NEW MATERIALS FOR FLUID FERTILIZERS

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Introduction

New materials, like new ideas, are rare. Often new products are merely old products slightly improved or used in a new way. So it is with the "new" materials discussed in this paper. Some are new but are built on a foundation of materials used in the past. Others are merely old materials used in new ways. This paper will be limited mostly to nitrogen products with brief discussion of phosphate compounds. Phosphate compounds will be covered in detail in another paper.

Shifts in Use of Aqua Ammonia

There was great interest in the direct application of aqua ammonia about 15 years ago. Aqua ammonia converters were purchased and used in great numbers because aqua was a way of getting low cost ammonia nitrogen into the soil without the use of the expensive high pressure equipment required for anhydrous ammonia. The aqua ammonia at that time usually contained only 20 percent nitrogen by weight because aqua of this strength has no vapor pressure at 100°F. Since that time, aqua ammonia has slowly disappeared from the direct application market, and except for a few areas has been completely replaced by anhydrous ammonia.

This shift was apparently caused by the cost of converting anhydrous to aqua in the field and on the cost of transporting low analysis aqua to the field. Since aqua is 20 percent nitrogen and anhydrous is 82.5 percent nitrogen, it appears that 4.1 trips must be made to the field with aqua for every trip made with anhydrous. However, since aqua ammonia is heavier than anhydrous and tanks can be completely filled rather than only 85 percent filled as with anhydrous ammonia, the number of trips is about 2.4 rather than 4.1.

Although aqua is not new, there is renewed interest in the aqua solutions. Aqua ammonia containing 41 percent nitrogen by weight (50% ammonia by weight) is of interest for the same reason that 20-percent nitrogen aqua was of interest in the 60's. It is a low-cost solution which does not release ammonia vapors as rapidly on exposure to the air as anhydrous ammonia. Forty-one percent nitrogen aqua is a compromise between nonpressure 20-percent nitrogen aqua and anhydrous ammonia. It requires only 1.26 trips to the field for every trip made with anhydrous, can be handled in medium pressure equipment and does not have to be knifed into the soil as deeply as anhydrous.

Forty-one percent nitrogen aqua ammonia has a vapor pressure of about 58 psig at 80°F and vessels in which it is stored and transported must conform to the appropriate ASME code. In areas where anhydrous ammonia cannot be stored due to local government regulations or where farmers are concerned about handling anhydrous ammonia, 41-percent nitrogen aqua ammonia could be a satisfactory compromise. If anhydrous cannot be handled at all, 41-percent nitrogen aqua could be shipped from a manufacturing plant or anhydrous could be shipped and converted to 50-percent aqua at a remote central location which would be acceptable to local governments.

Anhydrous ammonia can be converted to aqua ammonia using low cost equipment. A typical converter is shown in figure 1. Converters are available from a number of manufacturers and can be supplied with or without coolers. Coolers are necessary for high production rates; however, if the working pressure of the converter equipment is high enough for the vapor pressure of the aqua being produced and sufficient time is available, aqua can be produced without a cooler. When this is done, the total amount of water needed is usually pumped into the final storage tank and then circulated through a mixing device where it is mixed with anhydrous and moved back into the storage tank. Because there is a large amount of water and a small amount of ammonia in the beginning, heat and pressure do not build up until the aqua begins to reach its final concentration. If a cooler is not available, ammonia addition is slowed down so that the pressure for which the tank relief valve is set is not exceeded. If a suitable cooler is available, it can be used to cool the aqua at this stage and speed the mixing. Also, as shown in figure 1, anhydrous can merely be bubbled into a measured amount of water in a suitable tank. Plants which start without a cooler usually add coolers after a year or two to speed up mixing.

Rather than starting with a measured amount of water, anhydrous ammonia can be mixed continuously with water in a mixing device to produce final strength aqua. A cooler is required for this process because the resulting solution generates heat which must be dissipated before it is put into storage to lower its vapor pressure below the working pressure of the tank. Care should be taken to ensure that no system containing aqua or anhydrous ammonia is connected directly to a potable water system. Usually an "air-gap" tank is used to isolate the converter from the water system. A thorough discussion of aqua converters and their operation is given in the NFSA Liquid Fertilizer Manual. This information should be studied before an aqua converter is installed or operated.

Patented applicators are available which will produce aqua ammonia as it is applied in the field. Aqua produced this way overcomes some of the disadvantages of aqua ammonia produced at a base plant. Anhydrous ammonia is taken to the field in a conventional anhydrous ammonia application tank along with an empty water tank. The water tank is filled as near the application site as possible. Supplementary water and ammonia can be taken to the field in nurse tanks if desired. Aqua ammonia is then prepared and applied directly to the soil by mixing ammonia and water in the patented mixer. Any strength aqua can be produced. Also ammonia has been mixed in the device with a pre-mixed 14 percent K_2O potash solution.

Using Heat of Solution

Most aqua converters must dissipate the heat of solution generated when anhydrous ammonia is mixed with water, either through radiation and/or convection or through transfer into a cooling media such as water. A system has been devised to use this heat of solution to dissolve urea. If 20-percent nitrogen aqua ammonia is mixed from 50°F anhydrous ammonia and 60°F water, as shown on figure 2, the temperature of the mixture will be about 132°F. It is necessary to cool this strength aqua to 100°F if it is to be stored in nonpressure containers, as is usually the case (see figure 3). It requires heat, about 108 Btu's, to dissolve one pound of urea. If an 18.7 percent nitrogen urea solution with a 32°F salt-out is produced, heat must be added to the solution to dissolve the urea.

The device shown in figure 4 uses the heat produced by the solution of ammonia in water to dissolve the urea. The proper amount of urea and water are weighed into one mix tank and the agitator started. Circulation is then started through the shell-and-tube heat exchanger and back to the mix tank. The aqua ammonia is passed through an auxiliary cooler (shown as an evaporative cooler on the sketch), when urea solution is not being produced. When urea solution is being produced, flow is shifted through the shell-and-tube heat exchanger. Circulation is continued until all the urea is dissolved. The product is then pumped to storage and recirculation started from the second tank where a batch has been assembled while the first batch was being dissolved.

Urea solution can be used both for direct application and as supplementary nitrogen for mixed liquid fertilizers containing potash. When potash is present, urea used as supplementary nitrogen usually produces a liquid fertilizer with a lower salt-out temperature than that produced using urea-ammonia nitrate solution. An example of this is shown in figure 5.

Another device which is used to dissolve urea is shown in figure 6. A premeasured volume of water in the tank is preheated to 180°F. Urea is then blown from a pneumatic truck into the water while the mixture is circulated through a centrifugal pump. Circulation continues until all of the urea dissolves. This system works very satisfactorily; however, fossil fuel is required to produce the heat to dissolve the urea. The dissolution rate depends upon the amount of heat supplied and the capacity of the pump.

The economics of producing urea solution depend upon the delivered price of solid urea as compared to the delivered price of urea-ammonium nitrate solution. Some companies producing urea solution use it to produce both liquid mixed fertilizer and liquid feeds.

Fluid Clay

The suspending agent most frequently used in the production of suspension fertilizers is an attapulgite-type clay which is normally received dry in bulk or bags. It is a colloidal gelling-type clay that can be mixed with water to make a fluid containing approximately 10 percent by weight of clay. A more concentrated clay-water mixture usually cannot be made successfully without a dispersing agent since it is generally too viscous or thick to handle properly with the equipment normally used in the production of suspension fertilizers. Clay that is properly gelled in a fluid fertilizer is desirable because partially gelled clay is not satisfactory since it causes variations in the thickness and suspending action of the product from batch to batch. These variations may result in solids settling in one batch of product while another batch made by the same formulation and procedure may be too thick to pump or apply evenly. The use of dry clay in suspension fertilizers can be an arduous and dusty operation. Also about 5 minutes or more is required to mix the dry clay-water solution to assure gelling of the clay.

Because of these disadvantages of using dry clay, more suspension producers are showing interest in using predispersed fluid clay. Normally this is a fluid made either with water or urea solution containing a dispersing agent and about 25 percent clay. It is being produced by both batch and continuous processes. TVA uses a continuous process to produce a dispersed clay slurry containing 9 percent nitrogen from urea and 25 percent clay. About 11 pounds of tetrasodium pyrophosphate (TSPP) is used per ton of product as a dispersing agent. Other dispersing agents could be used; however, TSPP is readily available at a comparatively reasonable price.

Figure 7 is a schematic of TVA's 10-ton-per-hour demonstration plant for making nitrogen fluid clay (9-0-0-25% clay). In this plant, sufficient TSPP is mixed with water at 160°F to make about 400-gallon batches of a 20% TSPP solution. The 20% TSPP solution, 75% urea solution, and water are metered continuously into a mixing funnel which discharges simultaneously with preweighed dry clay into a dispersing tank. In this tank, which has a retention time of about 1.7 minutes, the solution mixture and clay are mixed by a small propeller-type agitator having a tip speed of 35 feet per second. The clay slurry overflows from the dispersing tank through a trough which discharges at the bottom of the mix tank near the suction side of a centrifugal pump where it is recycled through the mix tank. The pump is rated at 350 gallons per minute and has an impeller tip speed of about 50 feet per second. Additional mixing and shear are provided in the mix tank by a turbine-type agitator having a tip speed of about 92 feet per second. The mix tank provides about 8.5 minutes retention time. From the mix tank the product is pumped to storage.

Some producers are making batches of fluid clay in their mix tanks or storage tanks. The first operation in making fluid clay in these tanks is to thoroughly flush the system with water to ensure a clean system. The system is considered sufficiently clean when a teaspoon of the flush water does not cause "clabbering" when mixed with a pint of fluid clay. The entire mix system must be clean and free of fertilizer salts such as ammonium nitrate contained in UAN, potassium chloride, and ammonium phosphates from mixed grades. As little as 0.3% UAN by weight mixed with dispersed clay slurry will gel much of the clay into soft but solid lumps which will plug pipes and pumps.

To produce dispersed clay slurry by this process, all of the water is added to the mix tank followed by the TSPP and urea if it is used. These are completely dissolved before using an eductor system to add the clay. One company reports making a dispersed clay slurry at the rate of 25 tons per hour using $50^{\circ}F$ water. Warmer water is desirable to hasten dissolution of both TSPP and urea. Urea is included to reduce the freezing temperature of the dispersed clay slurry from $32^{\circ}F$ to about $15^{\circ}F$.

Advantages of fluid clay are: there is no dust; it pumps and handles easily; it stores well; and for many grades less clay per ton of product is needed to produce satisfactory suspension products. Although it is thixotropic the gel is easily broken by agitation. Its principal disadvantage is that as a 25 percent clay concentrate, it is almost instantly gelled by the slight contamination with any electrolytic fertilizer salts. Therefore, clean and separate storage tanks, as well as lines and pumps, are required to prevent contamination. If water is used to make the clay slurry instead of urea solution, the nitrogen-free slurry will freeze at 32°F, and being a water slurry, it can rupture storage tanks or lines.

Nitrogen Suspensions

With slight modifications, the plant for producing nitrogen fluid clay shown in figure 7 can be used to produce urea-ammonium nitrate suspension (30-0-0-2% clay). These changes include addition of a second centrifugal pump with an impeller having a high tip speed of about 75 feet per second for gelling the clay and adding a UAN solution feedline. The UAN and dispersed clay slurry mix in a short pipe which is located to empty into the gelling tank near the suction side of the above-mentioned pump. A schematic sketch of this plant which makes about 30 tons per hour of 30-0-0-2% clay is shown in figure 8.

One of the main uses anticipated for this UAN suspension will be as a source of supplemental N at plants and satellites producing high nitrogen suspension from base grades. In making such grades, additional clay must frequently be included in the formulations. Usually there is insufficient water in the formulations in which to gel the clay, and attempts are made to gel dry clay in UAN solutions. Experience demonstrates this is very difficult without violent and prolonged agitation. As a result, solids in products made in this manner may fall out during transportation to the field. Another expected use of the UAN suspension is the production of low- or no-phosphate grades such as X-0-X and nitrogen-limestone mixtures.

Limestone Suspensions

Limestone-water, limestone-urea-ammonium nitrate, and other limestone-plant nutrient suspension combinations have been established as products for the fluid fertilizer industry. TVA has produced limestone suspensions using TVA urea-ammonium nitrate suspensions which are similar to the limestone-urea-ammonium nitrate suspensions made with dry clay. The advantage is that no dry clay or dispersant needs to be added, since these materials are already in the suspension. Also, similar suspensions have been produced with dry urea, TVA dispersed clay slurry (9-0-0-25% clay), and limestone. Several grades produced using these materials are shown in tables I and II.

Phosphates

Phosphates will be discussed in the next section of this workshop; however, a recent development is worth mentioning here. Large quantities of spent phosphoric acid containing aluminum are used by the fertilizer industry to produce mixed liquids because this acid is usually cheaper than wet-process acid. When this acid is ammoniated to a 1 to 3 $N:P_2O_5$ ratio, the usual ratio produced, the aluminum precipitates and the product must be handled somewhat like a suspension. If the pH is raised to about 9.0, the aluminum will usually go back into solution producing a clear grade suitable for application through gravity flow equipment. The usual base grade produced is about 10-22-0. This grade will not salt-out at 32°F; however, if it is placed in storage, it will lose some ammonia and after two or three days, probably will form a gel. When the gel first forms, it can be broken easily by air sparging; however, after about a week, the gel becomes so strong that it is difficult to break. A major benefit that can be derived by using this type of spent acid is to produce a clear liquid fertilizer which will not be stored but applied immediately as a starter fertilizer through planter equipment. This technique should be tried with caution becuase it is new and results obtained so far vary between batches.

Conclusion

New products are built on foundations of data supplied by predecessors. This process will continue. It is hoped that the idea presented here will provide information for other new materials.

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TABLE 1

Limestone Suspensions Using TVA Urea-Ammonium Nitrate Suspension

Sample No.	Approx. Grade	Limestone (lb/ton)[a]	UAN 31-0-0 (lb/ton)	% Limestone	% Clay	Viscosity[b] at 70°F (cps)
1	30.4-0-0-1 CaO	40	1960	2.0	2.0	450
2	30.1-0-0-1.3 CaO	60	1940	3.0	1.94	460
3	29.8-0-0-1.8 CaO	80	1920	4.0	1.92	470
4	27.9-0-0-4.4 CaO	200	1800	10.00	1.8	530
5	24.8-0-0-8.8 CaO	400	1600	20.0	1.6	550
6	21.7-0-0-13.2 CaO	600	1400	30.0	1.4	850
7	15.5-0-0-22.0 CaO	1000	1000	50.0	1.0	1220

a. Limestone 78.5% $CaCO_3$

b. RVT model Brookfield Viscometer, No. 2 spindle at 100 rpm.

TABLE 2

Limestone Suspensions Using Urea and TVA Fluid Clay

Sample No.	Approximate Grade	Limestone (lb/ton)	Urea[a] (lb/ton)	Fluid Clay[b] (lb/ton)	Water (lb/ton)	% Limestone[c]	% Clay	Initial Viscosity At 70°F (cps)
1	21.7-0-0-13.2 CaO	600	920	120	360	30	1.5	1420
2	23.2-0-0-11.0 CaO	500	988	120	392	25	1.5	750
3	24.8-0-0-8.8 CaO	400	1055	120	425	20	1.5	310

a. 46% N

b. 9% N, 25% clay

c. 44% CaO

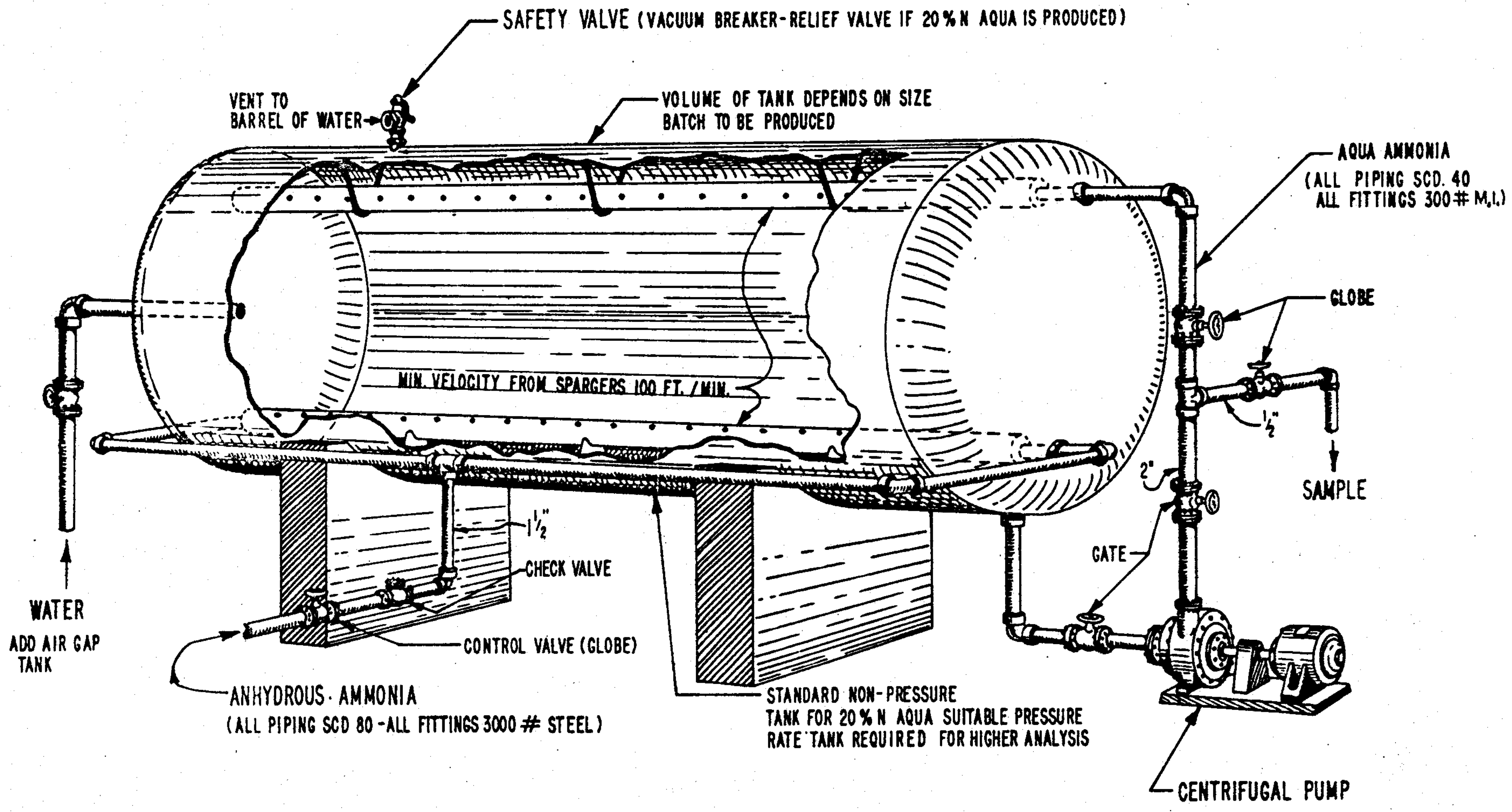


FIGURE I
AQUA AMMONIA CONVERTER

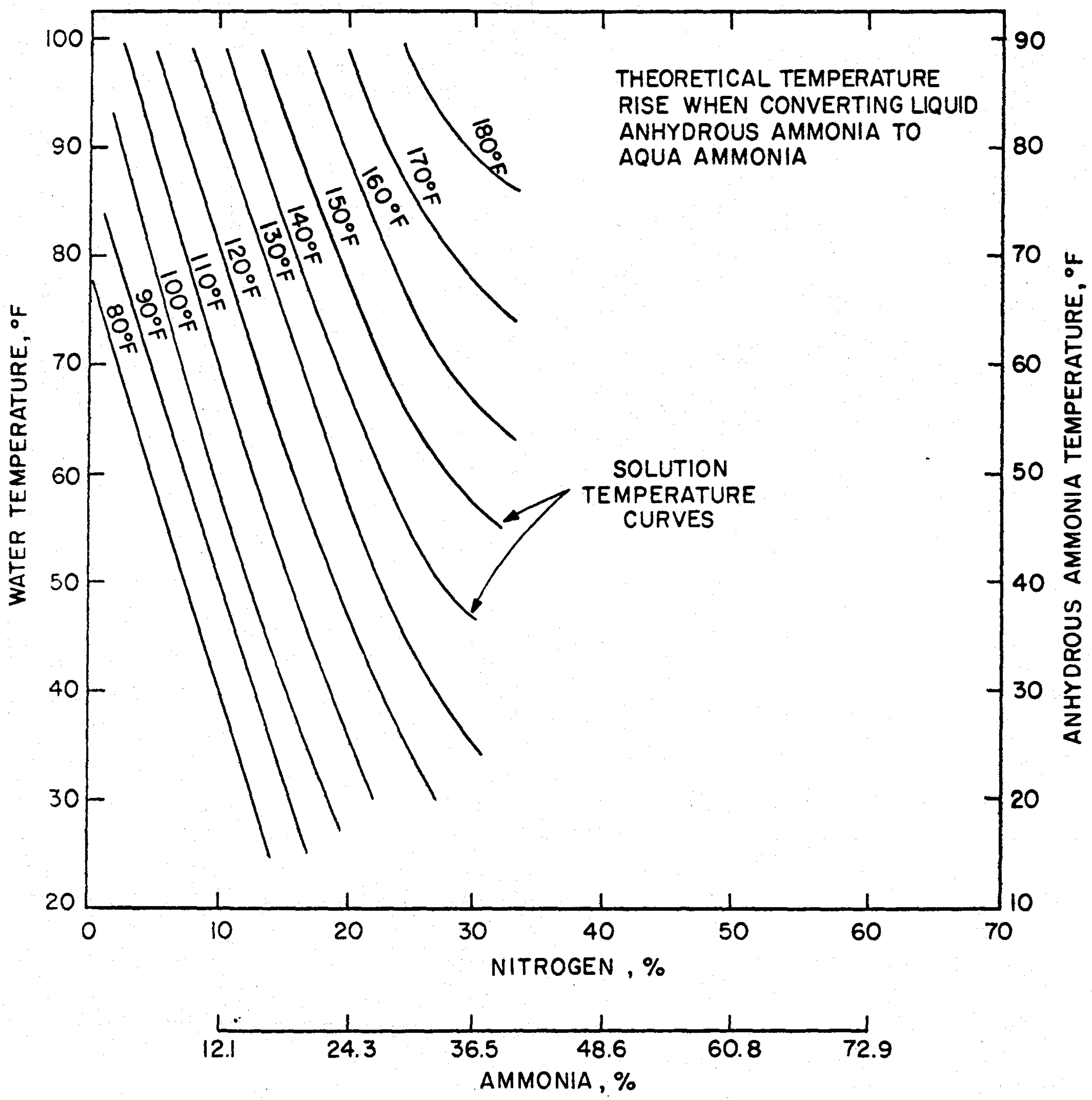

THEORETICAL TEMPERATURE RISE WHEN CONVERTING LIQUID ANHYDROUS AMMONIA TO AQUA AMMONIA
SOLUTION TEMPERATURE CURVES
80°F
90°F
100°F
110°F
120°F
130°F
140°F
150°F
160°F
170°F
180°F
WATER TEMPERATURE, °F
20
30
40
50
60
70
80
90
100
ANHYDROUS AMMONIA TEMPERATURE, °F
10
20
30
40
50
60
70
80
90
NITROGEN , %
0
10
20
30
40
50
60
70
AMMONIA , %
12.1
24.3
36.5
48.6
60.8
72.9

FIGURE 2

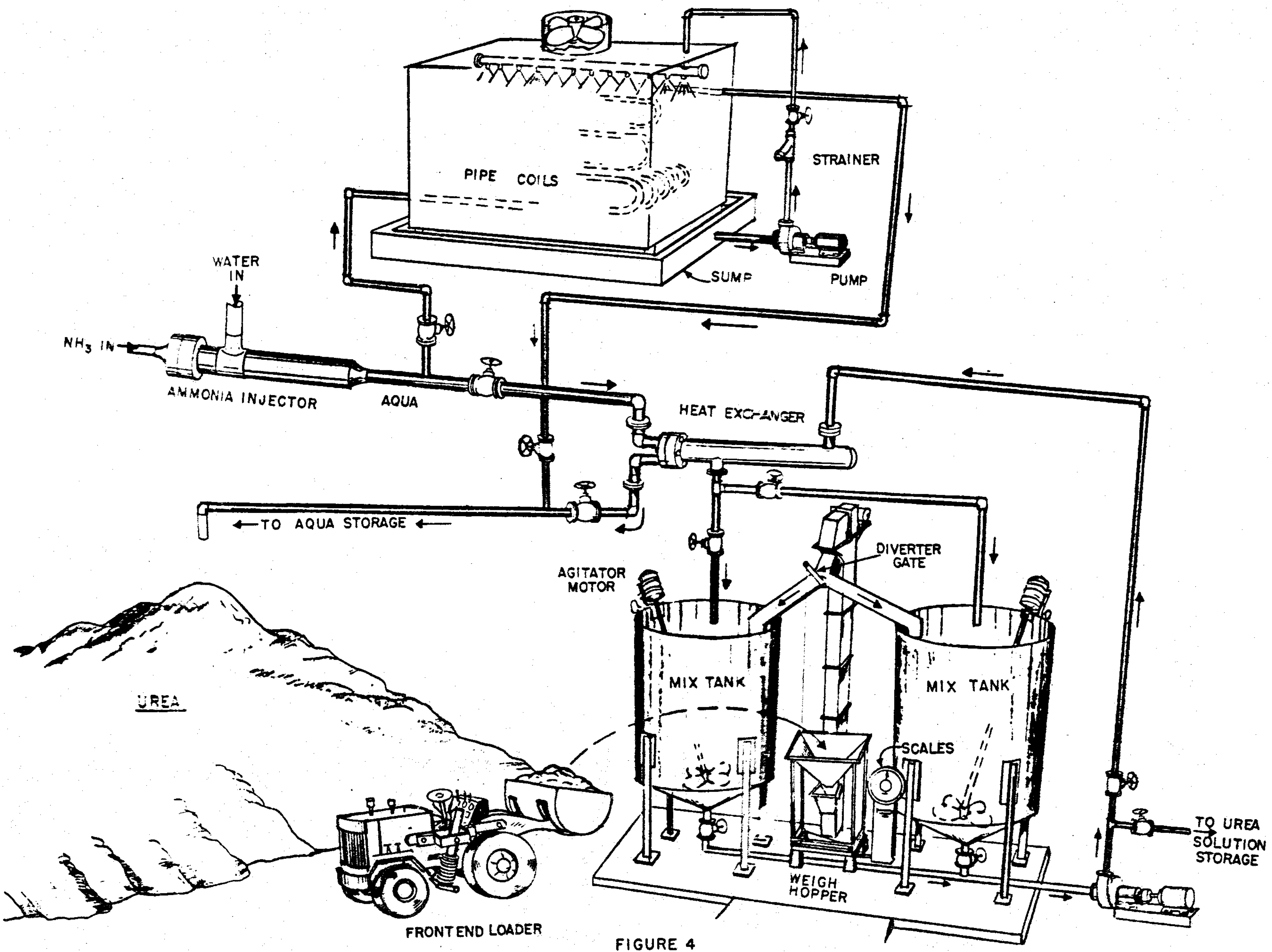


FIGURE 4

AQUA CONVERTER UREA DISSOLVER

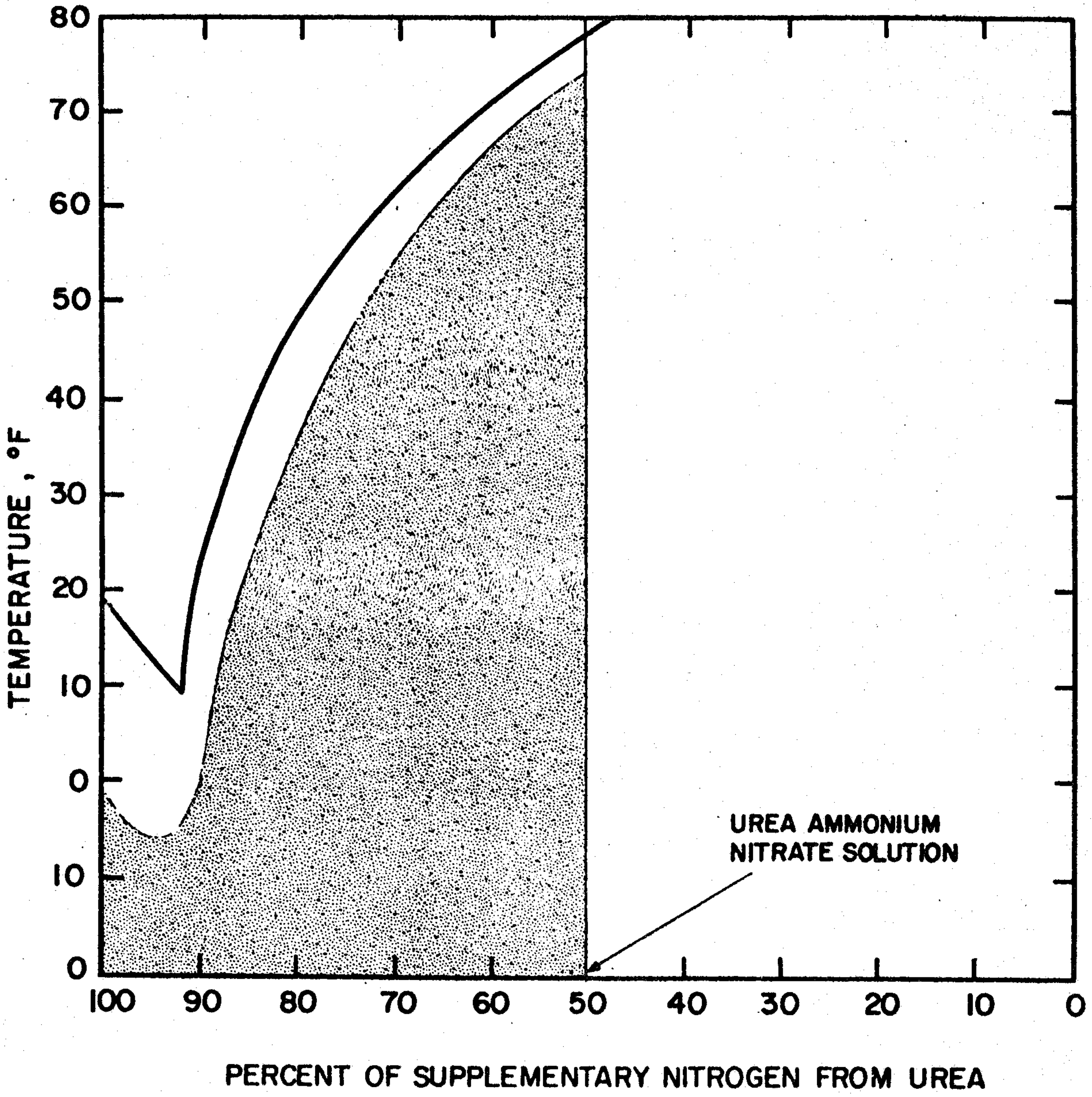


FIGURE 5

EFFECT OF UREA ON SALT-OUT TEMPERATURE OF 14-7-7 SOLUTION

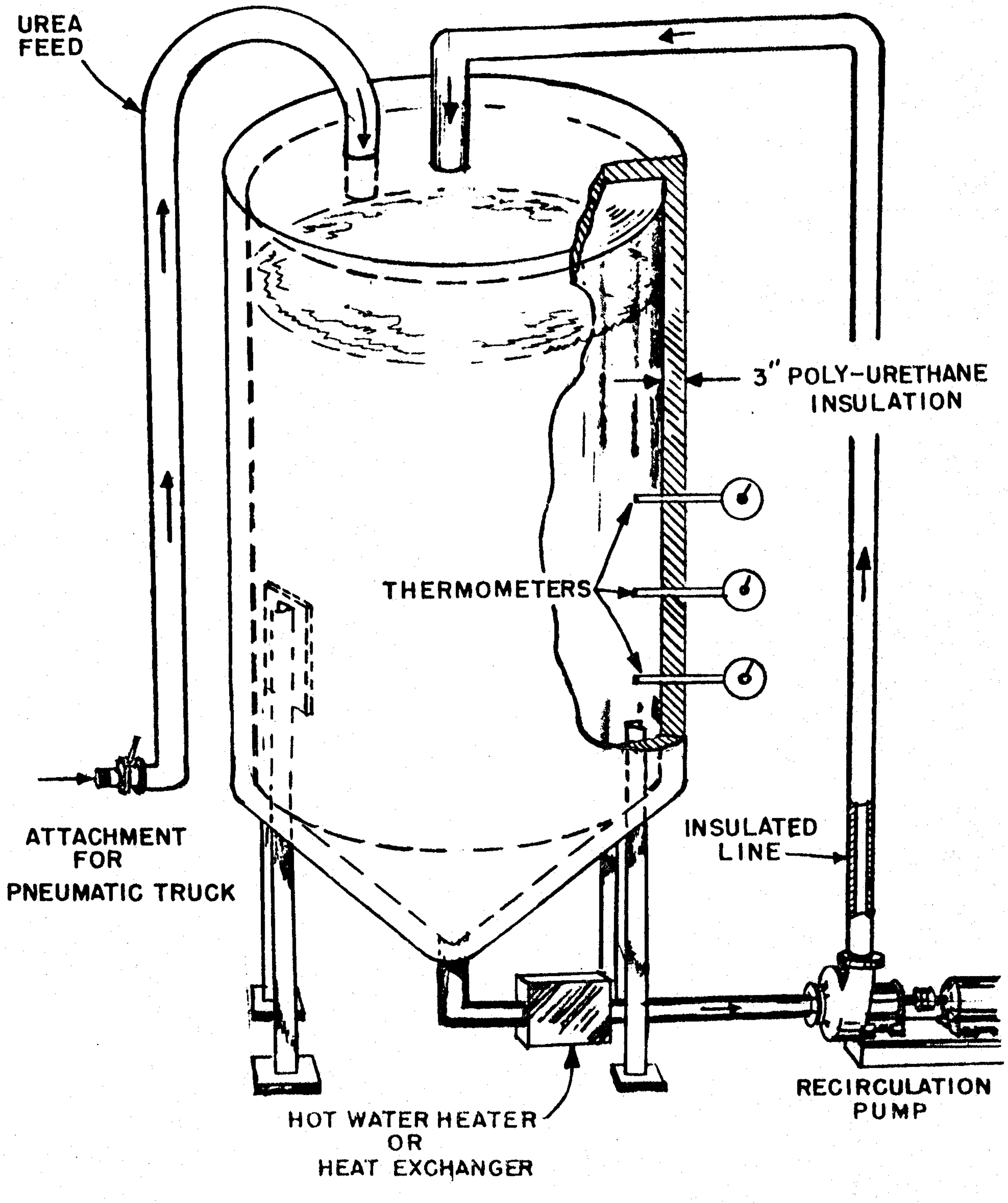
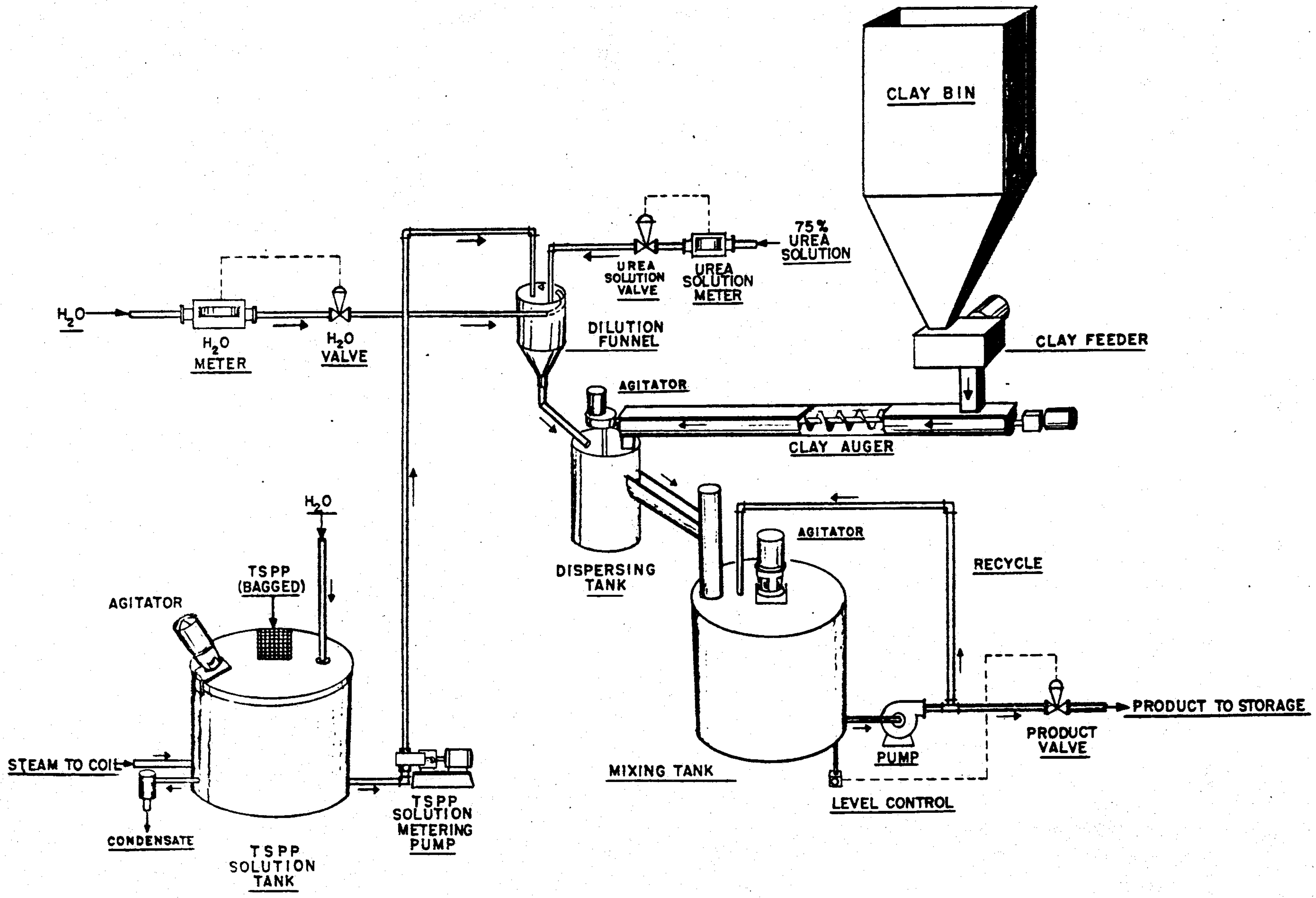
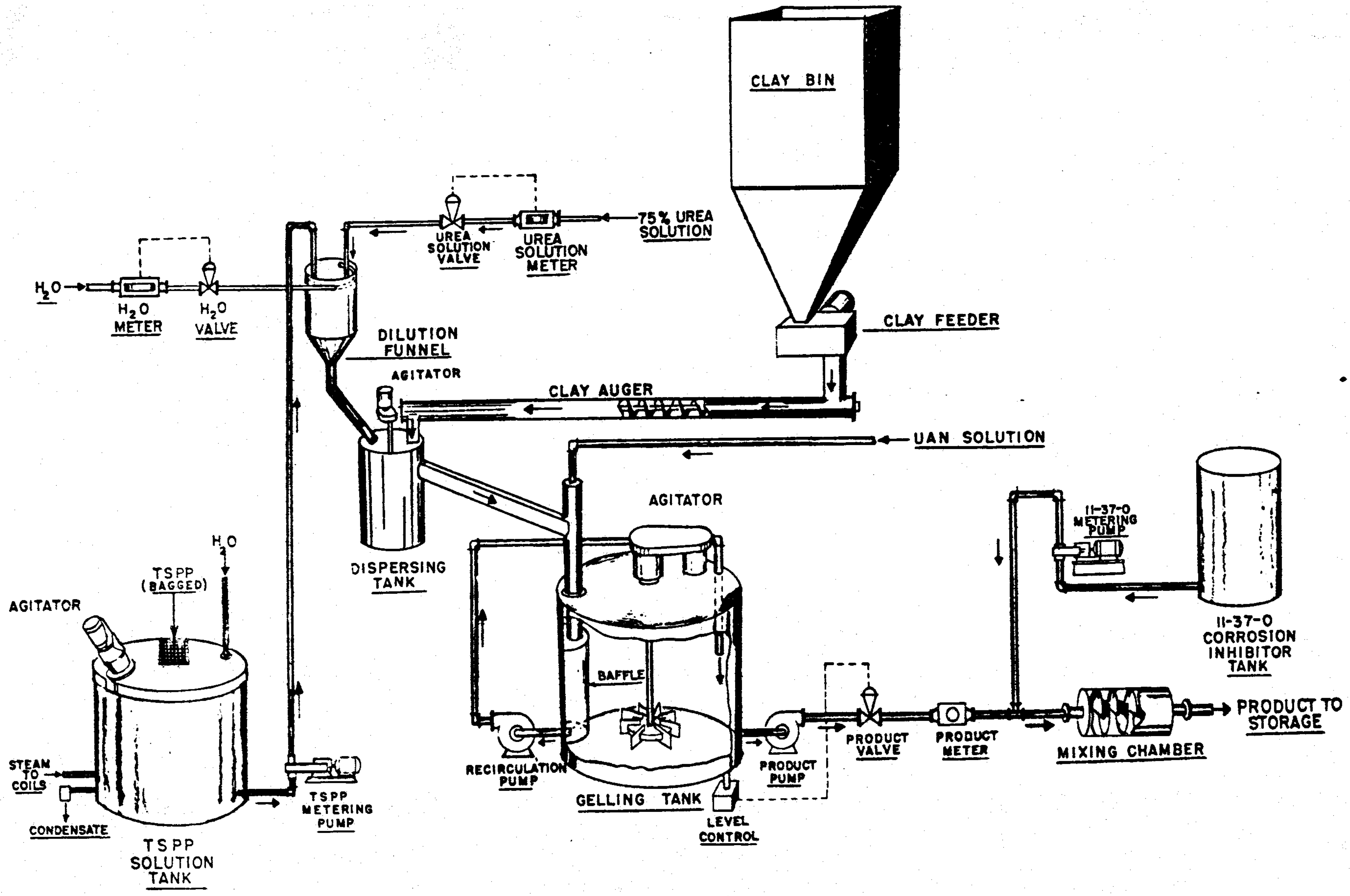


FIGURE 6

URFA DISSOLVING TANK



PLANT FOR PRODUCTION OF NITROGEN FLUID CLAY
FIGURE 7



PLANT FOR PRODUCTION OF UREA-AMMONIUM NITRATE SUSPENSION FERTILIZER

Figure 8