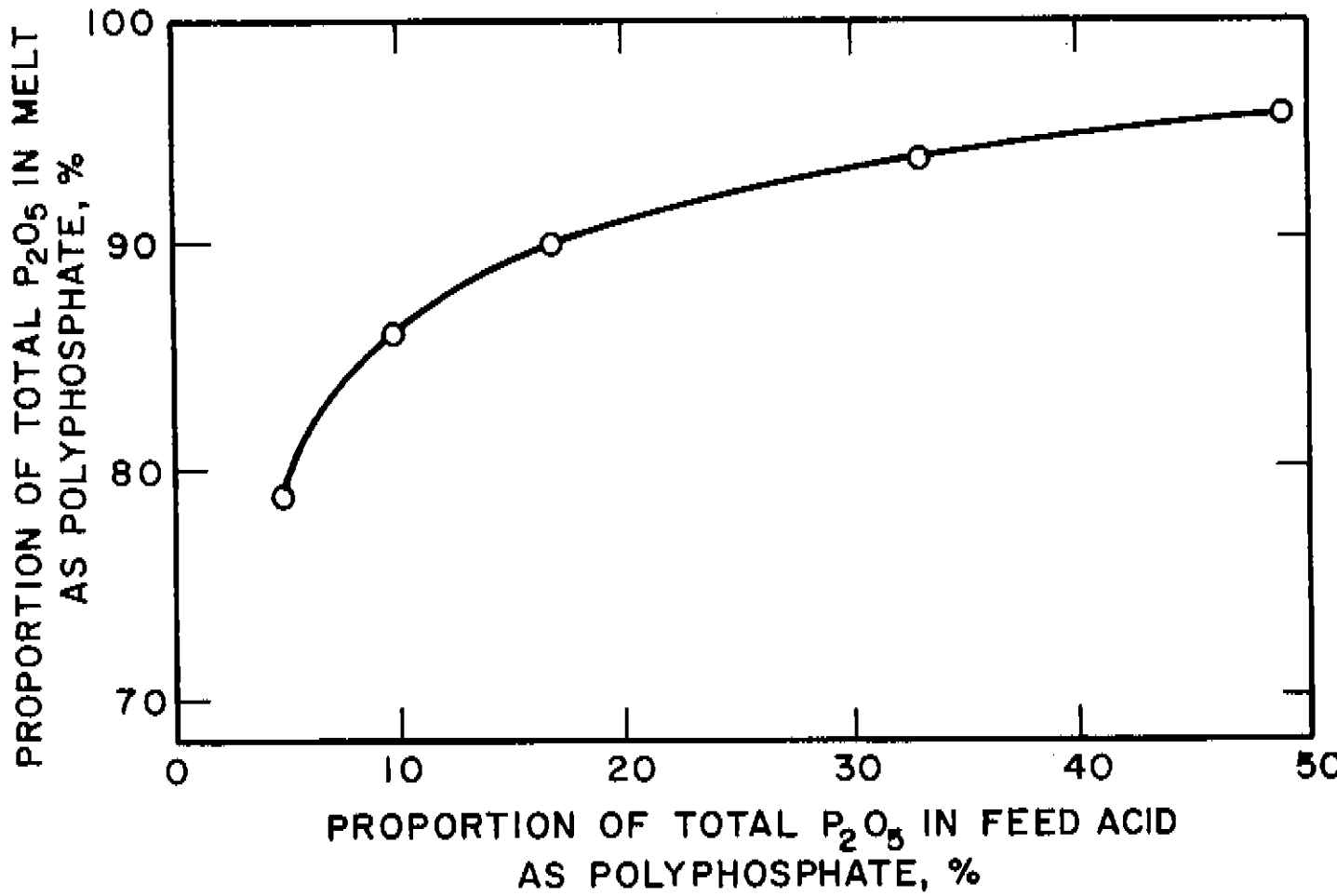


Figure 3: Effect of Polyphosphate Content of Feed Acid on Polyphosphate Content of Melt

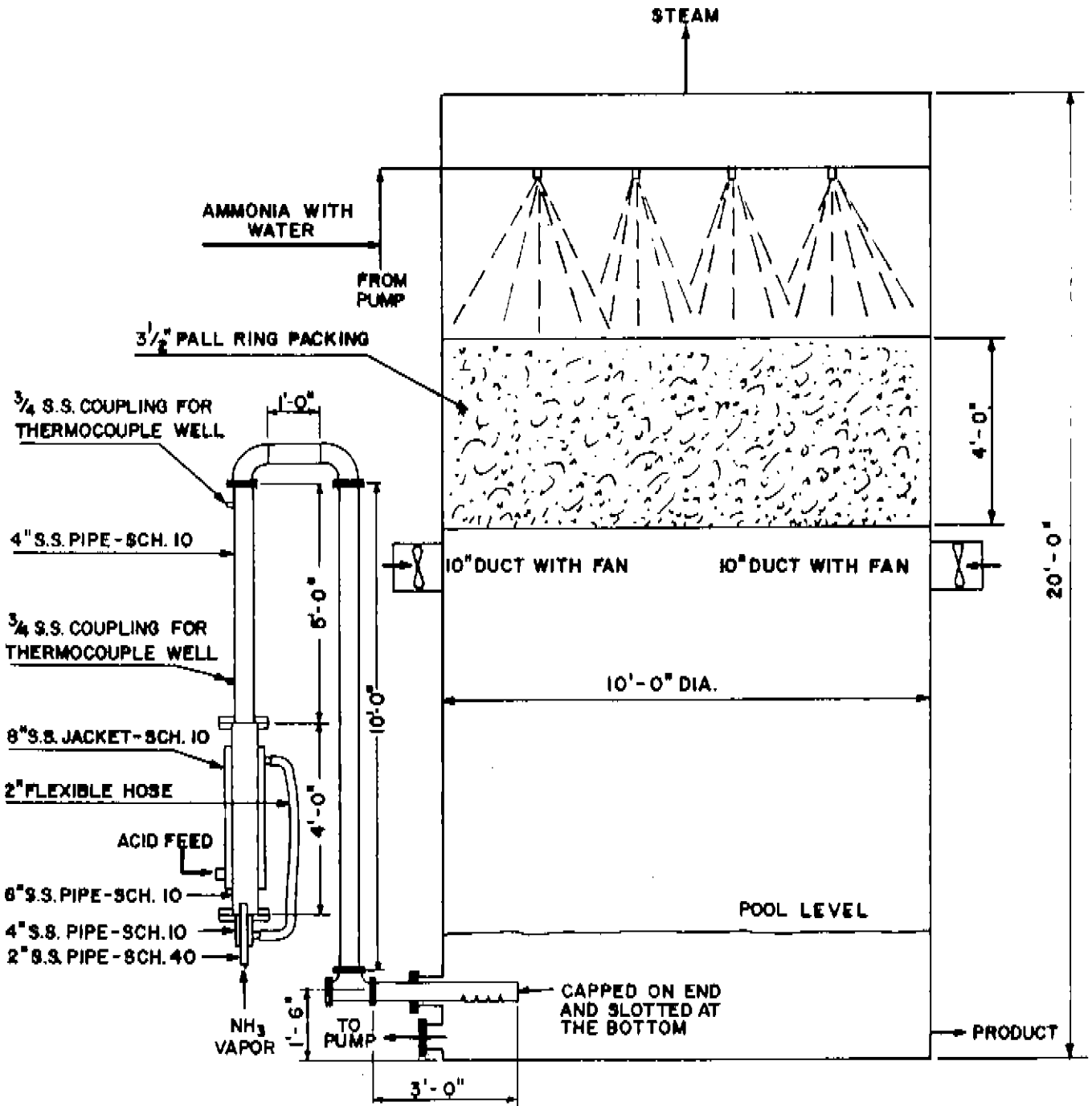


Figure 4: Typical Design of Commercial Plant Using TVA Pipe Reactor Process for Production of High-Polyphosphate Liquid Fertilizer

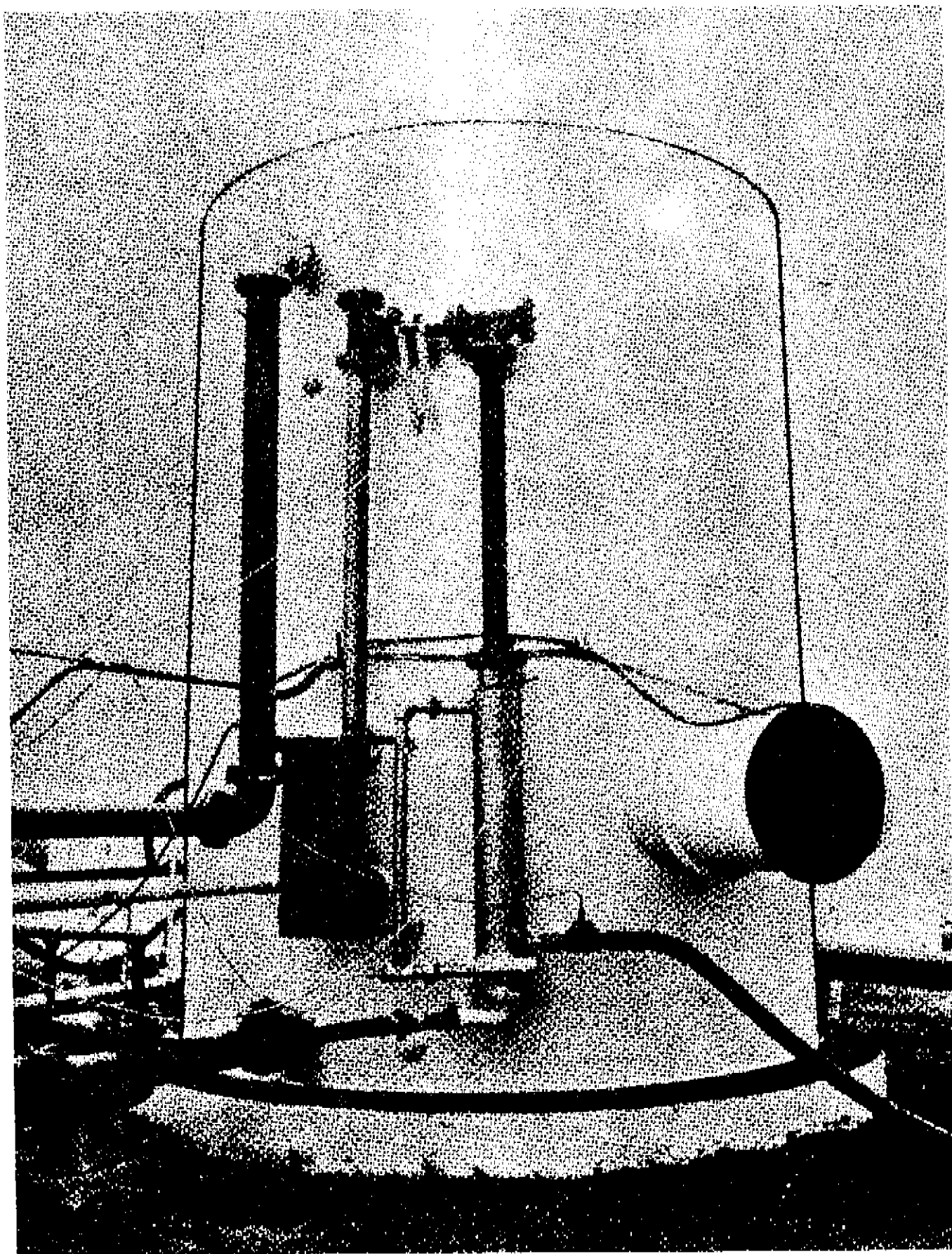


Figure 5: Commercial Production Unit for High-Polyphosphate Liquid Fertilizer Using TVA Pipe Reactor Process

DISCUSSIONMr. R.S. MELINE (Tennessee Valley Authority, U.S.A.)

A number of years ago TVA developed a process for producing liquid fertilizer from superphosphoric acid. All of the polyphosphate contained in the product was present in the feed acid.

Slide 1

In this process the super acid was neutralized with either anhydrous or equal ammonia in a reaction vessel on a continuous basis. Sufficient water was added to produce the desired grade product, usually an 11-37-0 or 10-34-0. The heat of reaction was removed by some method of cooling to prevent hydrolysis of the polyphosphates. This process produced a good quality product when thermal super acid was used which contained little or no impurities. Problems did develop when commercial producers began using wet-process super acid because this type acid normally contains impurities and the maximum practical level of polyphosphate is about 50%. This level of polyphosphate in many acids is too low to yield a liquid fertilizer that can be stored for a reasonable period of time without precipitation of the impurities. Magnesium is a particularly difficult problem with some acids.

Slide 2

To provide for higher levels of polyphosphate in the liquid fertilizer, TVA developed the simple pipe reactor process. This process is based on earlier TVA work using merchant-grade ortho wet-process phosphoric acid in a tee reactor. In this process the major portion of the neutralization is carried out in a pipe reactor and the heat of reaction is used to condense additional amounts of ortho P_2O_5 to the polyphosphate. The reaction results in a melt containing about 10% N and 65% P_2O_5 ; reaction temperature is 600° to 650°F (315°-345°C). About 80% of the P_2O_5 is in the polyphosphate form when using feed acids containing only 20 to 30% polyphosphate. The melt with little or no loss of polyphosphate is dissolved in a circulating stream of liquid fertilizer which passes through a cooler to maintain the temperature below 180°F (87°C) to prevent hydrolysis. Various types of coolers can be used. Liquid fertilizers containing this level of polyphosphate have been made from acids containing as little as 5% polyphosphate. Such products containing relatively high impurity levels can be stored for extended periods without precipitation.

Slide 3

The process has been well accepted by industry and more than 60 plants of this type are known to be in operation. This is a flowsheet of a typical commercial plant. It does have one feature that has not proven to be satisfactory--that is, the use of feed acid as the media in the jacket to provide the cooling required to retard scale formation and corrosion in the initial few feet of the pipe reactor. Water has proven to be the most satisfactory cooling media. Most commercial plants use the evaporative-type cooling tower to provide the major cooling requirements necessary for the liquid fertilizer product.

Slides 4 through 10

I would like to include several slides showing details of the design of a commercial plant which has consistently produced a 10-34-0 product with a polyphosphate content of 75% or more when using a feed acid containing 25 to 30% polyphosphate.

Slide 4 : Overall view of plant while in operation

Slide 5 : Pipe reactor

Slide 6 : Discharge end of pipe reactor

Slide 7 : Prime entrance area for air passing through the cooling tower

Slide 8 : Mist eliminator at top of cooling tower

Slide 9 : Air exhaust fan and secondary air inlet at top of cooling tower

Slide 10 : Same portion of tower while in operation

Slide 11

This is a view of a typical portable unit mounted on a flat bed trailer. There are a number of such units. They can be easily moved from one location to another and can service a wide area.

Slide 12

This is a section of the 1-inch pilot-plant pipe reactor showing the scale which was removed after the pipe had been cut into sections.

Slide 13

This is a section of a 6-inch commercial pipe reactor showing the scale formation and corrosion which will usually occur in the first few feet of the pipe at some time during the life of the pipe reactor. To further minimize or completely eliminate this problem is the aspect of the process that needs further development and TVA does plan to continue work in this area.

Slide 14

I would like to comment on a paper presented by TVA at the 1970 meeting of this group which described a process in the pilot-plant stage at that time for producing granular fertilizers by use of a low-polyphosphate melt produced from merchant-grade orthophosphoric acid in a pipe reactor. TVA recently started operation of such a plant in our demonstration-scale program and we are now producing 28-28-0 urea-ammonium phosphate at the design rate of about 16 tons per hour. The production rate for this grade is limited to this value by the capacity of our urea plant which is about 8-1/3 tons per hour. A second grade produced is 12-57-0 at the design rate of 12 tons per hour. This is the grade obtained when only the melt is granulated. Operation of the plant has been successful when producing both products; chemical and physical properties have been very good. The products require no conditioning agent.

Mr. TROJAN (Research Institute of Inorganic Chemistry, Czechoslovakia)

In recent years a remarkable upward trend in the production and consumption of fluid complex fertilizers (both clear liquids and suspensions) has been recorded. The results of the research efforts of TVA to develop progressive technological processes and, at the same time, introduce new products possessing the highest possible agronomic efficiency, represent a fundamental contribution to the technical groundwork of the mentioned trend, which is currently no more typical for the U.S.A. only, but is extending in Europe as well as in other regions. It is obvious that the introduction of production and more extensive application of such new products in agriculture requires that a certain technical and economic basis has to be built up, which differs considerably from that established for the use of solid fertilizers. On the other hand, the simplification of manufacturing processes, savings on energy and on labour, which is particularly important for the farm enterprises, and a wide and flexible range of product grades - these factors motivate all the authorities concerned to study carefully the conditions and possibilities of a switch to an extensive use of fluid fertilizers in the near future. In Czechoslovakia, too, this problem has been given due attention by several research institutions. Our conditions, characterized by the existence of comparatively very large farming enterprises cultivating up to several thousand hectares and by the progressing rationalisation and unification of the fertiliser distribution system, offer a very favourable basis for an extensive use of liquid fertilizers. The response to the recently launched experimental production of a nitrogen solution as well as to the start-up of a pilot-scale installation for the manufacture of an N-P solution has proved that our farmers are very seriously interested in these products, which are something entirely new in Czechoslovakia.

The paper by Mr. Robert Malina describes a further feasible and technically very interesting step in the development of processes for the manufacture of a basic intermediate for liquid fertilizers, i.e. a concentrated N-P solution based on ammonium polyphosphate. The process is carried out in a pipe reactor; this type of apparatus was applied by TVA for the direct preparation of ammonium polyphosphate from wet process phosphoric acid some years ago and it is known that many producers in the USA and some firms in Europe have been using the method.

As follows from the paper, several important improvements have been accomplished by TVA during the continuing research, of which I should like to emphasize, in the first place :

- widening of the reaction zone of the reactor by incorporating a water-cooled jacket and a considerable decrease of corrosion resulting thereof;
- the changed design of the reactor shape enabling an easier discharge of product, and
- the process makes it possible to produce a higher quality and more concentrated product, based, in fact, on wet process phosphoric acid as the primary raw material.

I should now like to ask the author a few questions :

1. As documented in the paper, the new TVA process discussed enables to make a product at a comparatively high content of polyphosphates higher than pentapolyphosphate. What is the solubility of these compounds in the given system and to what level would amount the P_2O_5 loss due to their limited solubility ?
2. According to our experience, as gained when modelling similar processes, the maximum mass transfer between a gas and liquid is attained at certain flow regime that can be characterized by a Reynolds number from within a rather narrow interval of the Re values. What nature of flow is to be considered the most suitable ?
3. We should like to know the author's opinion with respect to the economic advantages of the new process, described in the paper, over the process of a direct synthesis of ammonium polyphosphate from wet process phosphoric acid in a pipe reactor as developed by the TVA earlier.

Mr. MELINE

Now, loss due to polyphosphate beyond the penta. We have had no experience with any problem as such. We have had liquid fertilizers that contained as high as a total 94% polyphosphate. To tell you the exact species distribution I cannot. There was a lot of long chain polyphosphates but the product as made contained no insoluble material. But it should also be noted that when we get beyond the penta the life duration of such polyphosphate is not long. They hydrolyse back to a low level. So I do not look on it as a problem other than the fact that, as hydrolysis takes place, the pH begins to drop and a low pH encourages more hydrolysis, so the polyphosphate can go down quite rapidly if you are not in a right area or I should say too high. We have concluded that about 83% polyphosphate is the highest you want to go.

Second question, heat transfer, what is the nature of flow be considered the most suitable ? I think I will answer that question starting from the backward position. The most suitable is a very turbulent flow, the turbulence being caused by the reaction. When we use an acid made from calcined rock, which has a relatively low viscosity, the reaction will take place and proceed to completion in a short length. If we use an acid made from an uncalcined rock, the reaction starts out slower; so we have two choices : to preheat the feed acid to some higher temperature or make the pipe longer.

The third question compares the economics of the so-called direct process from ortho-acid and the process for making liquid from superacid : there really is not a comparison there because you are not making the same product. By the direct process, the best we have been able to do is about 50% polyphosphate and at that level of polyphosphate we recommend that a suspension fertilizer be made while from the superacid we recommend of course so-called clear liquid fertilizer be made. The cost of materials in the United States, the phosphoric acid is produced either on the East Coast or in the Far West. Most of the acid is shipped to the Mid West and converted to liquid fertilizer and by the

time it gets to the Mid West the costs are fairly well equalized because of the higher concentration of the superacid.

Now the cost of construction of the 2 plants, the quoted cost of a pipe reactor you saw here. You can get a complete plant excluding storage of acid and storage of product, in the United States for about 45,000 \$. For a direct process plant I would have to say the cost will be in a range of 4 to 5 times greater because there is a two stage process and you have problems of corrosion particularly in that first stage scrubber. In fact hastelloy G we have determined is necessary and then, in addition to that, you have to have a fluorine scrubber. It depends on what you want to make really.

Mr. DAVISTER (Soc. de Prayon, Belgium)

I understand that the removal of heat of reaction is one of the main problems in using the T reactor. Did you consider using a vacuum flash cooler for that operation ?

Mr. MELINE

The removal of the heat of reaction is a necessity from the liquid fertiliser to avoid hydrolysis. You must keep the liquid fertiliser in a circulating phase of it no higher than 82°C. We have not tried a vacuum evaporator, no. I can see that it could possibly do the job. The so-called evaporative cooler has been established and has worked so good that it more or less became the standard method of cooling in the U.S. on the 63 plants that I have mentioned.