

7
0-106 0-106

#162 ?

FLUID FERTILIZER
Chapter ●17

For
Fertilizer Technology Manual
(F. T. Nielsson, editor; M. Dekker, publisher)

MANUEL OF FERTILIZER PROCESSING.
1986.

by
Frank P. Achorn, Senior Scientist
Division of Agricultural Development
National Fertilizer Development Center

668.62
M 294
M

TENNESSEE VALLEY AUTHORITY
Muscle Shoals, Alabama

FLUID FERTILIZER Chapter 6

The term "fluid fertilizer" as used in this chapter refers to fertilizers such as anhydrous ammonia, aqua ammonia, nonpressure nitrogen solutions, liquid mixed fertilizers, and suspensions. Production of anhydrous ammonia has been considered at many international conferences and will not be presented here, although its use will be briefly discussed. Discussion is based mainly on the production and use of fluids in the U.S. where there has been more emphasis on fluids than in any other part of the world. However, developments in other areas are identified.

Large scale manufacture of fluid fertilizers is a new industry for most of the world. Manufacture and use of fluid fertilizers, particularly nitrogen solution, have increased. Several countries produce large quantities of anhydrous ammonia. Many of these countries ship most of their solutions to the U.S. and Canada for use in fluid marketing systems.

Published data, however, show that countries such as Belgium, Canada, Colombia, Denmark, France, Mexico, the Netherlands, and the United Kingdom consume significant amounts of fluid fertilizers for direct application. For example, in 1978 it was reported that Denmark used 127,100 tonnes per year of ammonia for direct application (1). In the United Kingdom, clear liquid mixtures have been used with excellent results and suspensions are being tested (2). Agricultural practices in South America are especially well adapted to use of fluids; Colombia has begun using them and Brazil is conducting market tests with nitrogen solution and suspensions.

In recent years, liquids have been used extensively in France. Ammonium polyphosphate solution of grade 10-34-0 is produced using the new pipe reactor technology. Nitrogen solution (urea-ammonium nitrate) is popular. Although test marketing of suspensions has begun in Belgium and

the Netherlands, fluids have not had positive results. Other reports show that small amounts of fluids have been used in China, India, Japan, Spain, and Sweden.

During the past 30 years, the fluid fertilizer marketing system has matured into a major marketing system in the U.S. The Department of Agriculture has developed a reasonably accurate system for reporting the quantities of all fluid fertilizers consumed.

Statistics for 1981 show that the world has capacity to produce 120.3 million (MM) tonnes of anhydrous ammonia. About 17 MM tonnes of fluid fertilizers were used in the U.S. during 1980. The type of fluids used and their increase in use in the U.S. since 1960 are shown in the following tabulation:

| <u>Material</u> | <u>Thousands of tons (tonnes) (3)</u> | | | | | | | |
|--------------------|---------------------------------------|--------|-------------|--------|-------------|---------|-------------|---------|
| | <u>1960</u> | | <u>1967</u> | | <u>1977</u> | | <u>1980</u> | |
| Anhydrous ammonia | 709 | (643) | 2405 | (2183) | 4924 | (4469) | 5485 | (4976) |
| Aqua ammonia | 427 | (387) | 863 | (783) | 655 | (594) | 662 | (601) |
| Nitrogen solutions | 650 | (590) | 2561 | (2324) | 5793 | (5257) | 6612 | (5998) |
| Liquid mixtures | 579 | (525) | 1827 | (1658) | 3998 | (3628) | 4637 | (4207) |
| Total | 2365 | (2145) | 7656 | (5292) | 15370 | (13948) | 17396 | (15782) |

Use of liquids has increased seven-fold in 20 years whereas the total tonnage of all fertilizers doubled during that period. These and other data indicate that about 61 percent of the total N applied in the U.S. is applied in fluid form; about 16 percent of the P₂O₅ and 8 percent of the K₂O are applied as fluids. Fluid mixtures represent 20 percent of the total mixtures (both fluid and dry) applied in the U.S. Some reasons for the popularity of fluid fertilizers are:

1. Low cost raw materials are either used directly or manufactured into other products. For example, during the past 20 years anhydrous ammonia has been the most economical source of nitrogen for direct application.
2. Fluids allow ideal placement of fertilizer such as row application as starter fertilizer or addition to irrigation systems.
3. Fluids are excellent carriers of micronutrients. A small amount of micronutrient can be dissolved or suspended in fluid. It is easy to obtain a uniform application of the micronutrient.
4. Fluids are excellent carriers of pesticides, herbicides, and insecticides. By using fluid fertilizer-pesticide mixtures, it is possible to avoid one application across the field. Because fluid fertilizers can be uniformly applied, it is also possible to apply the pesticide to obtain uniform weed or insecticide control. This is not always possible when using granular fertilizers.
5. Fluid fertilizers are usually much easier to handle than solid materials. For example, it would be much safer and easier to ship nonpressure urea-ammonium nitrate solution and unload it in a developing country than to ship either ammonium nitrate or urea.

One of the main disadvantages in handling fluid fertilizers is that they require special storage and handling equipment. In many developing countries it would be impractical to ship and handle small quantities of fluids, whereas bagged granular fertilizers can be readily used. Also,

fluids such as anhydrous ammonia and suspensions require special application equipment that is not readily available in most developing countries. Sometimes problems occur in the storage of fluids; however, equally serious problems occur in the storage of granular materials.

The U.S. fluid marketing systems may be used as guides for use in other countries; however, the subject should be studied thoroughly before using these marketing systems. This paper will provide for evaluation information concerning fluid fertilizer marketing systems.

Anhydrous Ammonia

This section is devoted to the use of anhydrous ammonia. Some physical characteristics of liquid ammonia are shown in the following tabulation:

| <u>Characteristics</u> | <u>Value</u> |
|---|----------------------------------|
| Boiling point ^a | -33.4°C (-28°F) |
| Freezing point ^a | -77.7°C (-108°F) |
| Latent heat of evaporation ^a | 327.4 KCal/gr (589 Btu/lb) |
| Solubility in water at 25°C ^a | 0.456 gr per gr H ₂ O |
| Vapor pressure Kg/cm ² (psig) ^b | |
| -18°C (0°F) | 0.32 (4.6) |
| 0°C (32°F) | 3.35 (47.0) |
| 38°C (100°F) | 13.87 (197.2) |
| Specific gravity | |
| -18°C (0°F) | 0.6749 |
| 0°C (32°F) | 0.6385 |
| 38°C (100°F) | 0.5831 |
| Explosive mixture | 16-25% NH ₃ in air |

^a at atmospheric pressure

^b gauge pressure

In the U.S. 4.1 MM tons (3.64 MM tonnes) per year of nitrogen, about 40 percent of the total nitrogen used, is supplied by direct application of anhydrous ammonia. This popularity of anhydrous ammonia results from its low cost which largely is the result of the excellent facilities for transporting and storing liquid ammonia.

There are now two pipeline systems for transporting ammonia from producing plants to the major consuming area; more pipelines are being planned. Many large atmospheric storage tanks with capacities ranging from 5,500 to 27,000 tonnes also are in use in the U.S. These tanks are maintained at atmospheric pressure by using ammonia as a refrigerant to keep the liquid at -33°C (-28°F). This is done by withdrawing and compressing ammonia gas from the tank, cooling it with water to liquify it, and vaporizing the resulting liquid in the tank to keep the contents cool.

Similar storage tanks are mounted on barges for transporting liquid ammonia on U.S. river systems. Figure 1 shows these inland waterways and the pipeline systems for ammonia and nitrogen solutions. Most major nitrogen-consuming areas are reached by either pipeline or barge. Also, tank cars are readily available that contain pressure tanks for storing 24 to 73 tonnes of anhydrous ammonia. It is common to have "whole train" shipments of ammonia that have as many as 100 cars; all of the cars are shipped directly from the producing plants to the consuming area. Because of these excellent transportation facilities, anhydrous ammonia can be delivered at relatively low cost.

Anhydrous Ammonia Dealer Operations

Usually most anhydrous ammonia dealers have pressure-type storage tanks varying in size from 12,000 gallons (45,420 liters) to 30,000 gallons (114,000 liters). The pressure in these tanks should not exceed about 265 psig (19 kgr/sq. cm). Liquid ammonia is transferred from the railway tanks car to the storage tank with an ammonia compressor or a positive displacement pump. Use of an ammonia compressor is the most often used method. Transfer is accomplished by removing vapor from the storage tank and

pumping it into a railroad car. Removing vapor from the storage tank causes its contents to cool; compressing the gas causes it to be heated, and hot gas causes the contents of the tank car to increase in temperature. These temperature changes cause a pressure differential between the railroad tank car and the storage tank, allowing the liquid ammonia to be easily transferred from the tank car to storage.

Pressure tanks having a capacity of 1,000 to 2,000 gallons (3,785 to 7,570 liters) are often used to transport ammonia from the dealer terminal to the farm. At the farm the ammonia is transferred from nurse to applicator tanks. Figure 2 shows how a vapor transfer pump is used to transfer ammonia from a nurse tank to an applicator. Some farmers fill the applicator by simply bleeding ammonia gas from the applicator tank into the atmosphere. Thus the vapor pressure of the ammonia in the nurse tank causes the liquid to be transferred to the applicator.

Application of Anhydrous Ammonia

Because it is applied as a volatile liquid, anhydrous ammonia must be injected 6 to 12 inches (15-30 cm) below the surface of the soil. This usually is accomplished by application knives such as those shown in figure 3. In sandy and loose soil, ammonia is often applied by an ammonia chisel, also shown in figure 3. Anhydrous ammonia usually is metered by a variable orifice meter or by a piston pump. The rate of application using the orifice meter is determined by the speed of the applicator, the swath width, and the orifice opening. Piston pumps are usually actuated by a drive-chain driven by a sprocket attached to a wheel of the applicator. Application rate is changed by changing the length of stroke of the piston, the rate being independent of the applicator speed.

Ammonia applicators range in size from small 5-row rigs to the large rigs which have swath widths up to 65 feet and are pulled by crawler tractors as shown in figure 4 (4).

The estimated application cost for anhydrous ammonia is about \$6.00 per acre (\$14.82 per hectare). This cost varies widely; however, most companies report that the cost for applying ammonia is usually about double that of applying nonpressure solutions.

Safety in Handling Ammonia

There are some hazards involved in handling anhydrous ammonia as with any fluid under pressure. Countries considering use of anhydrous ammonia should ensure that merchants and farmers are aware of the vapor pressure characteristics of ammonia so that tank ruptures can be avoided. At liquid temperatures up to 70°F (21°C)--normal summer temperatures for most consuming regions--the gauge vapor pressure is about 114 psig (8 kg cm²). At higher summer temperature, 100°F (38°C), this pressure can be as high as 197 psig (13.9 kg cm²).

Ammonia is a highly reactive alkaline chemical which must be handled with caution. Liquid ammonia can cause serious burns. As a gas, it is extremely irritating to the eyes and respiratory system. High concentrations can cause death by asphyxiation. Fortunately the gas is so irritating that workers will voluntarily leave the danger area before injury occurs. Of course this is no safeguard against a sudden encounter with liquid or a concentrated accumulation of the gas. Specific safety precautions for handling ammonia are given in U.S. agricultural publications such as the Agricultural Anhydrous Ammonia Operator's Manual by The Fertilizer Institute (5).

Aqua Ammonia

Aqua ammonia is not nearly as popular in the U.S. as anhydrous ammonia; but, it is safer to use. Because of the safety factor, it is a more practical material for use in developing countries.

The most popular aqua ammonia solution contains 20 percent N and exerts no gauge pressure at temperatures below 97°F (36°C). Therefore, aqua ammonia of this concentration is stored in covered nonpressure storage tanks usually built to withstand 5 psig (0.35 kg/cm²) and equipped with pressure and vacuum safety valves. These valves are set to open at 1.051 and 0.991 absolute atmospheric pressure.

Aqua ammonia usually is produced in a plant in which anhydrous ammonia, water, and recycled cool aqua ammonia are mixed continuously in a simple pipe mixing chamber. Enough water is added to adjust the specific gravity of the liquid to that of aqua ammonia containing 20 percent nitrogen or other desired concentrations. A 50-ton tank car of anhydrous ammonia can be converted to 206 tons of aqua ammonia in 5 to 8 hours depending upon the plant's cooling capacity.

Because aqua ammonia has a low vapor pressure, it does not need to be injected as deeply into the soil as does anhydrous ammonia. Most operators have found they do not have excessive ammonia losses if they inject the aqua ammonia about 3 to 5 inches (8 to 13 cm) beneath the surface. Applicators used for applying aqua ammonia are similar to those for anhydrous ammonia because they have injection knives. Since these knives penetrate about one-half the depth of anhydrous ammonia knives, much less power and energy is required to pull them. Also, aqua ammonia can be applied at a much faster rate. It can be applied during such field operations as plowing and discing without high ammonia loss.

Some companies apply aqua or anhydrous ammonia through ditch irrigation systems. This is done at very low concentrations and during early spring when the temperature of irrigation water is low. Enough ammonia is added to produce a slight ammonia odor in the irrigation water. Possibly this technique may help developing countries with application.

Nonpressure Nitrogen Solutions

The second most popular liquid material for direct application in the U.S. is nonpressure nitrogen solutions. Use of these solutions is increasing faster than that of anhydrous ammonia. The tabulation given earlier shows that during 1980 about 6.6 MM tons of these solutions were used in the U.S. The most frequently mentioned reasons for the increased popularity of the solutions are usually the same as for fluid mixtures. In addition to the advantages mentioned for fluid mixtures, the reasons most dealers and farmers prefer to handle these solutions instead of anhydrous ammonia are:

1. Nitrogen solutions are safer to handle, store, transport and apply.
2. Storage and transport equipment costs are less for nonpressure nitrogen solutions.
3. Application speed is much higher for nonpressure nitrogen solutions which results in lower application costs.

Nitrogen solutions usually are produced from urea, ammonium nitrate, and water. They contain a corrosion inhibitor and can be stored and used in mild steel (carbon steel) equipment. Solutions sold in the U.S. have three concentrations: 28, 30, and 32 percent N. Their salt-out temperatures vary directly with their plant nutrient concentrations. Some of the physical and chemical characteristics of the three nonpressure solutions are shown in the following tabulation (6):

| <u>Grade, % N</u> | <u>28</u> | <u>30</u> | <u>32</u> |
|--|-----------|-----------|-----------|
| <u>Composition, % by weight</u> | | | |
| Ammonium nitrate | 40.1 | 42.2 | 44.3 |
| Urea | 30.0 | 32.7 | 35.4 |
| Water | 29.9 | 25.1 | 20.3 |
| <u>Specific gravity, 60°F (15.6°C)</u> | 1.283 | 1.303 | 1.32 |
| <u>Salt-out temperature, °F (°C)</u> | -1 (-18) | +14 (-10) | 28 (-2) |

The inhibiting agent most often used in these solutions is a small quantity of anhydrous ammonia; usually about 10 pounds of ammonia/ton (5 kg of NH₃/tonne) of product is added to adjust the pH of the solution to 7.0. Another effective inhibiting agent is ammonium phosphate. Only a small quantity of ammonium phosphate (0.2% P₂O₅) is required to inhibit the solution. This phosphate material reacts with the mild steel tank to form a corrosion inhibiting iron phosphate film.

Production of Nonpressure Nitrogen Solutions

Two types of production processes are used--batch and continuous. Both are fairly simple; in each process concentrated urea and ammonium nitrate solutions are measured, mixed, and then cooled. In the batch process solutions are weighed in a mix tank and the inhibitor is weighed separately and added to the mix tank. Finished product is cooled after it is mixed. The continuous process is similar except the nitrogen solution, water, and inhibiting agent are metered and fed continuously to a mixing chamber similar to the simple baffled mixer shown in figure 5. Material from the mixing chamber is cooled and pumped to storage.

Recently in the U.S. there has been some interest in producing nitrogen solution from prilled urea and ammonium nitrate. When using a batch mix tank to produce solution from these solid materials, hot water is required to speed dissolution of the materials. Usually enough heat is supplied so that all solids will be dissolved at the end of the 30-minute mixing time. About 50 lbs/ton (25 kg/tonne) of saturated steam is required for a reasonable mixing time. This process is more expensive than the solution process; however, special pricing policies can make it desirable to produce a solution from solid materials. Also, it may be practical to use this procedure in some developing countries where solid materials are available.

Recently, one ammonia pipeline company, which also has a river terminal close to the pipeline, decided that it was economical to produce hot ammonium nitrate solution from ammonia at the pipeline and mix it with prilled urea received by barge. A similar procedure may be advisable for countries receiving anhydrous ammonia and prilled urea by ship. At the point of delivery, anhydrous ammonia could be converted to nitric acid and then to hot ammonium nitrate solution. This ammonium nitrate solution could then be mixed with the prilled urea to produce the nonpressure urea-ammonium nitrate solution.

Application of Nitrogen Solutions

While most nitrogen solutions are used for direct application, much is used to produce fluid mixtures. Most of the solutions are applied by broadcasting with spray nozzles. Figure 6 is a sketch of the nozzles usually used. On the right is a fan-type that emits fine droplets. Some applicator operators like fan-type nozzles to apply mixtures of nitrogen solution with herbicides. They report uniform response from the nitrogen and uniform kill

of weeds. Other operators report that under windy conditions there is too much fertilizer drift with these nozzles; they prefer to apply the solutions with flooding or hollow cone nozzles such as shown on the left side and center of figure 6. Flooding nozzles emit drops about the same size as average rain drops; there is little or no drip. They also apply material uniformly across the swath. These are the same nozzles used to broadcast fluid mixed fertilizers.

Applicators used to broadcast nitrogen solutions vary in size from small ones pulled behind farm tractors (figure 7) to the large self-propelled high-flotation applicator (figure 8). The high-flotation types minimize compaction of the soil during fertilizer application so that the fertilizer can be applied during wet periods. These large applicators can apply fertilizer solutions at a rate of 1.75 acres/minute (0.71 hectares/minute).

Nonpressure nitrogen solutions are added through sprinkler, gated pipe, and ditch irrigation systems. The nitrogen solution is added to the irrigation water several times during the growing season. With several applications there is usually less leaching of the nitrogen and more efficient use of it by the crop. The apparatus for feeding these solutions to the irrigation unit usually consists of a storage tank and a piston-metering pump. The rate is varied by changing the length of stroke and speed of the piston pump.

Some solutions are mixed with other clear liquids, such as ammonium polyphosphates of grades 10-34-0 and 11-37-0, and potash to produce clear liquid mixtures. The solutions are also used to produce suspension mixtures.

Fluid Mixtures

The fluid mix fertilizer business in the U.S. is composed of two major segments, one in which solution mixtures are produced and one in which suspensions are produced. Solution mixtures usually are free of solids and clear enough to see through. The suspensions are of higher concentration and have small crystals of plant nutrients suspended in saturated fertilizer solutions. These crystals are suspended by a gelling clay such as attapulgite or sodium bentonite. These clays are usually low in cost; therefore, it is practical to use them to produce suspension mixtures.

Objectives of the fluid fertilizer production and marketing systems are much the same as in the manufacture of solid materials; namely, to produce a material with low raw material cost, low operating cost, high nutrient concentration, good quality, low pollutant emission, product homogeneity, product versatility, and a product that can be applied uniformly (7).

Many materials can be used to produce fluid mixtures and there has been considerable versatility by the fluid fertilizer industry in accepting new materials as they become economical.

Solution Fertilizer Mixtures

U.S. statistical data show that about 60 percent of all the fluid mixtures are used as solution fertilizers.

The marketing system usually consists of regional fertilizer plants which use wet-process superphosphoric acid in TVA's new pipe reactor process to produce an ammonium polyphosphate base solution of grade

10-34-0 (8). The superphosphoric acid is produced by concentrating merchant-grade orthophosphoric acid (54% P_2O_5) to superphosphoric acid in a vacuum or atmospheric concentrator. The superphosphoric acid usually contains about 68 to 70 percent total P_2O_5 of which 20 to 35 percent is present as polyphosphate. Physical and chemical characteristics of a typical superphosphoric acid are shown below:

Chemical Analysis, % by weight

| | |
|---|------|
| Total P_2O_5 | 70.0 |
| Polyphosphate, % of total P_2O_5 | 30.0 |
| Sulfate (SO_4) | 3.8 |
| Aluminum (Al_2O_3) | 1.1 |
| Iron (Fe_2O_3), % | 1.0 |
| Magnesium (MgO) | 0.4 |
| Fluorine (F) | 0.27 |
| Solids (Insol. in CH_3OH) | 0.15 |
| Solids (Insol. in H_2O) | 0.01 |
| <u>Specific gravity, 75°F (24°C)</u> | 1.96 |
| <u>Viscosity, centipoises, 126°F (52°C)</u> | 175 |

Nearly all polyphosphoric acid in the wet-process superphosphoric acid is in the form of pyrophosphate; the remaining phosphate is present as orthophosphoric acid. Conversion to superphosphoric acid increases the cost, but the long shipping distance in the U.S. generates freight savings that reduce or eliminate this disadvantage.

More than 130 U.S. plants use the TVA pipe reactor process to produce an estimated 1.5 MM tonnes of 10-34-0 or 11-37-0 grade product per year. Other countries such as Belgium, France, and the USSR also use this TVA process to produce an ammonium polyphosphate solution. Two typical plants are shown in figure 9. The plant on the left has a combination mix tank-cooler design. The upper part of the tank consists of a section filled

with plastic "Pall Ring" packing. Liquid is recirculated to this section while air is drawn through the section to partially cool the liquid. Liquid from the bottom of the tank is passed through a heat exchanger where it is further cooled before being pumped to storage. Anhydrous ammonia is passed through this same heat exchanger, vaporized, then passed into the tee section of the pipe reactor. Superphosphoric acid is pumped by a positive displacement pump to this same tee section, where the acid and gaseous ammonia react to form a hot melt at 600°F (316°C). Usually some ammonia is added to the recirculation line to adjust the pH of the liquid to 6.0 for production of the 10-34-0 grade. The water content is controlled by adding water to the recirculation line.

The plant on the right uses a separate mix tank and an evaporative cooler. The mix tank is used for mixing hot melt from the pipe reactor with recirculating liquid. By having a separate mix tank it is possible to maintain a high liquid temperature {180°F (82°C)}, which enhances mixing of the melt in the liquid and also provides an excellent means of evaporating and superheating the anhydrous ammonia used in the pipe reactor. Data indicate that plants with the separate mix tank usually produce an ammonium polyphosphate liquid of slightly higher polyphosphate content than those with the combination mix tank-cooler. Probably one reason this occurs is because of the high temperature of the ammonia used in the pipe reactor. Ammonia not added to the pipe reactor is usually added as liquid ammonia to the mix tank. Usually about 60 percent of the ammonia is added to the pipe reactor and 40 percent to the mix tank. This tank is equipped with a small scrubber in which cooled 10-34-0 grade product is used to scrub exit gases from the mix tank.

Both plants have efficient, inexpensive evaporative coolers. Very few contaminants are lost from either of the plants. There is a considerable loss of water as steam and water vapor.

Physical and chemical characteristics of a typical ammonium polyphosphate solution of grade 10-34-0 made by this process are tabulated below:

Chemical Analysis, % by weight

| | |
|---|----------|
| Nitrogen | 10 |
| P ₂ O ₅ | 34 |
| Polyphosphate, % of total P ₂ O ₅ | 65-70 |
| <u>Viscosity, centipoises, 80°F (24°C)</u> | 75 |
| <u>Specific gravity, 80°F (27°C)</u> | 1.400 |
| <u>Salt-out temperature, °F (°C)</u> | <32 (<0) |

A considerable amount of the 10-34-0 grade solution is used for direct application in the wheat belt and other areas in which potassium is not deficient. Most of the ammonium polyphosphate solutions of grade 10-34-0 or 11-37-0 are used in small mix plants to produce NPK mixtures. A typical plant is shown in figure 10. Ammonium polyphosphate solution is mixed with nitrogen solutions (urea-ammonium nitrate solutions) and potash to produce such clear liquid grades as 7-21-7, 8-8-8, and 21-7-0.

Sometimes the liquid mix plant produces a potash base solution such as a 2-6-12 or 4-11-11 grade and transports it to a satellite station where it is mixed with nitrogen solution, containing 28 to 32 percent N, and 10-34-0 grade ammonium polyphosphate solution to produce NPK mixtures. At the satellite station each liquid is metered and mixed in the farmer's nurse tank.

Equipment used to broadcast solution fertilizers is about the same as that used to broadcast nitrogen solution. Sometimes a pesticide (herbicide or insecticide) is transported separately in a can to the farm and mixed with the liquid at that location. In this way the danger of transporting a

pesticide fertilizer on roadways is avoided. Some applicators are equipped with a small eductor for adding pesticide to a recirculating stream of liquid from the applicator.

Many farmers in the U.S. corn belt and areas with short growing seasons like to add some liquid mixtures, usually of grade 7-21-7, in the row with the seed to enhance early "pop up" of the crop. Much of the clear liquids used in the U.S. are for this purpose. Liquid mixtures flow from a constant head tank by gravity through an orifice plate. Part of the liquid is often added directly with the seed and part is placed to the side of the seed.

Figure 11 shows a barrel that has been adapted as a constant head tank for adding solutions to ditch irrigation systems. This barrel is sometimes used on farming equipment for dribbling liquids in the seed row. This equipment is designed using the principle of Marriott's bottle and is similar to those used in laboratories. It has a breathing tube and an orifice plate at its discharge. A constant head is maintained at the orifice plate. This metering equipment has been used in Mexico and other countries to meter solutions into ditch irrigation units.

Suspension Fertilizers

Use of suspensions has grown very rapidly in the U.S. during the past 5 years. Some of the main reasons for the increased popularity of suspensions are the same as for other fluids. However, some of the reasons that suspensions are more popular than solution-type mixtures are:

1. Lower cost, less pure materials can be used to produce suspensions.
2. Higher analysis grades can be produced; this is especially true when grades containing potassium are to be used.
3. Usually larger quantities of micronutrients can be suspended in suspensions than can be dissolved in solution fertilizers. Therefore, when suspensions are used, in most instances all required micronutrients can be added by the suspension fertilizers.
4. Powdered herbicides and insecticides not normally soluble in solution fertilizers can be suspended and uniformly distributed throughout the suspension.

The main reason for the early production of suspensions was to produce high potash grades for use in regions requiring potassium. The most popular suspension grades are those having high potash content such as the 3-9-27, 3-10-30, 4-12-24, 6-18-18, and 7-21-21 grades. Recently high nitrogen suspensions such as 14-14-14, 20-5-10, 21-7-7, and 24-8-0 grades also have become popular. A recent survey of fluid fertilizer manufacturers shows that about 35 percent of the fluid fertilizer plants in the U.S. produce suspensions and 89 percent produce solutions. These plants use the following materials to produce suspensions:

| <u>Materials</u> | <u>% of Plants Reported</u> |
|------------------------|-----------------------------|
| Potash | 60 |
| Nitrogen solutions | 73 |
| Ammonia | 37 |
| 10-34-0 grade solution | 69 |
| Phosphoric acid | 7 |
| Solid phosphates | 32 |

These data show that the most popular phosphate material for suspensions is still the ammonium polyphosphate solutions. However, economic pressures have encouraged use of other materials. The next most popular phosphate source is solid ammonium phosphates. In the past two years, use of granular materials as a source of phosphate for the fluid fertilizer industry has become very popular; many plants have been installed for converting granular materials into fluids. Most companies that formerly used 10-34-0 grade solution for the production of suspensions plan to use either phosphoric acid or granular phosphate materials, or an ammonium phosphate base suspension for producing their suspensions.

Companies using ammonium polyphosphate solution of 10-34-0 grade or an orthophosphate base suspension of grades 13-38-0, 12-35-0, or 11-33-0 use a simple plant such as the one shown in figure 12. In this plant the base phosphate material of 10-34-0 or 13-38-0 grade is mixed with non-pressure nitrogen solution, containing 28-32 percent N, and potash. All materials in the formulation are weighed and mixed in the mix tank. This plant has a relatively low cost, about \$50,000, and there are a number of these plants located throughout the U.S. Probably the most economical source of phosphate materials for these plants is ammonium orthophosphate suspension of grade 13-38-0 produced from the wet-process orthophosphoric acid and ammonia.

TVA has developed a new three-stage ammoniation process for producing this orthophosphate suspension. A sketch of this plant is shown in figure 13. The first stage is a boiling reactor operating at 220°F (104°C) and an N:P₂O₅ weight ratio of 0.23:1. Retention time in the first reactor should be about 30 minutes and the specific gravity 1.5. Under these conditions impurities introduced by the wet-process orthophosphoric acid are precipitated in the form that can be suspended easily in the fluid.

In the second stage, more ammonia is added to adjust the N:P₂O₅ weight ratio to a range of 0.3-0.33:1. Fluid is recirculated from the second stage at a high rate to produce rapid cooling in the evaporative cooler. Because of the rapid cooling, crystals formed in the fluid are small and easily suspended. Part of the fluid from the cooler is recirculated to the second stage to maintain its temperature between 190 and 200°F (87.8 and 93.3°C). The remainder of the fluid is sent to a third stage reactor where a small quantity of ammonia is added to adjust the N:P₂O₅ weight ratio to 0.35-0.365:1. At this degree of ammoniation all crystals in the suspension are diammonium phosphate. It is desirable to have diammonium phosphate crystals in the suspension instead of monoammonium phosphate because of the low density of the diammonium phosphate and its smaller crystal size. The third stage reactor is maintained at 120°F (49°C) by cooling-water coils.

Gelling clay is added to the third stage so that the final product contains about 1.5 percent clay and has an analysis of 13.5 percent N and 38 percent P₂O₅. TVA has produced several thousand tons of this base suspension for use in its product development field programs. Field tests show the 13-38-0 grade product to be an excellent suspension that can be shipped long distances and stored up to 12 months without excessive gelling of small crystals. The suspensions have been used to produce mixtures, such as the 20-10-10, 7-21-21, and 14-14-14 grades, by adding nitrogen solution and potash. Actual production cost of the 13-38-0 grade for a basic phosphate producer would be less than comparable production costs of a granular diammonium phosphate of 18-46-0 grade. One company in the Netherlands has built a pilot plant for producing 13-38-0 grade suspension. Other companies have shown considerable interest in using the process.

Other companies use a batch ammoniation process for producing base suspensions or NPK mixtures from merchant-grade phosphoric acid (54% P_2O_5), anhydrous ammonia, and potash (9). A sketch of a typical batch plant using phosphoric acid and ammonia is shown in figure 14. This process includes a stainless steel (type 316) mix plant, stainless steel recirculation pump, and a wooden evaporative cooler which provides rapid cooling.

Acid is ammoniated to an N: P_2O_5 weight ratio of 0.33:1. With this procedure all crystals in the suspension are small diammonium phosphate crystals.

Use of Solid Materials in Suspensions--For the last few years it has been popular in the U.S. to use granular and powdered ammonium phosphates and nitrogen materials in the production of suspensions. Materials such as granular and powdered monoammonium phosphate, granular diammonium phosphate, and granular and prilled urea have been used.

Probably the main reason for using solid materials is that they are the most economical source of phosphate delivered to use areas. Also, when ammonia is added to the suspension, the material cost usually is less than comparable costs for bulk blended (dry mix) materials. Other reasons given for converting granular materials to fluids are:

1. Many merchants prefer to add pesticide to the fertilizer mixture after it has been delivered to the farm. This avoids the transporting of large quantities of fertilizer-pesticide mixtures on roadways as is necessary when granular fertilizer-pesticide mixtures are used.

2. A fluid can be applied more uniformly and accurately than a granular mixture. This is important when herbicide is incorporated into the fertilizer mixture; nonuniform application can cause toxicity in some spots in the field and ineffective weed control in others.
3. Small quantities of micronutrients can be uniformly applied as fluid mixtures. This is difficult to accomplish with bulk blended materials (10).
4. Many companies report that since they have fluid fertilizer application equipment for nitrogen solution, they must convert solids to fluids to utilize the equipment effectively.

These reasons certainly apply to other developed countries and some developing countries.

Five typical plants in which solid materials are used to produce suspensions are shown in figure 15. A dominant feature of these mix tanks is the large pumps used to recirculate liquid within the mix tank. One of the plants has a liquid grinder while the others have high intensity agitators. All tanks are equipped for adding ammonia and some for adding phosphoric acid. All can convert solid materials such as mono-ammonium phosphate (MAP), granular ammonium polyphosphate (APP), diammonium phosphate (DAP), ammonium sulfate, and urea to fluids.

Most producers of suspensions prefer to produce mixtures having the highest possible grade without exceeding practical viscosity limits. Application tests show that this viscosity should not exceed 1000 centipoises to avoid nonuniform application and difficulty in pumping and handling the suspension. Crystals formed in the suspension should be small and light enough to avoid excessive settling and plugging of nozzles during application. In producing

suspensions it would be desirable to adjust the N:P₂O₅ weight ratio to the point of highest solubility (0.3:1). However, at this ratio the lightest and smallest crystals are not produced. As was mentioned earlier for the production of 13-38-0 grade suspensions, it is important that the suspensions be ammoniated to an N:P₂O₅ weight ratio of 0.33:1 so that all of the crystals in the suspension are diammonium phosphate. Figure 16 is a photograph of MAP and DAP crystals. It is obvious that DAP crystals would have less tendency to plug a nozzle. Also, DAP is lighter than MAP (respective densities, 1.619 versus 1.803), and should have less tendency to settle during storage and application.

Typical formulations for production of 11-33-0 grade suspension from MAP, DAP, or APP are tabulated below:

| | <u>MAP</u> | <u>DAP</u> | <u>APP</u> |
|--|----------------|----------------|----------------|
| <u>Phosphate Material</u> | <u>11-52-0</u> | <u>18-46-0</u> | <u>11-55-0</u> |
| Formulation, lbs/ton of product | | | |
| 11-52-0 grade (MAP) | 1269 | - | - |
| 18-46-0 grade (DAP) | - | 1004 | - |
| 11-55-0 grade (APP) | - | - | 1200 |
| Phosphoric acid (54% P ₂ O ₅) | - | 367 | - |
| Anhydrous ammonia | 97 | 47 | 107 |
| Water | 604 | 552 | 663 |
| Gelling clay | 30 | 30 | 30 |

When either the MAP or APP materials are used, only anhydrous ammonia is required to adjust the N:P₂O₅ ratio; however, when DAP is used, some phosphoric acid must be added to the formulation to lower the N:P₂O₅ ratio and improve solubility of the ammonium phosphate portion of the mixture.

Interest in direct application of phosphate rock is being revived because of better methods for characterization of the rock (11). It is now known that finely ground uncalcined North Carolina rock and Morocco rock are good sources of phosphate for some soils. However, it is difficult to apply the small-sized dry rock without excessive dusting and subsequent loss.

Therefore, a logical solution to these problems is to produce suspensions from ground phosphate rock. Tests show that a suspension can be produced which contains 60 percent North Carolina rock (97% minus-100 mesh and 67% minus-325 mesh), 28.2% water, 0.5% attapulgite gelling clay, 0.3% tetrasodium pyrophosphate dispersant, and 1% nitrogen or ammonium phosphate electrolyte solutions. Such a product contains about 18% P_2O_5 , has a viscosity of less than 750 centipoises, and has excellent storage characteristics (12). Application of this suspension would eliminate problems associated with dustiness in dry application and mixing, facilitate inclusion of other plant nutrients, micronutrients, and herbicides, and eliminate separate application of the materials.

Direct application of this suspension is especially attractive in some developing countries, because it eliminates chemical processing of phosphate and offers a possible means of using local deposits.

Transportation and Application of Suspensions--When suspensions were first introduced in the U.S. they settled excessively during transport. Some means of agitation during transit was required. Figure 17 shows a trailer truck similar to trucks used to transport powdered bulk cement. The cone bottom of the truck is equipped with air spargers that can be used to keep materials suspended that tend to settle during transport. Another type of transportation truck (figure 18) has a round bottom but is equipped with a recirculation sparger. Material passing through the sparger tends to sweep the bottom of the tank and keeps the contents of the tank well mixed.

Applicators for suspensions are similar to those normally used for applying nitrogen solutions; many times the same equipment is used. When

suspensions are applied, a flooding-type nozzle must be used to avoid plugging of the nozzle. This is the large applicator that will apply suspensions at a rate of 1.75 acres (0.71 hectares) per minute. This applicator is also equipped with high flotation tires and can be used to apply fertilizer on wet soil without excessive compaction. It is equipped with a large recirculation pump and a drilled-pipe sparger. Streams of fluid from this pipe cause material within the tank to be mixed. This applicator costs about \$100,000.

Satellite Plants

Some companies produce NPK base grades (3-10-30, 4-12-24, and 7-21-21) and NP base materials (13-38-0 or 11-33-0 grade suspensions, or 10-34-0 grade solutions) and ship them along with nitrogen solutions to a satellite station such as that shown in figure 19. In this plant base materials and nitrogen solutions are mixed and weighed in a small mix tank mounted on scales. With these base materials it is possible for a small merchant to install an inexpensive plant for producing NPK suspensions or solution mixtures. Storage tests show that cone-bottom storage tanks are ideal for storage of suspensions; however, they are more expensive than flat-bottom tanks. Companies frequently use air spargers consisting of open-end pipes installed to introduce sparging air close to the bottom of the tank. Tanks with cone bottoms also have spargers. Experience has shown that it is preferable to agitate the suspensions once a day by blasting 300 gallons of air at 100 psig into the suspension so that it becomes well mixed.

Summary

Fluids have become a major source of plant nutrients in the U.S. and are becoming popular in countries such as Belgium, Canada, Denmark, France, Mexico, the Netherlands, and the United Kingdom. Other countries such as Columbia, India, Japan, Sweden and some other South American countries have also shown interest in fluid fertilizers. Probably nonpressure nitrogen solutions have the most potential for all countries. These solutions can be transported in conventional tank trucks and stored in mild steel storage tanks or in plastic-lined pits. It is conceivable that solutions of this type can even be unloaded from ships in developing countries where no docking facilities are available. Fluids have an excellent potential for use in irrigation systems and for direct application through existing wagons that have been used to spray herbicides or insecticides.

Although there are some hazards in the use of anhydrous or aqua ammonia, nonpressure solutions are completely safe to handle. Development of processes for producing superphosphoric acid has made it practical to produce high-analysis liquids, such as the ammonium polyphosphates of grades 10-34-0 and 11-37-0, which can be easily stored and applied. Equipment normally used to spray insecticides can easily be adapted for spraying these clear liquid solutions. One disadvantage of clear liquid mixtures is low-analysis potash grades. This can be overcome by producing suspension fertilizers containing crystals of plant nutrients suspended in saturated solutions. Usually if potash grades are produced, the plant nutrient concentration of suspensions is twice that of solution grades.

Sophisticated equipment has been developed for high speed application of fluids such as nonpressure solutions and suspension fertilizers. The

main advantage of using fluids is that they are excellent carriers of micronutrients and pesticides. These mixtures can be uniformly applied.

Solutions are likely to become a major source of plant nutrients in many countries because they are easy to handle and transport and have a lower production cost than many solid fertilizers.

References

1. Fertilizer International, No. 105, March 1978, p. 9.
2. Palgrave, D. A. Agricultural Progress, 43, 1968, pp. 15-24.
3. U.S. Department of Agriculture, "Commercial Fertilizer Consumption," for Year Ended June 30, 1977: Crop Reporting Board, Statistical Reporting Service.
4. Achorn, F. P., et al. "Latest Techniques in Application of Anhydrous Ammonia." TVA Fertilizer Conference, July 1977, pp. 36-45.
5. Agricultural Anhydrous Ammonia Operators' Manual, The Fertilizer Institute, March 1978.
6. National Fertilizer Solutions Manual, 1967.
7. Slack, A. V. and Achorn, F. P. "New Developments in Manufacture and Use of Liquid Fertilisers," The Fertiliser Society, London, England, 1973, pp. 64-74.
8. Meline, R. S., Lee, R. G., and Scott, W. C., Jr. "Production of Liquid Fertilizers with very High Polyphosphate Contents," Fertilizer Solutions, 16, (2), 1972, pp. 32-45.
9. Achorn, F. P. and Lewis, J. S. "Alternate Sources of Materials for Fluid Fertilizer Industry," NFSA Round-Up, St. Louis, Missouri, July 1974, pp. 8-13.
10. Achorn, F. P. and Mortvedt, John J. "Addition of Secondary and Micronutrients to Granular Fertilizers," Granular Fertilizers and Their Production, International Conference, London, England, November 1977, pp. 304-332.
11. Lehr, J. R. and McClellan, G. H. TVA Bulletin Y43, April 1972, "A Revised Laboratory Reactivity Scale for Evaluating Phosphate Rocks for Direct Application."
12. TVA 11th Demonstration, New Developments in Fertilizer Technology, October 5-6, 1976, pp. 70-74.

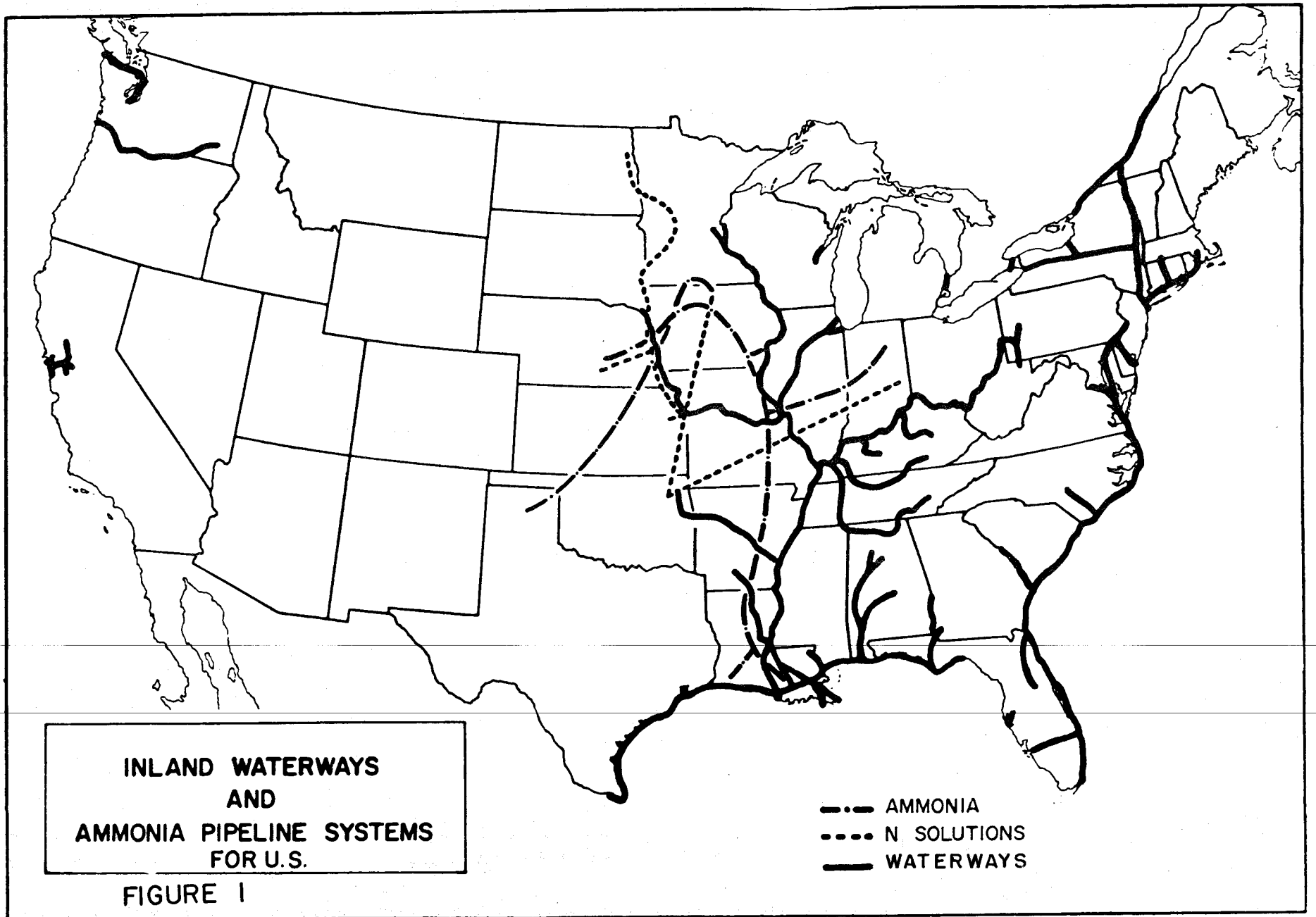
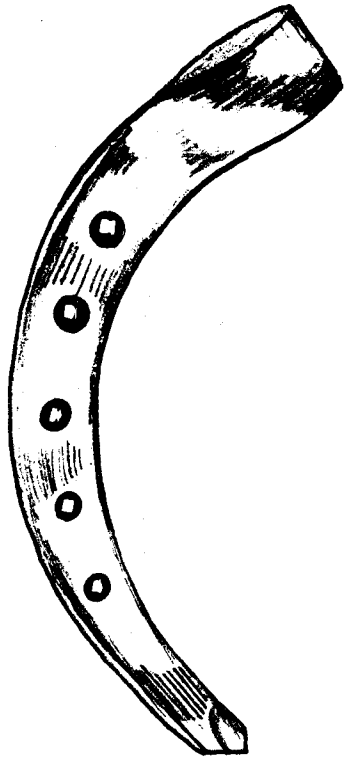
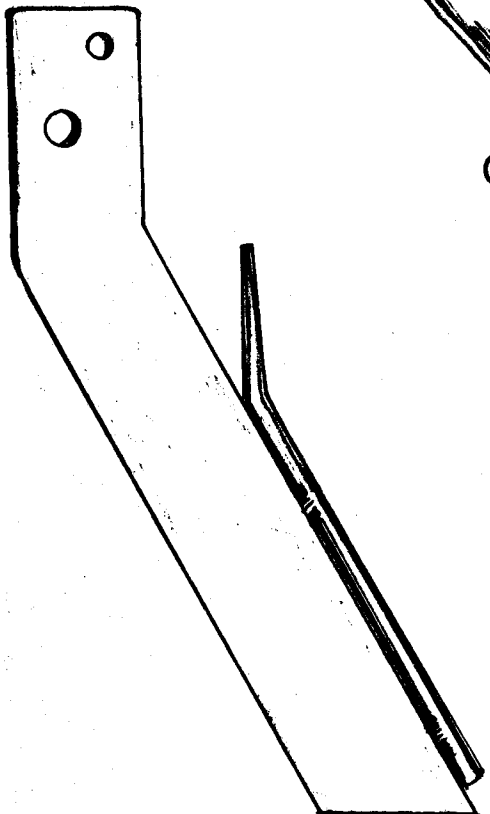




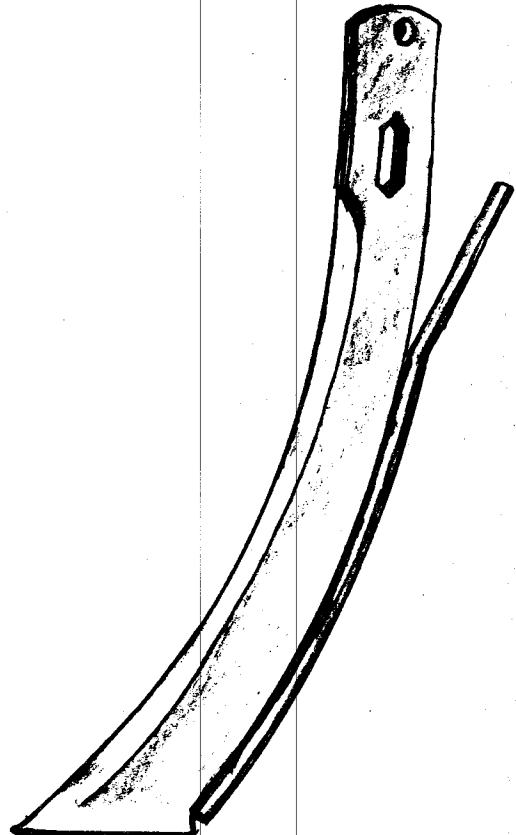
FIGURE 2
TRANSFER OF AMMONIA FROM NURSE TANK TO FARMER'S APPLICATOR
USING VAPOR TRANSFER PUMP



CHISEL



BACK SWEPT



FRONT SWEPT

FIGURE 3
KNIVES FOR APPLICATION OF AMMONIA

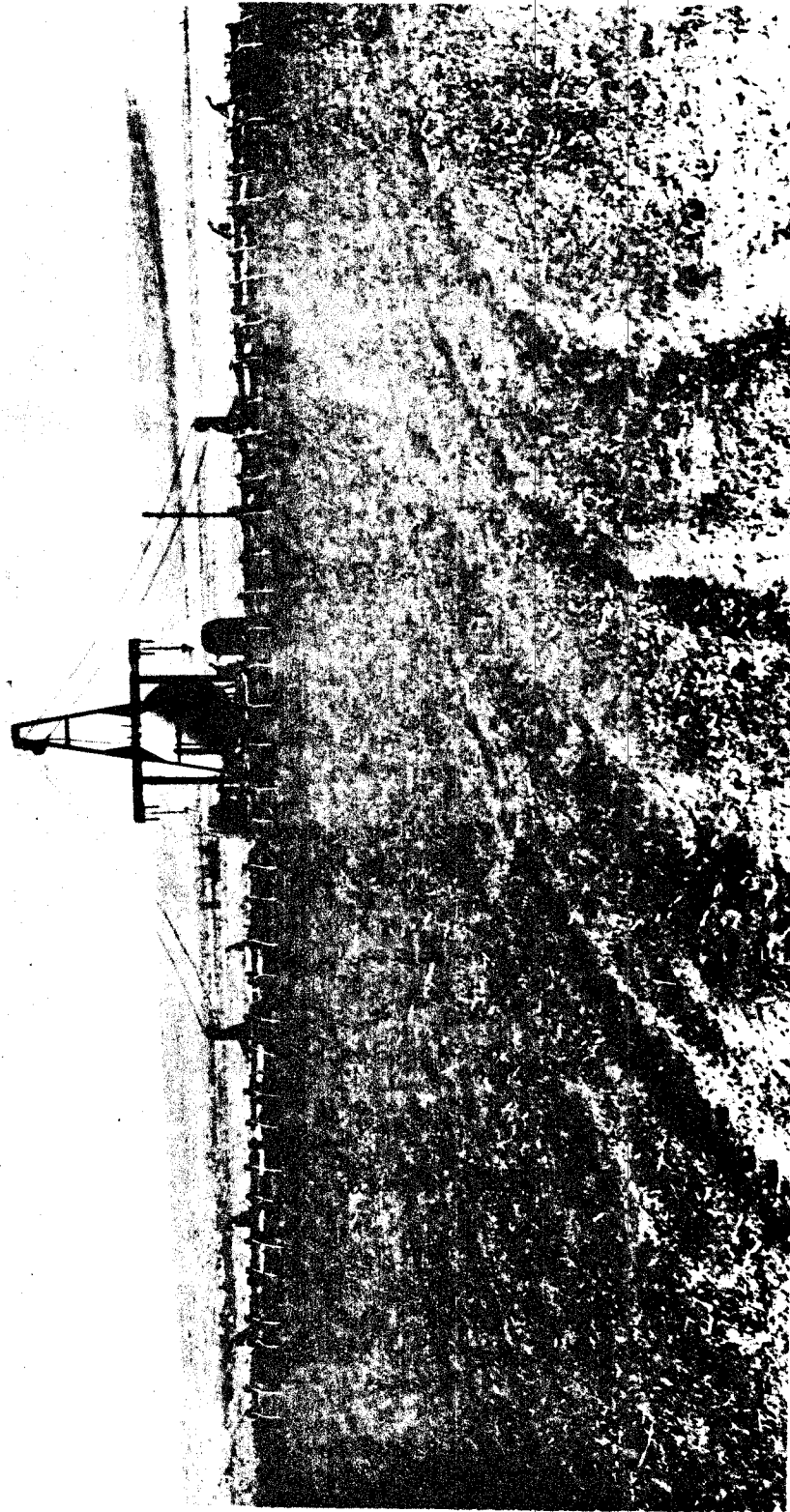


FIGURE 4
ANHYDROUS AMMONIA APPLICATOR
WITH 65-FOOT SWATH

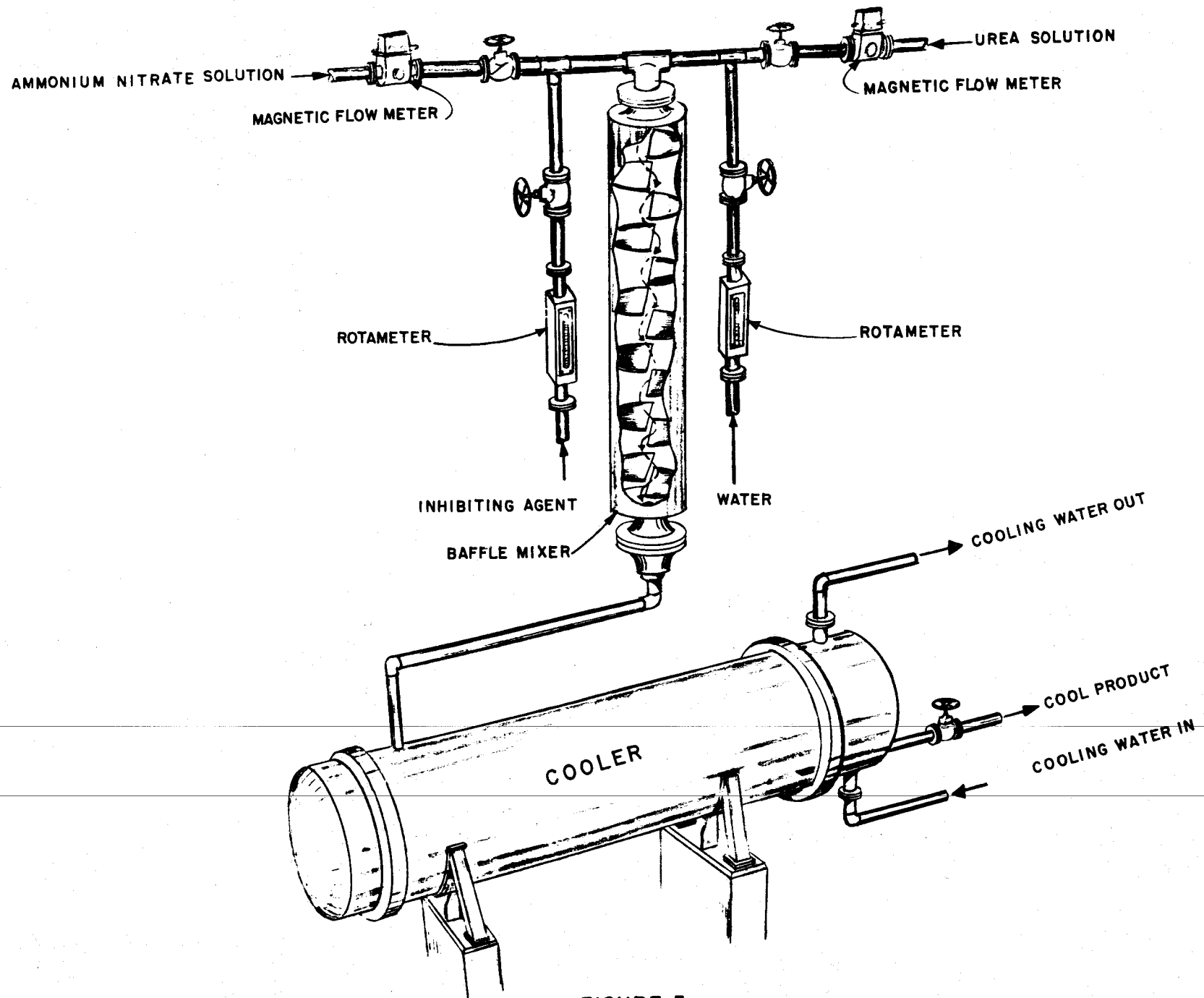


FIGURE 5
 TVA CONTINUOUS UREA-AMMONIUM NITRATE SOLUTION PLANT

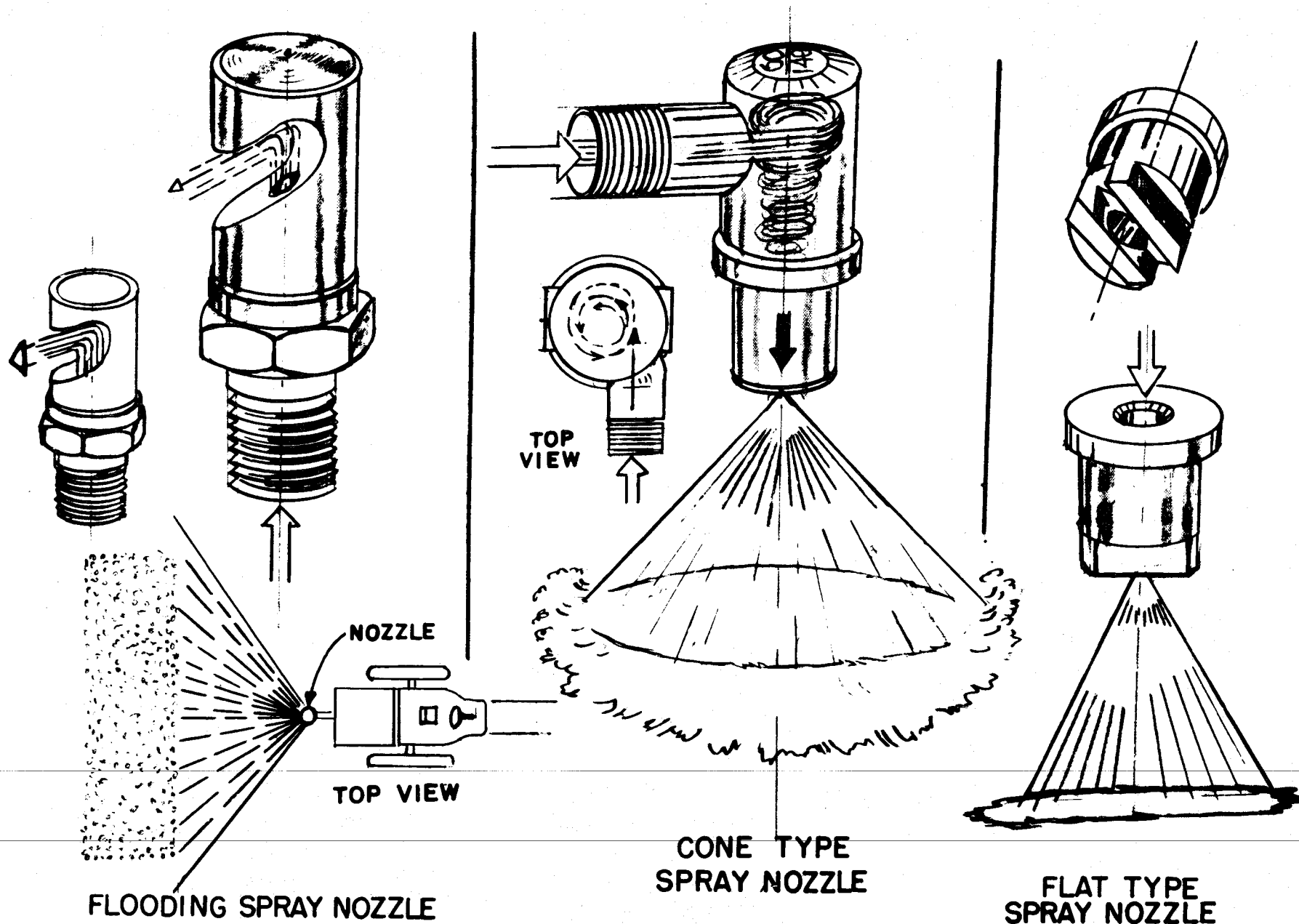


FIGURE 6

NOZZLES USED TO BROADCAST AND APPLY
FLUID FERTILIZERS

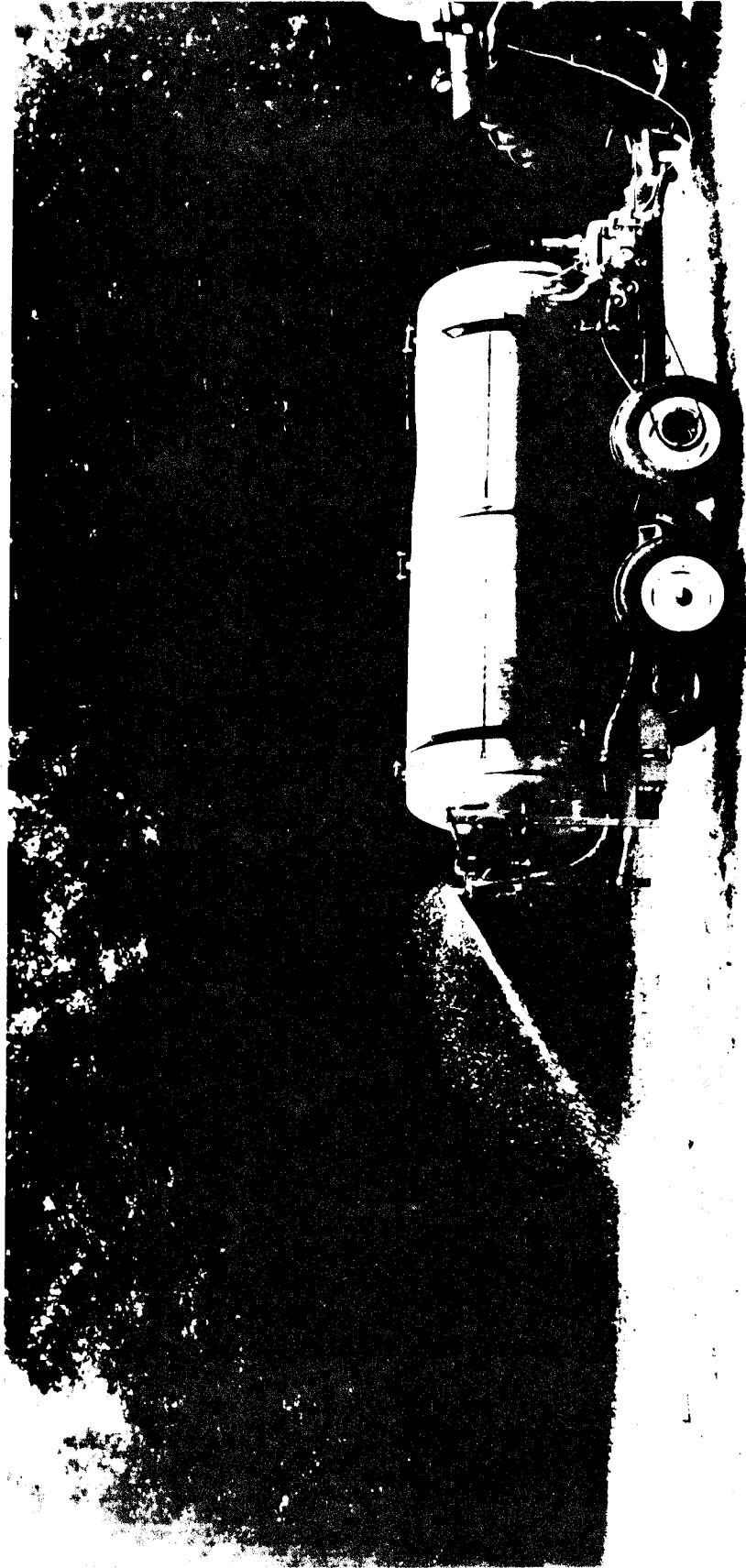


FIGURE 7
PULL TYPE APPLICATOR FOR FLUID FERTILIZERS

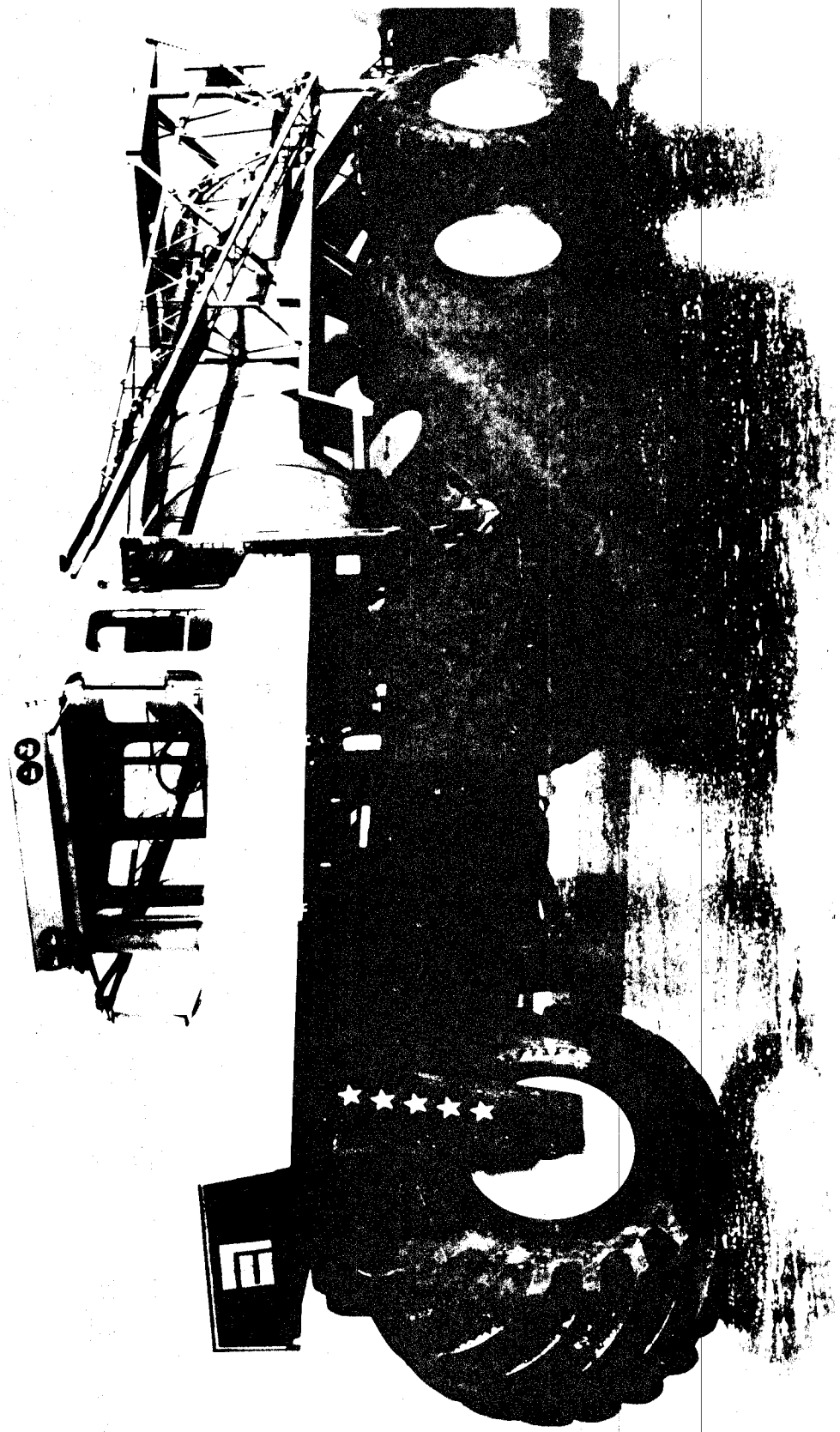
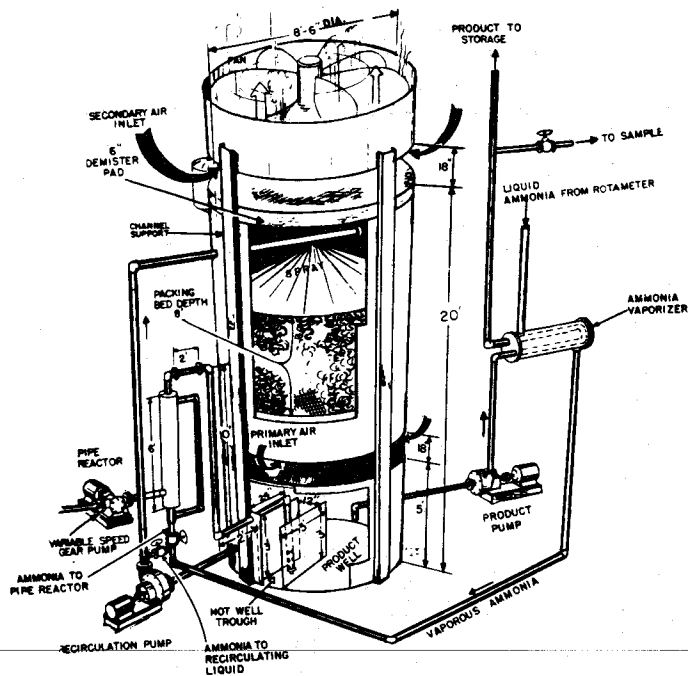
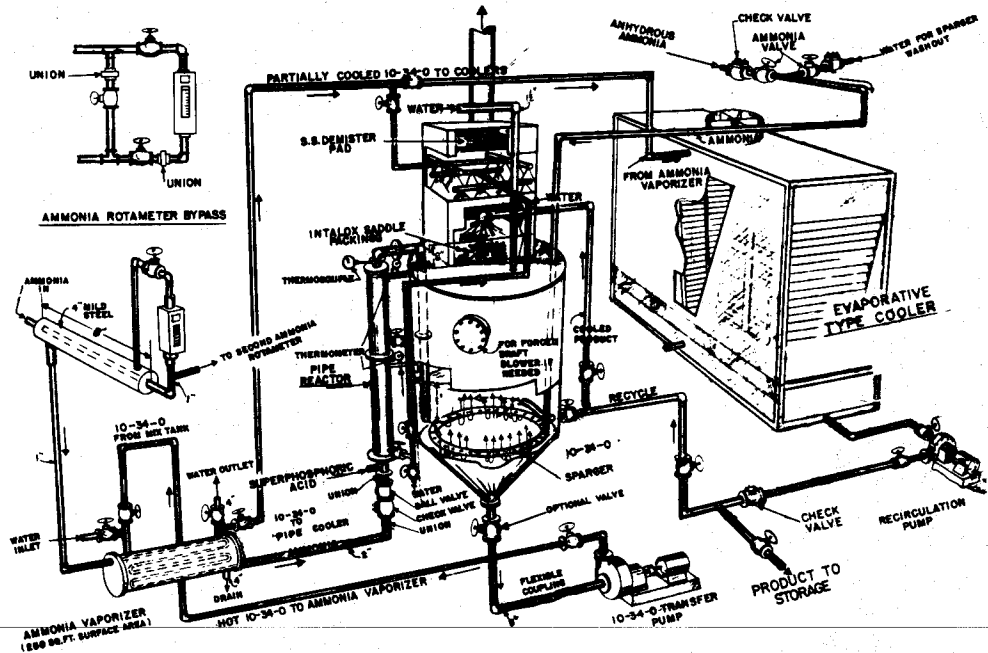


FIGURE 8
SELF PROPELLED APPLICATOR FOR FLUID FERTILIZERS



PLANT USING PIPE REACTOR PROCESS WITH INTEGRAL MIX-TANK,
COOLER AND SCRUBBER



PLANT USING PIPE-REACTOR
PROCESS SEPARATE MIX-TANK AND EVAPORATIVE COOLERS

FIGURE 9
TYPICAL PIPE-REACTOR PLANTS FOR PRODUCTION OF AMMONIUM
POLYPHOSPHATE SOLUTION

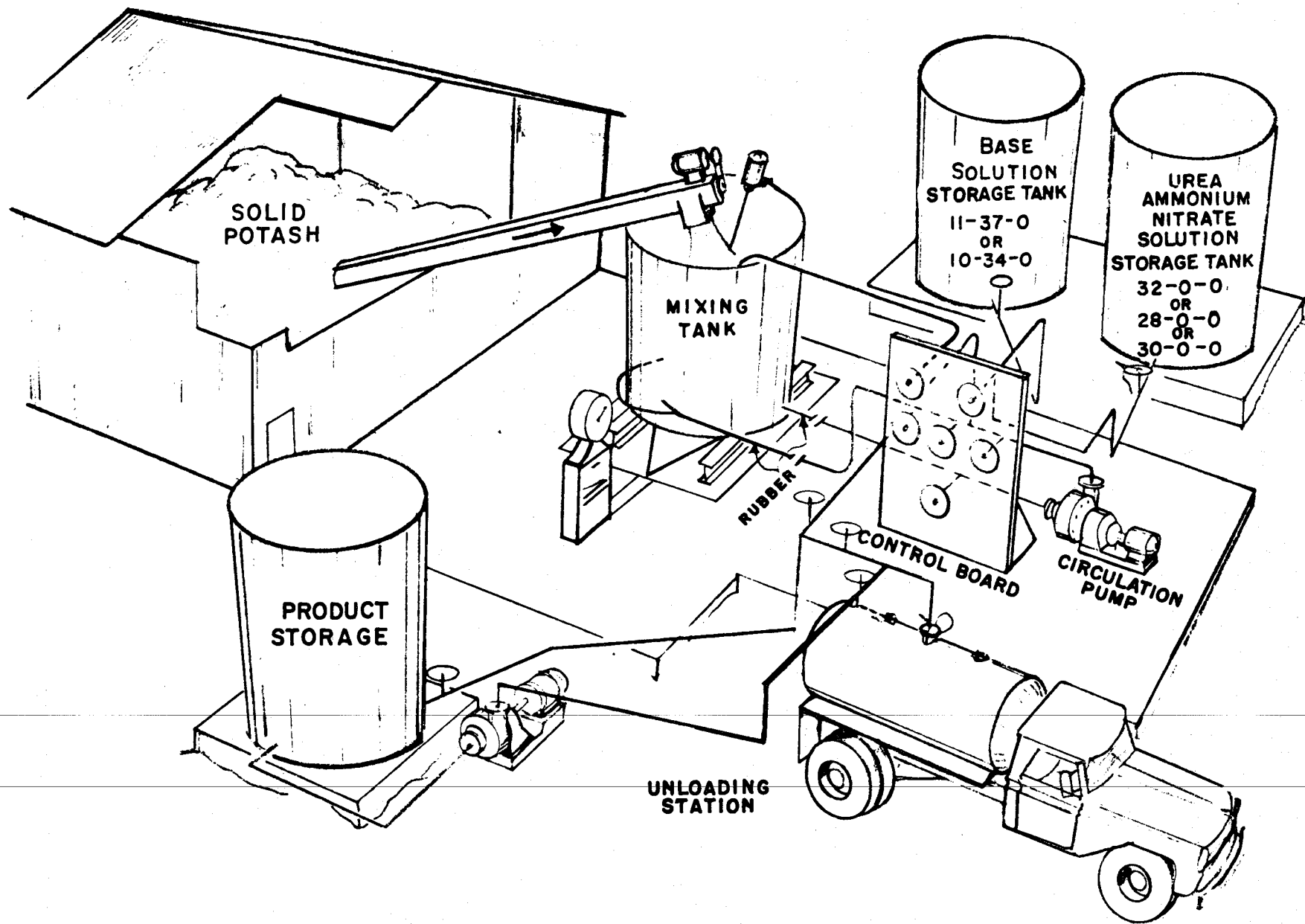


FIGURE 10
LIQUID FERTILIZER MIX PLANT

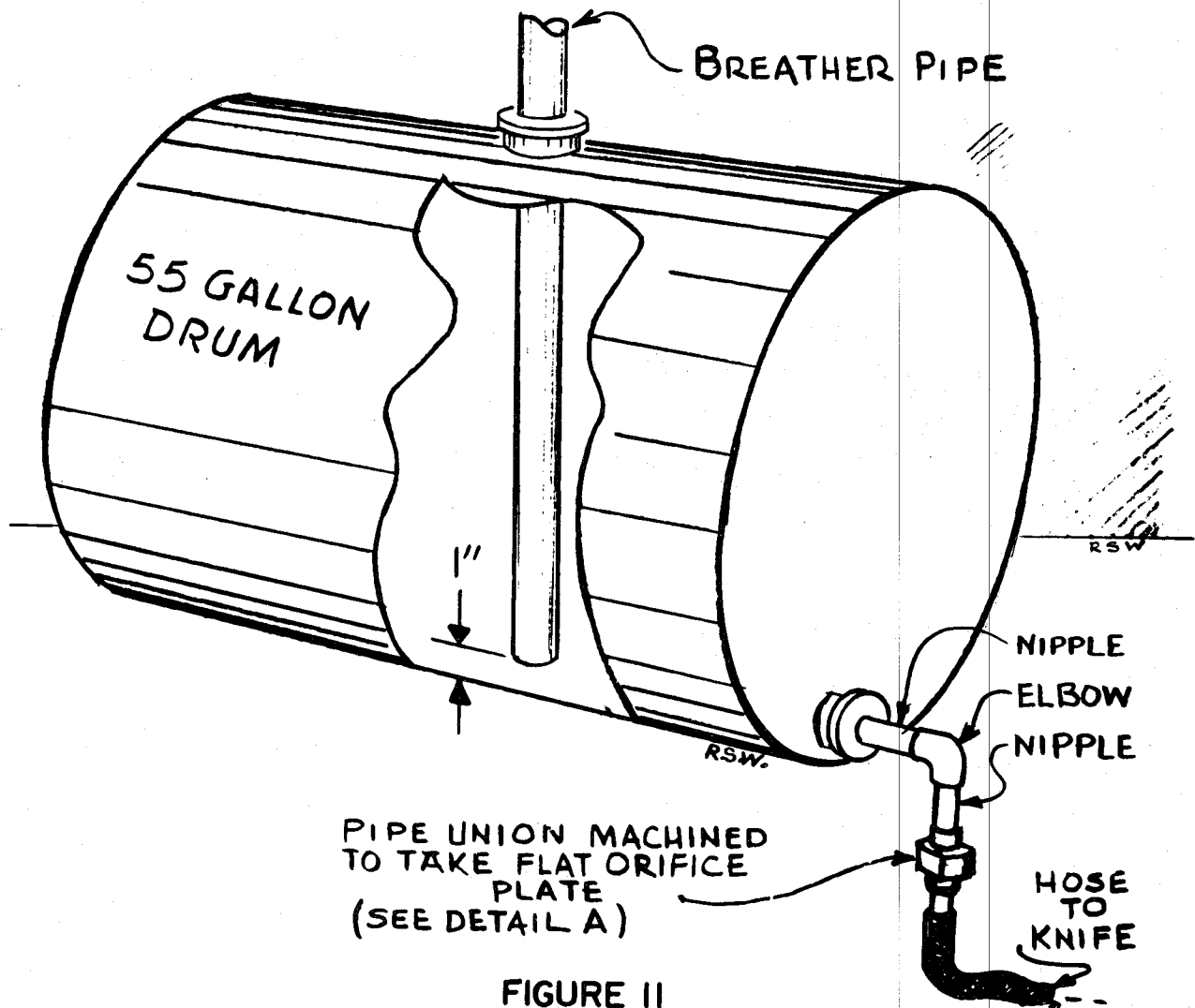
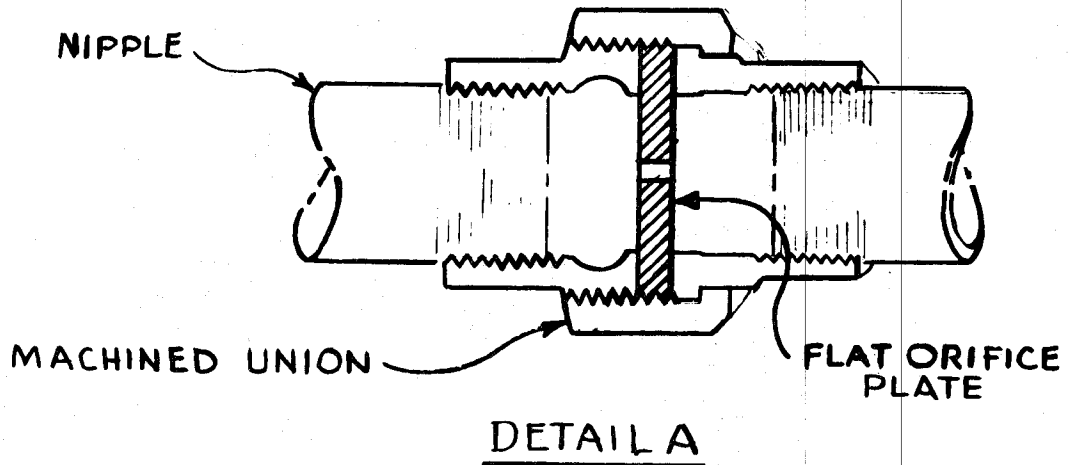


FIGURE II
BARREL ADAPTED AS A CONSTANT HEAD TANK FOR
ADDITION OF SOLUTIONS TO DITCH IRRIGATION SYSTEMS

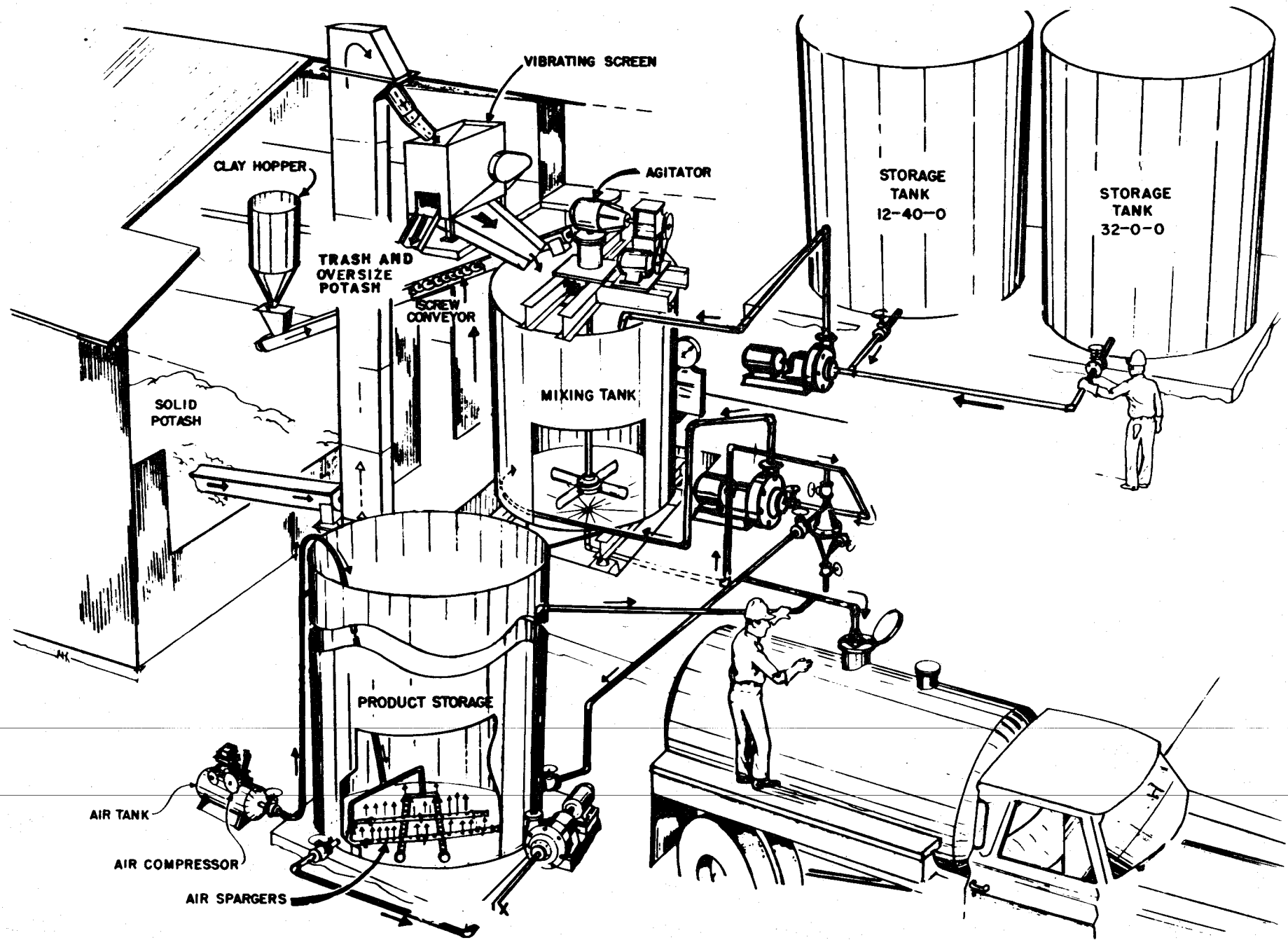


FIGURE 12
COLD-MIX PLANT FOR PRODUCTION OF SUSPENSION MIXTURES

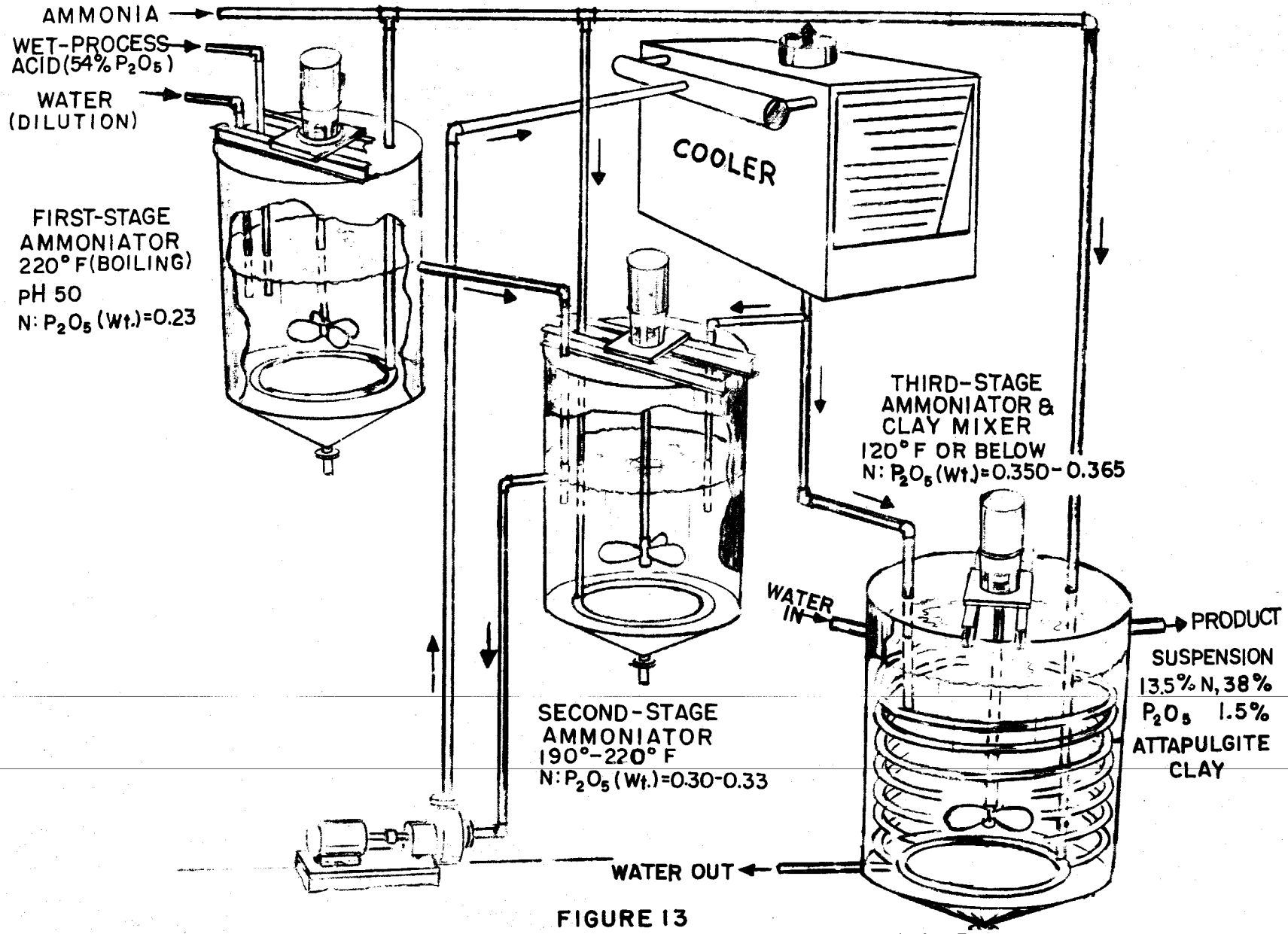


FIGURE 13
THREE STAGE CONTINUOUS AMMONIATION PROCESS FOR
PRODUCTION OF 13-35-0 AMMONIUM ORTHOPHOSPHATE
SUSPENSION

FORMULATION FOR 12-12-12 SUSPENSION

| ORDER OF ADDITION | MATERIALS | #/TON |
|-------------------|---|-------|
| 1 | WATER | 531 |
| 2 | PHOSPHORIC ACID (54% P ₂ O ₅) | 445 |
| 3 | AQUA-AMMONIA (20%N) | 97 |
| 4 | CLAY | 40 |
| 5 | POTASH (62% K ₂ O) | 387 |
| 6 | UAN (28% N) | 500 |

COOL TO 140°F THEN RECIRCULATE TO MIX TANK WHILE GELLING CLAY.

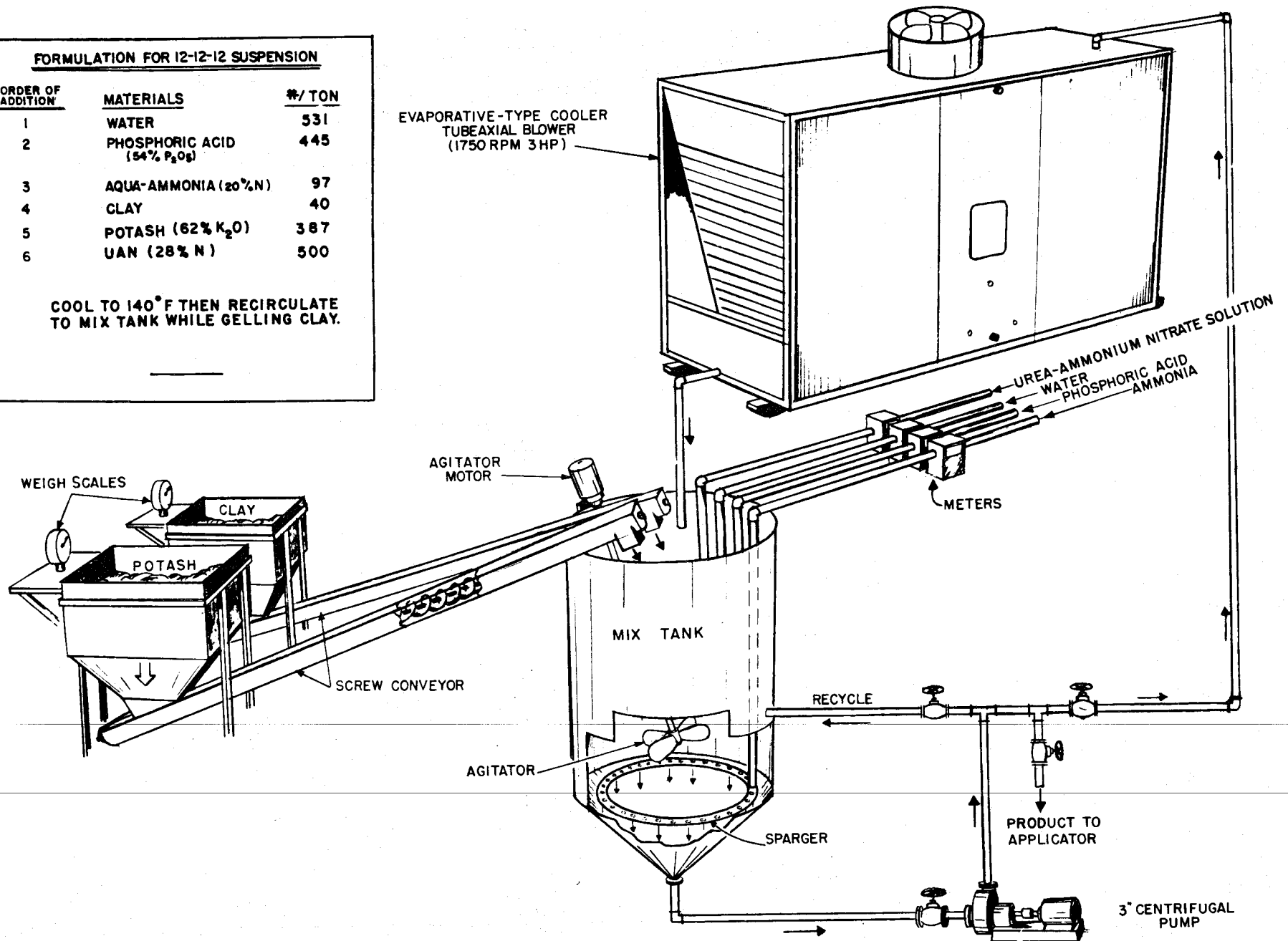


FIGURE 14
USE OF PHOSPHORIC ACID FOR NP AND NPK SUSPENSIONS

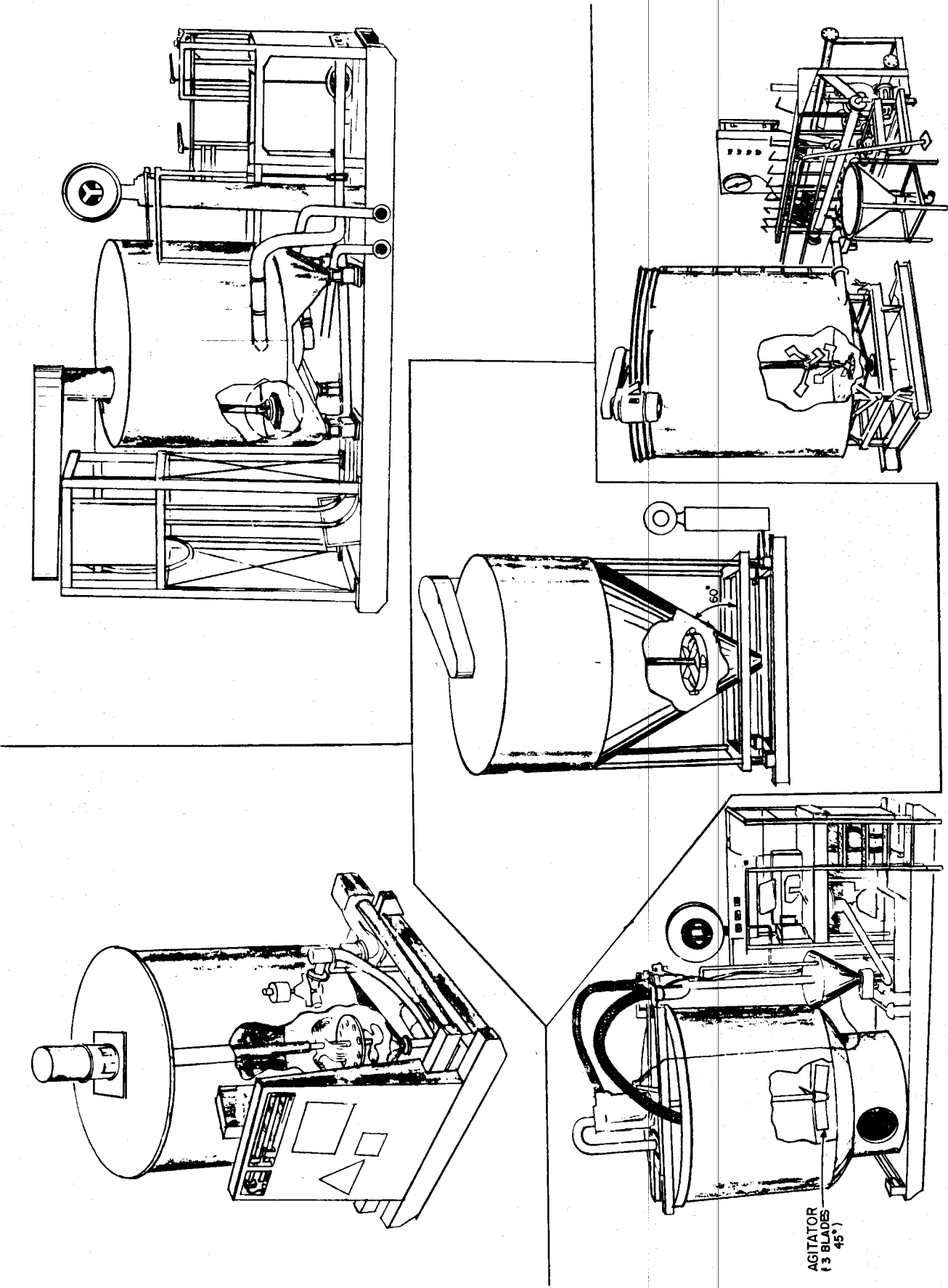
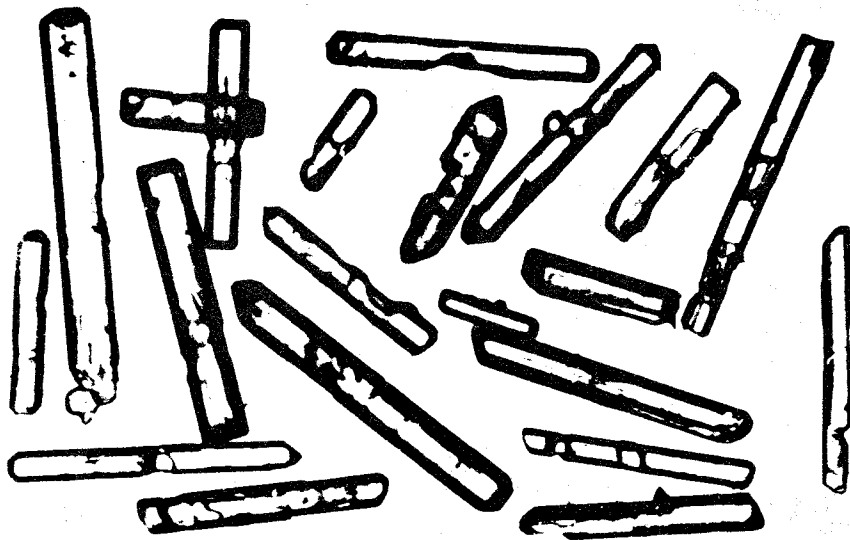
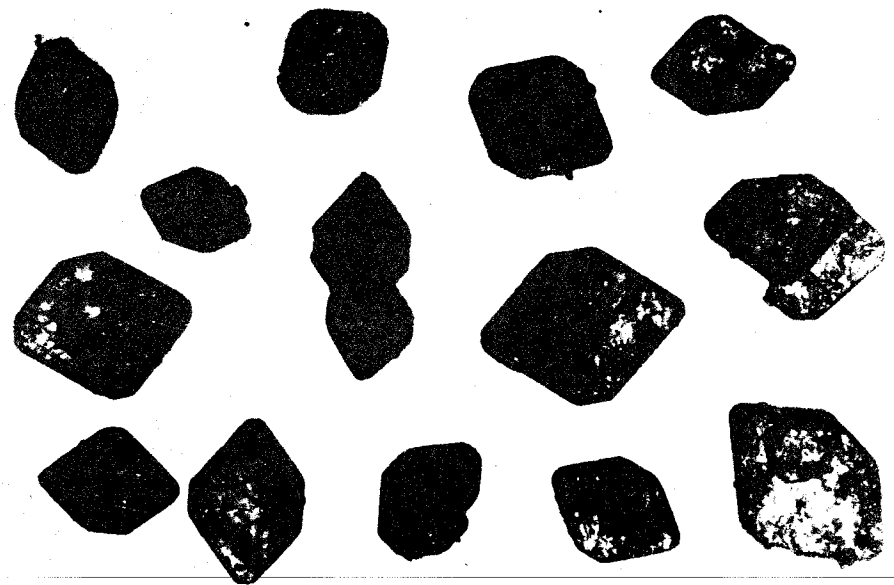


FIGURE 15
FIVE TYPES OF MIX TANKS FOR SUSPENSIONS

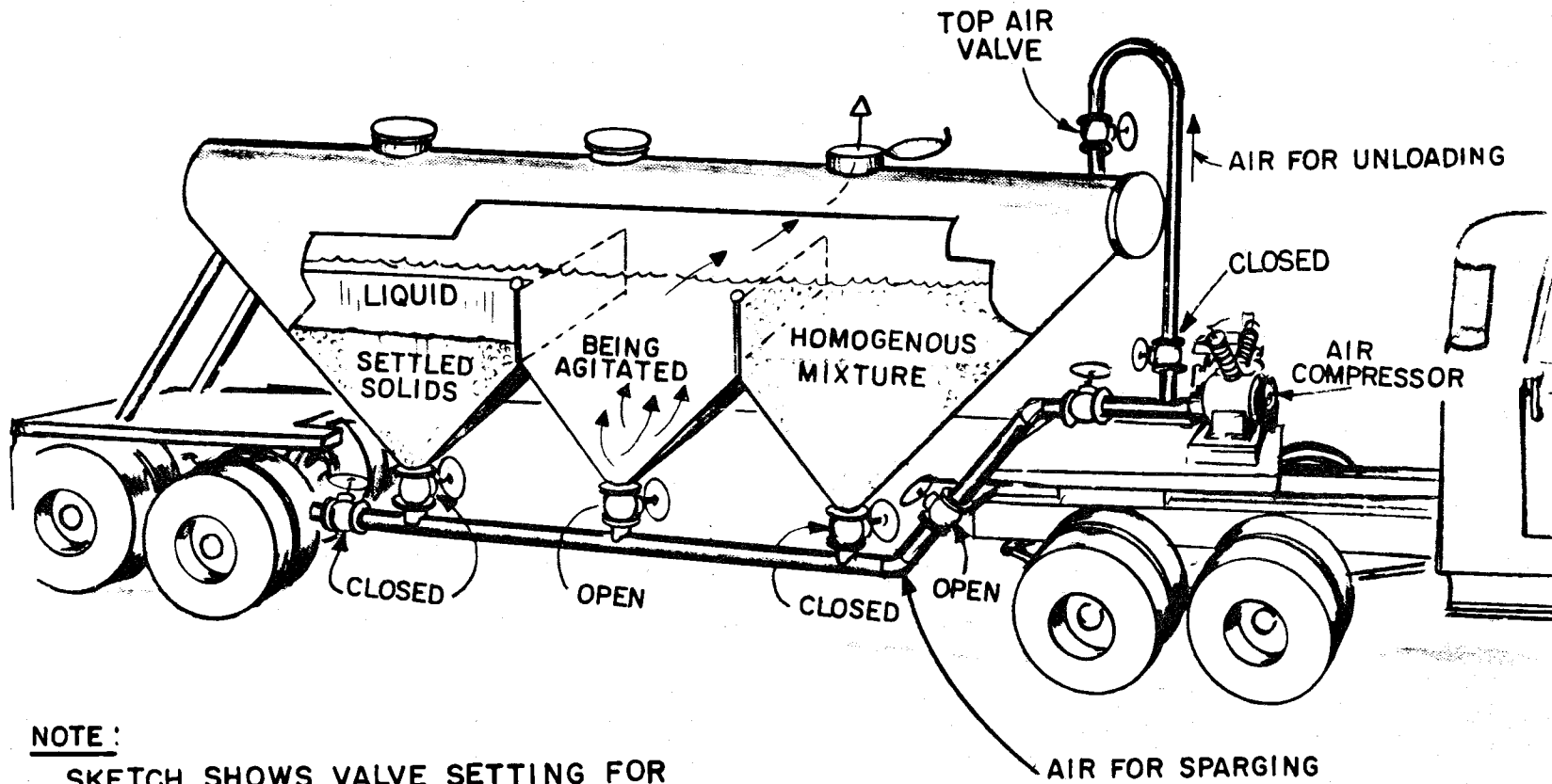


MONOAMMONIUM PHOSPHATE



DIAMMONIUM PHOSPHATE

FIGURE 16
MICROSCOPIC APPEARANCE OF MONOAMMONIUM PHOSPHATE
AND DIAMMONIUM PHOSPHATE CRYSTALS



NOTE :

SKETCH SHOWS VALVE SETTING FOR AIR AGITATION CENTER TANK. AIR PRESSURE ALSO USED TO FORCE SUSPENSION FROM TANKS.

FIGURE 17
CONE BOTTOM TRANSPORT

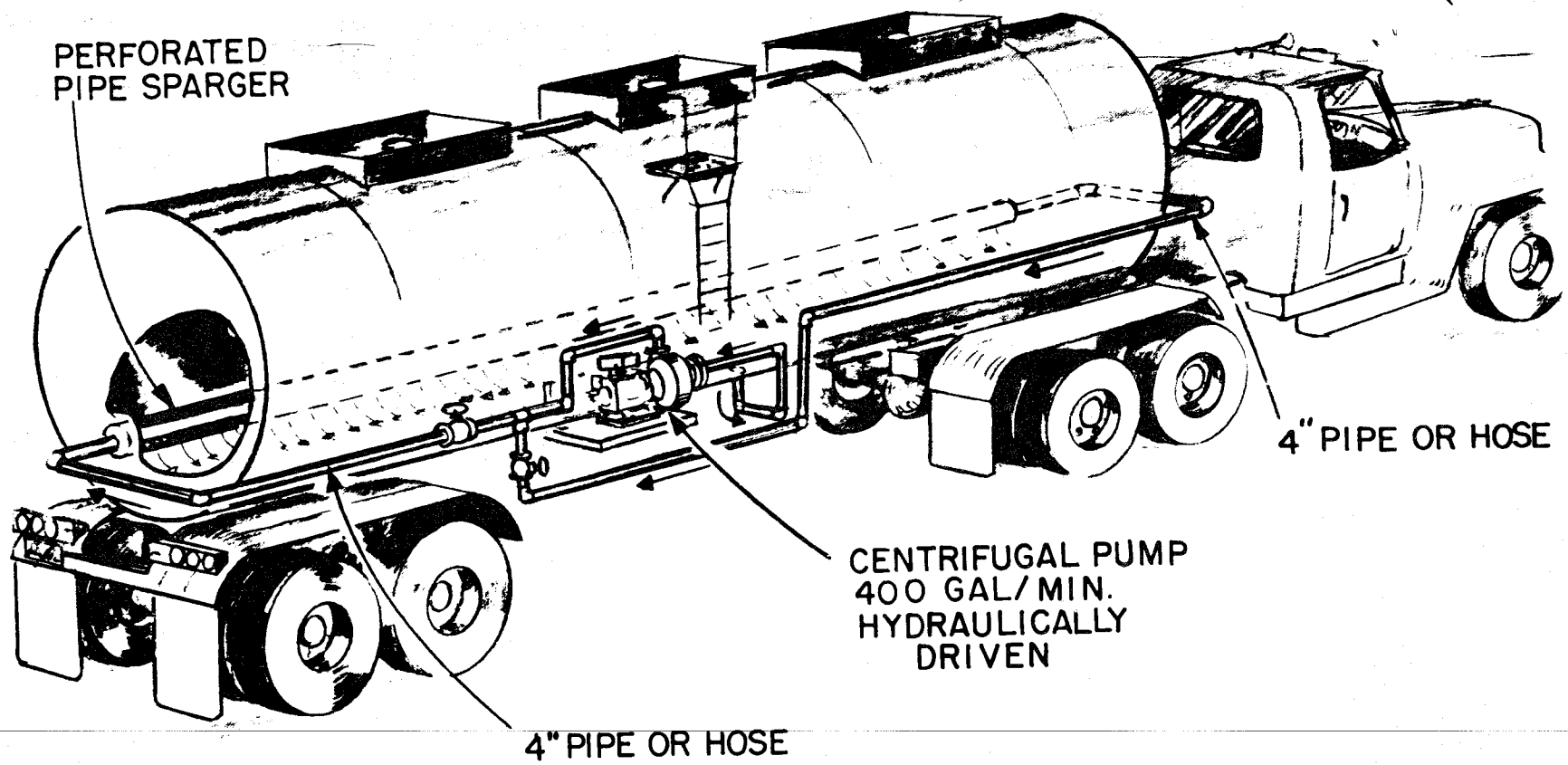


FIGURE 18

TRANSPORT TRUCK WITH PIPE SPARGER FOR SUSPENSION FERTILIZERS

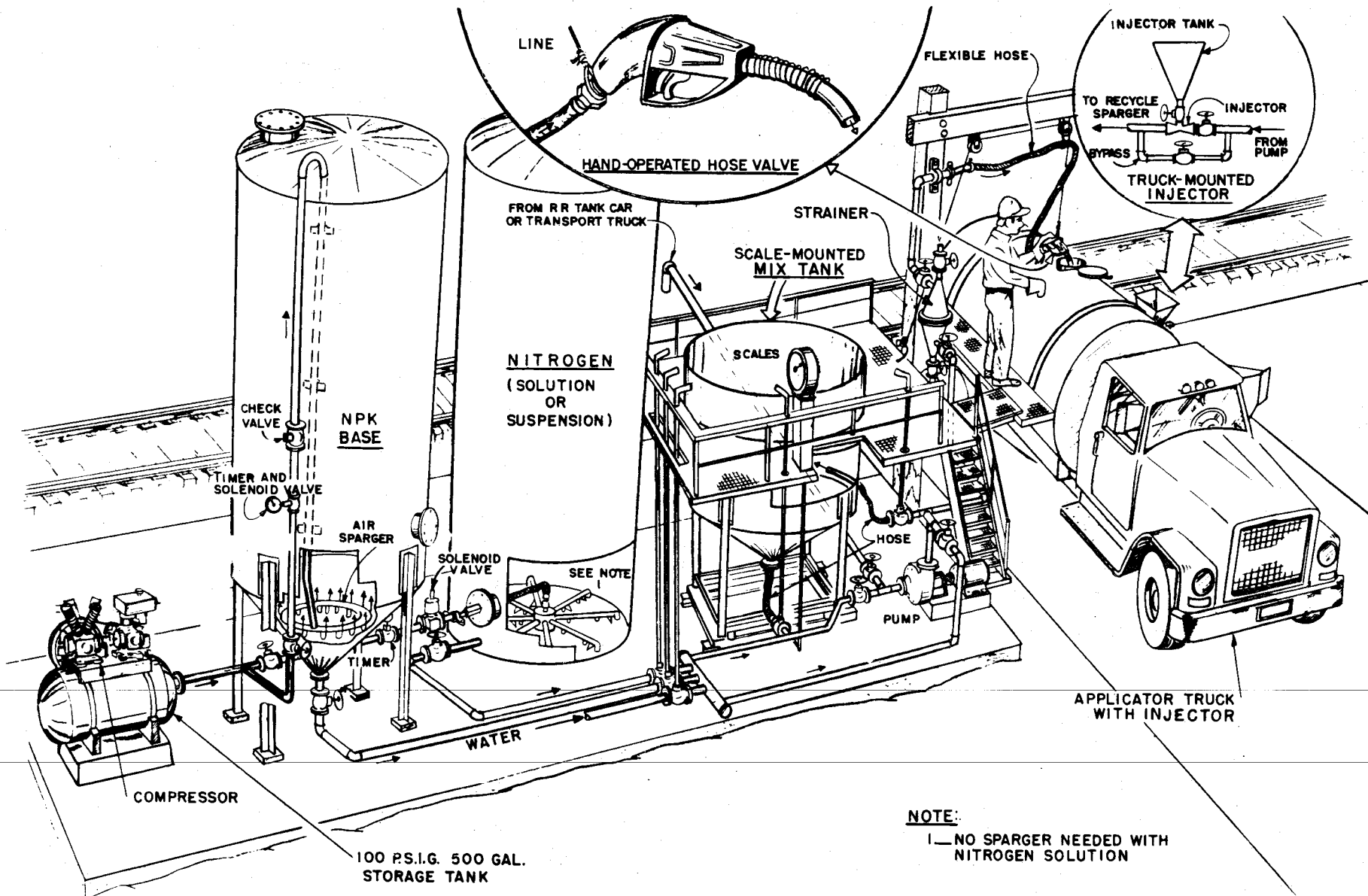


FIGURE 19
 SUSPENSION SATELLITE PLANT