LATEST DEVELOPMENTS IN PRODUCTION OF SUSPENSION MIXTURES

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Suspension mixtures have been steadily improved since they were first developed in the early 1960's. However, most suspension mixtures are still produced and quickly applied before large crystals can form or before the suspensions thicken as a result of precipitation of impurities derived from wet-process phosphoric acid.

Until recently most of these mixtures were broadcast on top of the soil by the fertilizer dealer because, even though research indicated that placing fertilizer near the seed (banding) was a more efficient way to get maximum effect from the fertilizer, broadcast application was less expensive. Fertilizer costs were low enough that even though extra fertilizer was required to achieve the same agronomic results, broadcasting was more cost efficient. Broadcasting is more tolerant of large crystals and sludges than is band application.

Recently farm profits have been reduced by high interest rates, high input costs (including the increased cost of fertilizer), and low farm prices. Because of this, many farmers are applying their own fertilizer and moving toward more agronomically efficient banding. This requires improved quality of suspension mixtures even though impurity content of many raw materials is increasing.

There are many ways of preparing suspension fertilizers for farm use. The best products are made from N-P_2O_5 bases prepared by a basic producer. Normally, basic producers have the equipment and technical knowledge to produce bases which store well and produce quality products. These bases are prepared ahead of use and combined by the fertilizer mixer with other ingredients such as urea-ammonium nitrate solution and potash.

Since the early 1960's TVA has developed techniques for producing a number of such bases. Products being used by industry which are being market tested by TVA or which are being produced by TVA processes are ammonium polyphosphate solution (10-34-0), ammonium orthophosphate suspension (13-38-0), solid ammonium polyphosphate (11-55-0, 25% polyphosphate), and solid diammonium phosphate (18-46-0). The most popular base, however, is commercial monoammonium phosphate which is usually produced in a diammonium phosphate plant. Some suspension bases are produced in the mixing plant by directly ammoniating orthophosphoric acid and by adding ammonia and phosphoric acid to 18-46-0 (1).

Surprisingly, much suspension fertilizer is still prepared from ammonium polyphosphate base solution (10-34-0) produced by the TVA pipe reactor process. This base solution presents few physical or chemical problems because impurities and dissolved salts are held in solution. The base is usually prepared by ammoniating superphosphoric acid containing about 10 percent polyphosphoric acid ($H_{n+2}P_nO_{3n+1}$), usually as pyrophosphoric acid ($H_4P_2O_7$), and 90 percent orthophosphoric acid (H_3PO_4). This base produces excellent suspensions but suspensions made from this base are more expensive than suspensions made directly from orthophosphoric acid because of the cost of equipment and fossil fuel required to concentrate orthophosphoric acid to polyphosphoric acid.

The TVA pipe reactor process uses the heat produced by reacting ammonia and superphosphoric acid to provide the energy to polymerize orthophosphates to polyphosphates. This is done by confining most of the reaction to a pipe reactor. Heat loss from such a pipe is low and a polyphosphate melt (about 10-65-0) is formed in the pipe at 600 to 650°F

(316-343°C). The melt is mixed with water and more ammonia to form a 10-34-0 or 11-37-0 product with 50 to 80 percent of the phosphates in the polymerized form. The amount of polymerized phosphate depends on the skill of the operator and quality of the superphosphoric acid used.

A popular base in the South is an ammonium orthophosphate base suspension (13-38-0) produced by ammoniating orthophosphoric acid using a continuous process developed by TVA (2). The acid is ammoniated in three stages. It is held at precise pH levels and temperatures in each stage: pH 5.4 and 230°F (110°C) in the first stage; pH 6.5 and 200°F (93°C) in the second stage; and pH 7.1 and 140°F (60°C) in the third stage. This precipitates metallic impurities as crystalline compounds which suspend better than amorphous gels which precipitate and thicken the mixture and reduce the grade when these controls are not used. After ammoniation the product is cooled and a suspending agent, attapulgite clay, added. The 13-38-0 is an excellent base if properly made and stores well in the South. No thermal energy other than that produced by the ammoniation reaction is needed.

Although this base is made from ammonia and low cost (as compared to polyphosphoric acid) orthophosphoric acid, it still contains considerable water and is expensive to ship from the base plant to the mixing plant. Also unless it is made near a phosphoric acid plant, merchant-grade acid must be used or special arrangements made to ship sludge or filter grade acid resulting in high costs for P_2O_5 or problems with solids in rail cars and storage tanks.

Satisfactory runs have been made in the TVA 13-38-0 demonstration-scale plant using sludge acid but extensive tests have not been made with either sludge or filter-grade acid. It appears, however, that a satisfactory base suspension can be made from these acids with the process.

Another disadvantage has been the cost of plant equipment. Even though the cost of a 13-38-0 plant is low compared to a diammonium phosphate plant producing solid ammonium phosphate at a similar production rate, the battery limits cost of a 20 ton-per-hour 13-38-0 plant including acid and product storage is still estimated to be more than $900,000. A flow diagram of the TVA 13-38-0 plant is shown in figure 1.

Recent bench-scale and pilot plant work indicate, however, that a similar base suspension can be made using a batch process. The batch process should be more economical than the three-stage continuous process because it is less complicated and requires less equipment. Figure 2 is a flow diagram showing the equipment configuration used in TVA pilot plant tests. This could easily be adapted to an industrial process. In the pilot plant 448-pound (203 kg) 13-38-0 batches were produced which consisted of 244 pounds (111 kgs) of 13-38-0 produced from orthophosphoric acid and ammonia and 244 pounds (111 kgs) left in the reactor each time as a "Heel." All of the acid and water in the formulation were added to the reactor during the first period of ammoniation. The "Heel" could be adjusted to control pH and temperature. Ammonia feed rate was adjusted to maintain pH of about 5.2 until all of the acid had been added. After waiting 30 minutes additional ammonia was added until the pH of the fluid reached 6.4. Temperature in the reactor was controlled at about 232°F (111°C) by addition of process water. The product was cooled and suspending clay added in a second vessel.

Several problems occurred in the batch process. Careful control of the acid and ammonia feed rate was necessary to prevent excessive foaming and boil-over. It was necessary to add a foam breaker to the reactor to help alleviate the boil-over problem. There was also some plugging of the ammonia spargers which was subsequently overcome by blowing air through the sparger when ammonia was not being added. The crystals produced were somewhat larger than the arbitrary TVA limit of 850 micrometers and the 13-38-0 grade could not be achieved without excessive viscosity. Refinements of the process should overcome these difficulties. Also TVA's requirements are probably more strict than those which would be used in a regional plant because TVA often ships 13-38-0 produced in the demonstration plant long distances in rail cars.

Development of a successful batch process will allow orthophosphoric acid and ammonia to be shipped to regional plants where it can be converted to a high quality 13-38-0 base in a simple low cost plant. The base can then be shipped from the regional plant to the final mix plant where it can be stored and used as a fluid. The lower capital cost of such a plant should make the base competitive with solid ammonium phosphates which are also made from orthophosphoric acid and ammonia and shipped and used as solids. It will allow low cost plants with simpler, less expensive equipment to be used to mix the final grades and will provide an ideal base for satellite plants.

Solid ammonium polyphosphate (11-55-0) containing 15 to 25 percent of its P_2O_5 as polyphosphate produced by TVA also has been a popular base for suspensions. This product is produced by reacting wet-process orthophosphoric acid and ammonia in a pipe reactor, passing it through a disengager to separate water from the melt before it can recombine with the polyphosphate and granulating the resulting melt in a pugmill. The process requires a cooler but because the melt is anhydrous no drying is needed. This product solves several problems which occur with fluid bases. It contains no water and its analysis is higher than fluid bases; therefore, its delivered freight rates are competitive with solids used in dry bulk blending. The 11-55-0 granules must be reduced in size by shearing and ammoniation, however, before a fluid can be made from them.

Until recently this product has been used by manufacturers to produce fairly low analysis (10-30-0 and 11-33-0 grades) suspensions. Although the polyphosphate content of this product produced base grades which were more fluid than those made by ammoniating ortho acid (because the impurities were sequestered and ammonium polyphosphate salts more soluble than the orthophosphate salts), problems still occurred with large crystal growth and sludge precipitation in long-term storage because the base suspension was usually allowed to cool slowly without agitation from a mixing temperature of 145-160°F (63-71°C) to ambient temperature. Since the size of the crystals in such a suspension is inversely proportional to the number of crystals in the suspension and to the crystallization rate (3), it was realized that if these suspensions could be cooled quickly, small crystals which would suspend well could be produced. Experience with the TVA 13-38-0 process showed that high circulation through an evaporative cooler provided the quick cooling necessary to produce small crystals. To make practical use of this information in the field a batch cooler similar to that shown in figure 3 was developed (3). The cooler does not contain packing because packing would quickly plug with crystals from the suspension. Also a conical distributor which would not plug had to be developed to distribute the fluid across the cross-section of the cooler. This distributor is shown in figure 3.

Several coolers based on this principle have been built by fluid fertilizer manufacturers. Usually they are similar to the example shown but other designs have been used. One example is shown in figure 4. Grades as high as 12-36-0 have been made from 11-55-0.

This system also works well with monoammonium phosphate (11-53-0 to 10-50-0). The base grades produced are usually lower than those produced using solid ammonium polyphosphate but they have been stored satisfactorily for several months. The mixing procedure is the same as that for the solid 11-55-0. The best $N:P_2O_5$ ratio is 0.33:1 and quick cooling with rapid agitation produces a grade which stores much better than grades produced and stored hot without agitation.

Satisfactory grades can be produced from monoammonium phosphate and ammonia without a cooler but mixing costs are usually increased. If a batch smaller than the normal batch is produced, cooled product from a previous batch or some other product, such as an ammonium polyphosphate solution prepared elsewhere, can be used. Enough cool product is usually added to bring the temperature of the batch to $100^{\circ}F$ ($38^{\circ}C$) before it is pumped to storage. Rapid agitation during cooling with an agitator or by recirculation through a pump is required to produce small crystals that will suspend well.

Some manufacturers avoid the problem of crystal formation completely by producing a base with all of the ammonium phosphate salts in solution. A popular grade is 8-24-0. The saturation temperature of 8-24-0 is about $19^{\circ}F$ ($-7^{\circ}C$). Usually 1 to 1-1/2 percent suspending clay is added to retard settling of the precipitated impurities. Sometimes a 9-27-0 is produced but the saturation temperature of this grade is about $45^{\circ}F$ ($7^{\circ}C$) and some ammonium phosphate salts can precipitate from this solution during cold weather storage. When monoammonium phosphate containing a high concentration of impurities is used as a phosphate source, 9-27-0 can thicken and become as viscous as suspensions of higher grades made from monoammonium phosphates with lower impurity concentrations.

A disadvantage of the low analysis bases is that high phosphate grades cannot be made. For example, a common grade made from a 10-30-0 suspension base is 7-20-20. If 8-24-0 is used as a base, the usual grade in this ratio is 6-17-17. That means that extra water must be hauled to the field and applied. However, the high nitrogen and high potash grades produced are usually near the same concentration as those produced from a 10-30-0 or higher analysis bases.

Quality of the suspensions produced varies, however, with the impurity level in the phosphoric acid from which P_2O_5 is produced. Large quantities of impurities tend to produce grades which become thick in storage and are difficult to handle. These gels are usually caused by an iron phosphate compound of the type $NH_3FePO_4.xH_2O$ (3). Plant and laboratory tests have shown that there is less tendency for this kind of suspension to gel if fluosilicic acid is added to the monoammonium phosphate solid to supply fluorine to adjust the fluorine:iron ratio. Best results are obtained when the $F:Fe_2O_3$ weight ratio of the suspension is above 0.78:1. This procedure is equally effective if the fluorine from ammonium fluoride or fluosilicic acid is added to the base suspension as it is prepared, but it is difficult to obtain fluorine compounds for use in the field at a price the fertilizer mixer can afford.

TVA has developed and recently demonstrated a process for making a 9-32-0 ammonium polyphosphate suspension containing 25 percent of the phosphate as polyphosphate. This product is gaining acceptance as a base for starter fertilizers. However, because it is a suspension and contains about 2-1/2 percent clay it must be applied with positive pressure such as air pressure or that supplied by a piston or hose pump.

All ammonium phosphate salts are in solution at 32°F (0°C) and as long as impurities do not precipitate the base can be handled as a solution except for the clay. The clay suspends precipitating salts at temperatures below 32°F (0°C) and impurities which precipitate during long-term storage. The clay interferes with application of the product through gravity flow planter applicators. Some physical and chemical properties of 9-32-0 are shown in table 1.

Merchant-grade wet-process acid and anhydrous ammonia are used to produce the product. A flow sheet of the pilot plant process is shown in figure 5 (4). The acid is pumped from a storage vessel to a plate and frame heat exchanger where it is heated to about 180°F with 200°F liquid from the melt dissolution tank. Liquid anhydrous ammonia is pumped from a liquid anhydrous storage tank through another heat exchanger in which it is vaporized and heated to about 180°F (82°C) with liquid that has passed through the acid heat exchanger. Hot acid and vaporous ammonia flow into a mixing tee connected to an inverted U-shaped pipe reactor tube where the acid is ammoniated and the polyphosphate formed. The usual operating temperature in the pipe is 450-500°F (232-260°C). Ammonium polyphosphate melt from the pipe reactor discharges under the surface of liquid in the melt dissolution tank where sufficient water is added to dissolve the melt and to obtain the desired density. Temperature in the melt dissolution tank usually ranges from 200-210°F (93-99°C) and is controlled by varying the amount of cooled liquid returned from an evaporative cooler. The final product is cooled to about 100°F (38°C) to slow hydrolysis of the phosphate and 2-1/2 percent attapulgite clay is added before the product is sent to storage.

A similar process involves adding sulfuric acid to the pipe reactor along with the orthophosphoric acid and ammonia. Sulfuric acid supplies extra heat which can be used to produce more polyphosphate. Grades with polyphosphate contents as high as 52 percent have been produced in the pilot plant with this process. A control test using the same equipment, raw materials and procedures but without sulfuric acid, produced only 37 percent polyphosphate (5). The optimum grade appears to be 12-31-3.0S with all sulfur from sulfuric acid. This process has yet to be proven in the field but it shows promise for producing medium polyphosphate fluids capable of satisfactory long-term winter storage without the expense of producing superphosphoric acid.

Monoammonium phosphate is rapidly becoming the major phosphate source for fluid suspensions. Producing base suspensions which store without thickening or large crystal formation is difficult with monoammonium phosphate but use of the batch cooling process works well with monoammonium phosphate although the grades are usually limited to 10-30-0 or 11-33-0 unless some polyphosphate is added to solve this problem. But there are other ways. When 10 percent of the P_2O_5 is included as nonorthophosphate, the product usually remains free of gels and crystals for several months. Polyphosphate usually can be obtained from ammonium polyphosphate solution (10-34-0 or 11-37-0) prepared from superphosphoric acid or a suspension such as 9-32-0 prepared from orthophosphoric acid and containing polyphosphate.

Preliminary tests indicate that ammonium phosphate bases can be made from monoammonium phosphate in a continous plant similar to that used to produce the TVA 13-38-0 grade. Only limited tests have been made with the continuous process; however, the process allows close pH and temperature control and continuous cooling with rapid recirculation in an evaporative cooler which improves the quality of the product. Shell and tube coolers can be used with the continuous process but the problems with cooling water supply and its disposal in most small fertilizer plants make use of the evaporative cooler attractive.

Fluids, especially suspensions, are relatively new forms of fertilizer, having been used for only about 20 years. These new physical forms of fertilizer offer a wide field in which new developments continue. In the early days of suspensions inadequate manufacturing and application equipment hindered development of new forms of suspensions; but with the adoption of modern chemical engineering principles to mixing and application equipment, most of these problems have been solved. This has opened up suspension fertilizer manufacture to a new and diverse array of raw materials and combinations.

The advantages of suspension fertilizers that have established them as a significant form of fertilizer seem likely to continue. Research developments which have reduced the problems of high raw material costs, low nutrient concentration, and low product quality appear to be mostly solved. Suspensions should occupy continued increasing importance in the fertilizer market.

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Table 1

Ammonium Polyphosphate Suspension
Chemical and Physical Properties

Analysis, % by weight	
N	9.5
P_2O_5	32
Clay	2.5
N-P_2O_5 wt ratio	0.3
P_2O_5 polyphosphate, % of total P_2O_5	22-25
pH	6.7
Density, lb/gal	11.7
Viscosity, cps at 80°F	200
0°F	500

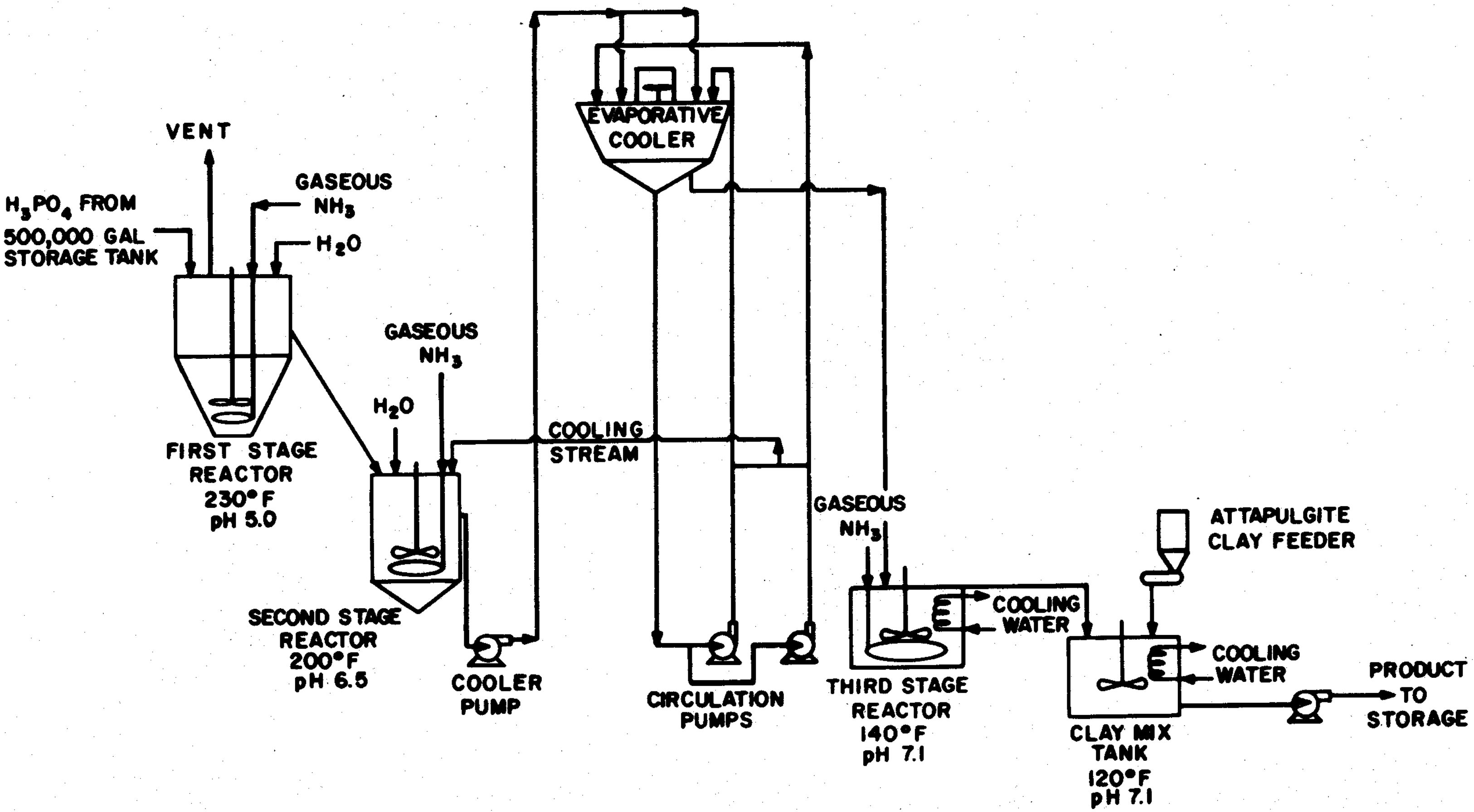

FIGURE I

FLOW DIAGRAM OF DEMONSTRATION-SCALE PLANT FOR PRODUCTION OF 13-38-0 AMMONIUM ORTHOPHOSPHATE SUSPENSION FERTILIZER

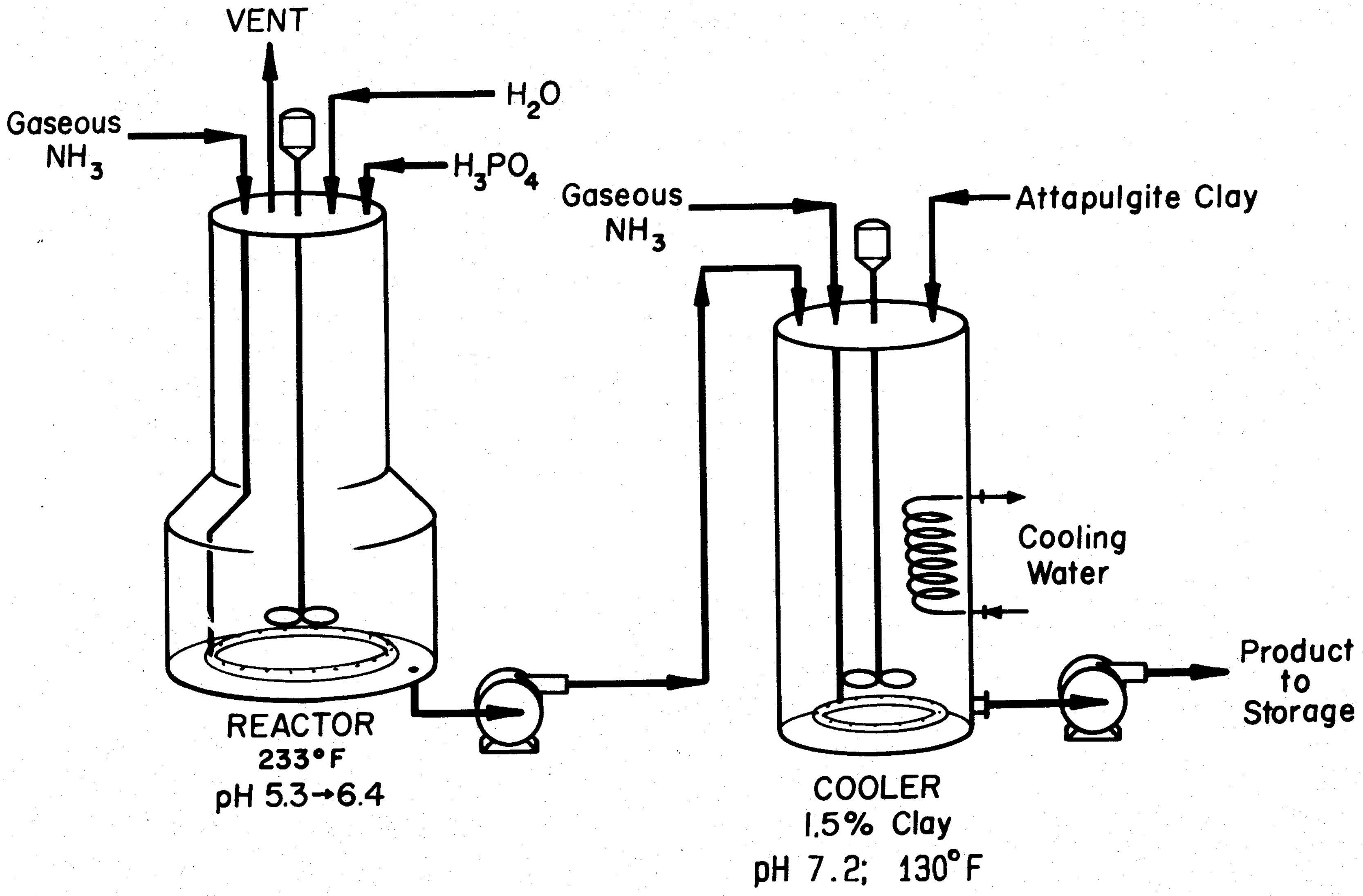

FIGURE 2

PILOT-PLANT BATCH PRODUCTION OF 13-38-0 GRADE AMMONIUM ORTHOPHOSPHATE SUSPENSION

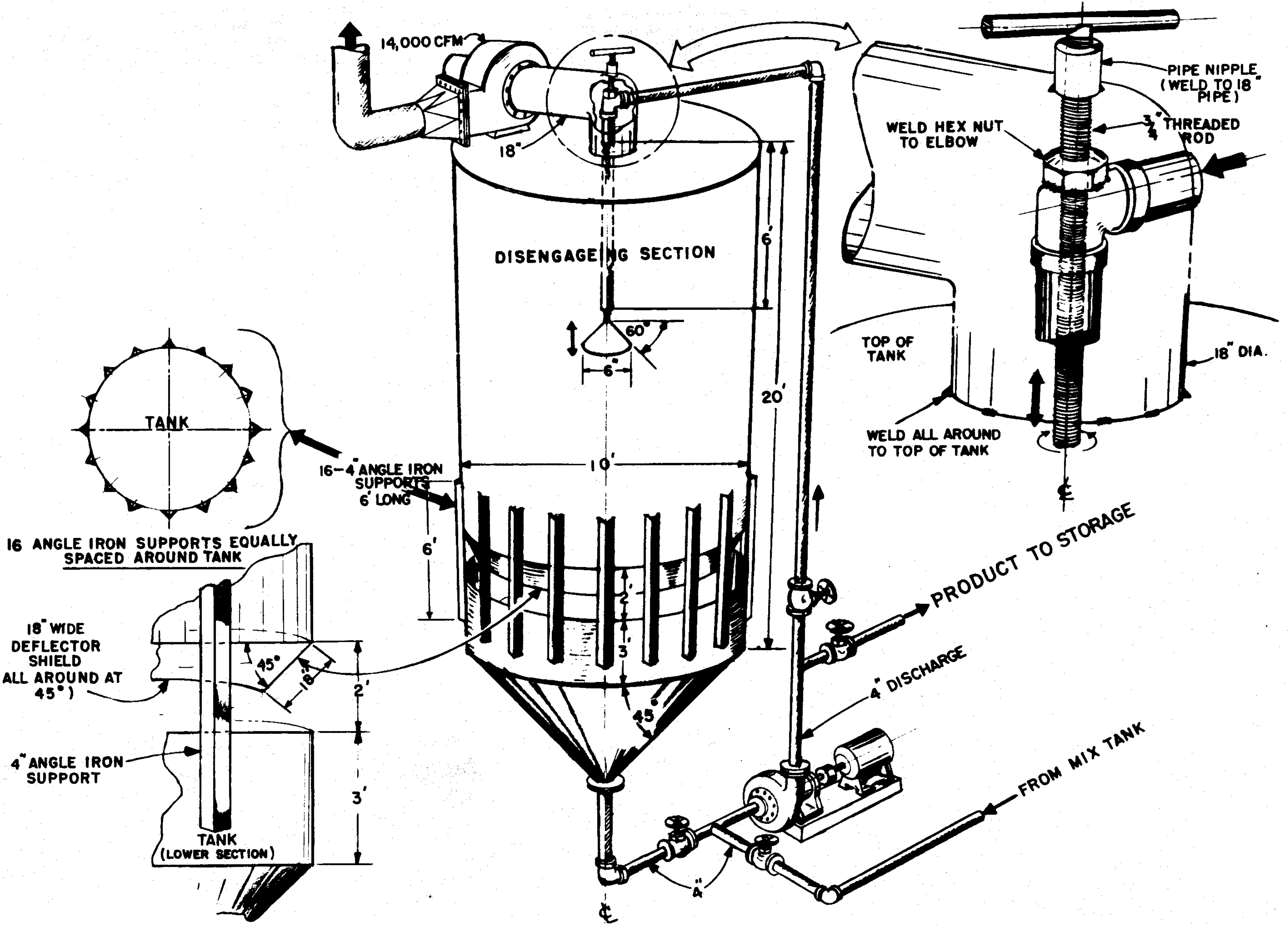

FIGURE 3
SUSPENSION COOLER
(NO PACKING)

PPI SEC.-TVA

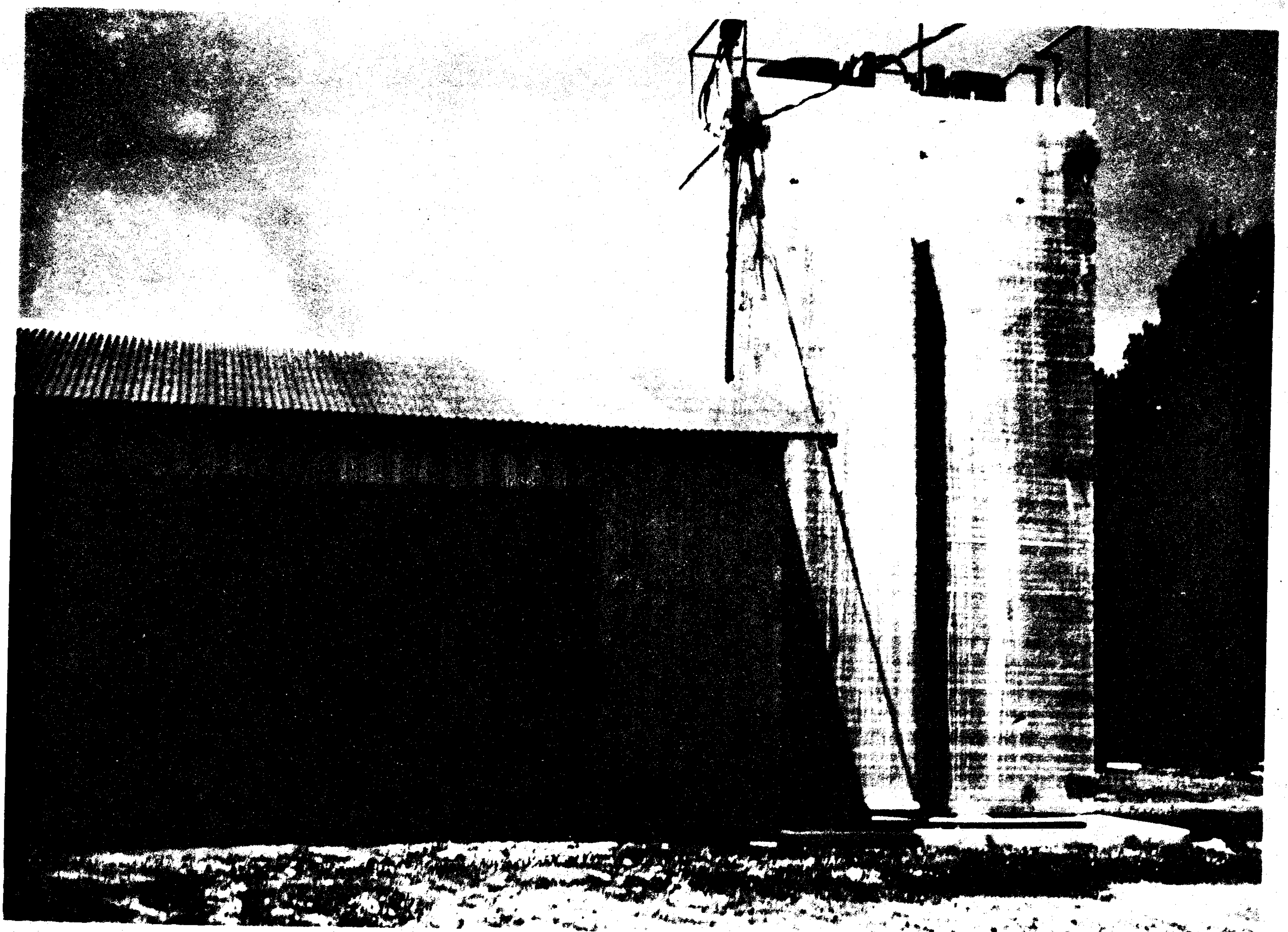

FIGURE 4

NONPACKED EVAPORATIVE COOLER MADE FROM
PRESTRESSED CONCRETE SLABS