0-195

0-195
AN-7204
RN-3157

PROCESS AND PRODUCT CONSIDERATIONS OF FLUID LIME

For Presentation At

American Chemical Society
Las Vegas, Nevada
August 26, 1980

by

Hubert L. Balay
Chemical Engineer

and

David G. Salladay
Chemical Engineer

Process and Product Improvement Section
Division of Agricultural Development
National Fertilizer Development Center

TENNESSEE VALLEY AUTHORITY
Muscle Shoals, Alabama

PROCESS AND PRODUCT CONSIDERATIONS OF FLUID LIME

No other mineral has as many uses as limestone. It is used extensively in the construction industry for aggregate, cement manufacture, and building stone. Limestone and products derived from it are used in agriculture, metallurgy, glass manufacture, refractories, fillers, abrasives, and in many chemical processes including fume scrubbing, pulp and paper manufacture, and sugar refining. The lime industry extends worldwide. Carbonate rocks form about 15 percent of the earth's sedimentary crust. They are quarried from deposits dating from Precambrian to a recent period. Limestone has been used since earliest recorded history. Primitive man prepared plaster and mortar from limestone; and sand-lime mortar was used to build great structures of the Egyptian, Greek, and Roman civilizations.

Limestone in Agriculture

Crushed limestone has been used to raise the pH of soil for almost as long as it has been used in mortar. Surveys show, however, that soil pH in many parts of the U.S. is still too low to produce maximum crop yields and that many U.S. farmers do not use enough limestone. Effectiveness of some of the available limestone also has been questioned. Scientific study and constant use have shown that rate of reaction of limestone in soil depends upon particle size as well as chemical composition (calcium carbonate equivalent) of the rock. It is generally accepted that all liming material passing a 100-mesh sieve and 60 percent passing a 20-mesh sieve (Tyler standard screen-scale) will react within the first year after application. Some use the ENV (effective neutralizing value) rating which is a relative value expressing effectiveness of limestone in neutralizing soil acidity. ENV considers fineness of grind as well as chemical quality. One method of calculating ENV is shown in figure 1. The finer the grind of limestone the more desirable the limestone; however, fineness of agricultural limestone has been limited because of difficulties in grinding, storing, handling, and applying fine limestone to the soil.

Fluid Lime

In the late 1960's growing interest in suspension fertilizer led to an interest in applying finely-ground limestone as a suspension. Since limestone was the only material sold by suspension plant operators which had to be applied dry, extra investment in dry application equipment was required. In 1969 TVA successfully produced fluid limestone suspensions in the laboratory from -20, -60, and -100 mesh limestones. Part of this work was reported in TVA's 8th Demonstration held on October 6-7, 1970. The demonstration emphasized that with suspension lime:

(1) There would be no dust during handling or spreading.

(2) Very fine limestone could be used which would promote rapid reaction in the soil.

(3) Suspension fertilizer manufacturers with equipment for broadcasting suspension fertilizer could use the same equipment to apply limestone, thereby eliminating need for extra dry spreading equipment.

These data were presented to suspension fertilizer manufacturers but were not accepted because standard agricultural limestone, the only limestone available in quantity at that time, consisted of widely varying particle sizes which were difficult to suspend. It also appeared that the extra cost of handling, suspending, and applying the limestone could not be recovered. In 1976 further information was published on the formulation of limestone suspensions. At that time a good supply of finely-ground limestone was becoming available. Many quarries had installed dust collection equipment and were looking for a market for this product. Also, finely divided limestone became available from quarries which were grinding fine limestone for industrial customers. Equipment for producing suspensions also improved. Small liquid mix units with 3-hp propeller agitators and 2-inch centrifugal pumps powered with 3-hp motors were being replaced by units having turbine agitators driven by up to 60-hp motors and 6-inch centrifugal pumps driven by 40- and 50-hp motors.

Mixing Equipment

Sketches of typical plants used to produce suspension fertilizer and fluid lime are shown in figure 2. These plants do an excellent job of producing limestone suspension in 5- to 10-ton batches; however, finely ground limestone must be stored and added to the mix tank in batches. Usually equipment used to add limestone to the mix tank is conventional solid handling equipment such as bucket elevators, conveyor belts, drag chains, and augers. However, none of this equipment is capable of efficiently handling finely divided limestone without discharging an unacceptable amount of dust into the workroom. A formula for producing a 10-ton batch of 50 percent limestone mixture in a conventional batch mixer is shown in table 1. The usual procedure is to add water to the mixer, add and shear the clay, add limestone, then agitate the mixture until the limestone is thoroughly suspended. Some operators add 2 to 5 pounds of ammonium nitrate per ton of limestone suspension at this point to help gel the clay. Ammonium nitrate usually is added as ammonium nitrate solution containing

18 percent N or as urea-ammonium nitrate solution containing 32 percent N. Attapulgite clay must be properly gelled to provide enough suspending strength to keep the limestone from settling out.

Combination Mixing-Storage

Systems have been devised to avoid storage and handling problems associated with batch production of fluid clay. These vary from old tank cars mounted on piers and equipped with multiple propeller agitators to large vertical cone-bottomed mixing tanks equipped with large recirculation systems, clay injectors, strainers, and pumps. The major advantage of these systems is their ability to convert a complete truck or hopper car load of finely divided limestone into a suspension, thereby eliminating troublesome storage of finely divided dry limestone. The dry limestone usually is handled pneumatically and discharged either into a recirculating stream of fluid or beneath the surface of the fluid in the mixing tank.

A typical system is shown in figure 3. A coned-bottom tank, usually of 15,000-18,000 gallons capacity, is used as a mixing tank. A second tank, usually of 30,000-40,000 gallons capacity, is used for storage of finished product. Mixing is done by a large (usually 6" x 5" or 6" x 6") centrifugal pump on the small tank, and is done exclusively by recirculation. A second pump on the large tank keeps finished product in suspension by recirculation, and serves as a standby pump for the mixing pump and for filling applicators. Pumps are installed so they can be used independently or in parallel. The mixing pump discharges tangentially into the mixing tank to impart a swirling action to the mixture in the tank. The storage tank pump usually discharges tangentially at two levels as shown in figure 3 so that any limestone which settles during storage can be completely resuspended before being pumped into application equipment.

Limestone is delivered in pneumatic trucks or hopper cars and is blown directly into the mix tank through a pneumatic tube which discharges below the surface of the liquid at a point near where the recirculation stream discharges into the tank.

When a batch is prepared, a load of limestone is ordered from the quarry. Arrangements are usually made with the quarry to supply the mixer operator with the weight of limestone shipped as soon as it is available. As soon as the weight is received, the plant operator calculates the amount of water and suspending clay (usually attapulgite clay) required to prepare a suspension of the desired concentration. The correct amount of water is then pumped into the tank. The amount of water is usually determined volumetrically and is measured by use of a sight-gage on the mix tank. As soon as water is in the tank, recirculation is started and the proper amount of clay added. If dry clay is used, it is added through a clay inductor. Fluid clay, if used, is pumped into the tank. If dry clay is used, it must be sheared and gelled to perform properly. Shearing is accomplished by recirculating the water-clay mixture through the plant pump. Frequently, as with the batch system, ammonium nitrate or urea-ammonium nitrate solution is added at this time. When the limestone arrives, it is blown into the tank. Then recirculation is continued until a proper suspension is obtained. The suspension is then pumped from the mix tank to the holding tank where it is stored until needed.

There are several variations of the system shown in figure 3, but the only important difference is that some operators place a liquid jet eductor on the pump discharge to enhance pump mixing action. When an eductor is used, kinetic energy of the pump discharge causes the surrounding fluid and limestone to be sucked into the pump discharge stream. After all limestone is added, circulation is continued through the pump and eductor and back into the mix tank until a good suspension is formed. The time required to produce a good suspension depends upon size of equipment used and physical properties of the limestone.

A similar tank for mixing and storing lime suspension is shown in figure 4. It consists of a horizontal tank with a recirculation system. An air sparging system is used with the recirculation pump; recirculation, instead of being returned tangentially to the tank, is distributed across the surface of the fluid in the tank. The mixing procedure is slightly different from that described for cone-bottomed vertical tanks. The clay-water mixture is prepared while a weighed amount of limestone is being delivered to the site in a pneumatic truck. Upon arrival the limestone is blown below the surface of the water-clay mixture while the mixture is circulated and air blown through the sparger into the tank. After the mixture is completed, it is stored in the tank until needed. If some limestone suspension remains from a previous batch, it is mixed with the new batch. With this arrangement it is necessary to anticipate the rate at which the limestone suspension will be sold so there will be enough room in the tank to accommodate each new batch of limestone.

Byproduct Sources of Limestone and Lime for Suspensions

Most dry agricultural limestone is ground to pass a 60-mesh screen (Tyler standard sieve series). For example, Alabama law requires that 90 percent of limestone pass through a 10-mesh screen and 50 percent through a 60-mesh screen. For this reason, standard agricultural limestone will not make good suspensions and the -100 to -200 mesh limestone required for suspension fertilizers must be supplied from material collected at limestone quarries in pollution control equipment or ground in ring-roller crushers for industrial uses. Because of this, the amount of finely divided limestone available to fluid lime manufacturers is limited and often expensive. Searches have been made for byproduct materials suitable for use in limestone suspensions to supplement conventional sources. The most important such material is precipitated flue dust from Portland cement plants.

Analyses of three samples of flue dust from two plants are shown in table 2. These analyses show that flue dust usually has a calcium carbonate equivalent of 70 to 80 percent and contains a useable amount of K_2O. The major neutralizing source is CaO, a compound which reacts with water to evolve heat and cause thickening of suspensions made from it. Early work showed that flue dust would not make a satisfactory suspension unless it was mixed with an appropriate amount of a lignosulfonate, usually about 10 pounds per ton of product. This result was expected since lignosulfonic acids and their salts are known as class one admixtures (setting retardants) for concrete in ASTM nomenclature.

Use of flue dust to make suspension lime, however, has not been widely accepted because the flue dust-lignosulfonate suspension, although it mixes and applies fairly well if applied soon after manufacture, sticks to the interior walls of application equipment and cannot be removed by washing. When the application equipment is then used for fertilizer, the flue dust reacts with the phosphates forming hard lumps which can be removed only by scraping. Also, any residue left in valves, pumps, and lines tends to set and interfere with future operation of the equipment. Reported use of lignosulfonates to retard the thickening of flue dust suspensions led to investigation of other compounds which cause delays in setting of concrete. Sugar, carbohydrate derivatives, soluble zinc salt, and soluble borates are a few of the compounds used as retarders that show promise. It was found that as little as 0.05 percent by weight of sugar in the flue dust would retard the setting action and as little as 0.2 percent would prevent setting almost entirely for extended periods. Subsequent laboratory investigations revealed that molasses normally used in fluid cattle feed (55 percent sugar) would also retard setting of flue dust suspension and prevent its sticking to laboratory equipment. This was important since molasses is readily available and cheaper than sugar. Laboratory results with sugar are shown in table 3 and with molasses in table 4.

Only limited field trials have been made with flue dust-sugar suspensions; however, this appears to be a promising use of a byproduct material which normally would present a disposal problem. Mechanics of the sugar-flue dust reaction is not known. However, most starches, sugars, cellulose products, acids, and salts of acids used as retarders for cement contain one or more hydroxyl groups. These three classes of compounds all have the HOCH group in common. That alone does not appear to explain the retarding action since other compounds, such as alcohols, contain this group and do not act as retarders. It seems probable that the HOCH group is adsorbed on the grains of $3CaO.SiO_2$ and $3CaO.Al_2O_3$ in the cement protecting them for a time from attack by water. When calcium or sodium lignosulfonate is used, the retarding action is apparently due to adsorption of the anion.

As shown in table 2, there are differences in analysis between flue dust sources, and results obtained depend upon the chemical composition of the dust. For this reason, performance of the dust and any additives should be determined by trial mixes with the actual dust to be used.

Laboratory tests performed by others have shown that when CaO-containing suspensions are mixed with urea-ammonium nitrate solution, nitrogen in the form of ammonia is liberated from the ammoniacal portion of the solution. Tests at TVA show that this reaction does not occur when urea solution or dry urea is used as the nitrogen source. Acceptable grades with up to 10 percent nitrogen and 50 percent flue dust have been prepared. However, grades with 40 percent flue dust appear to be most acceptable.

A mixture of 60 percent limestone and 40 percent flue dust makes an acceptable suspension without retarders but this does not totally prevent sticking of flue dust to application equipment.

Other byproducts suitable for soil neutralizing suspensions are available from sugar refining. Limestone is used in both cane and beet-sugar refining. For every pound of beet sugar produced a little more than half a pound of limestone is required. Most of this is reused, but some is discarded with waste and if properly salvaged could be a source of liming material.

The pulp and paper industry uses both lime and limestone in preparing cooking liquors. About 300 pounds of limestone is consumed for every ton of pulp produced by the sulfite process and a waste product with liming value which also could be a raw material source for suspensions is produced. Other possible sources of suspension liming material are waste products from calcium carbide and cyanamide production; the leather industry; water and waste treatment; and the insecticide, fungicide, and disinfectant industries.

Another possible source of limestone slurry is the flue-gas scrubbers in power plants. Limestone is used to remove SO_2 from stacks of coal-fired power plants. After the SO_2 removal ability of the limestone has been exhausted, about 50 percent of the liming value of the original limestone remains. The slurry also contains calcium sulfur compounds and can be a valuable source of sulfur nutrient.

A problem common to most byproduct sources of soil neutralizing material is dilution of neutralizing power of the limestone. The byproduct also may be mixed with foreign matter which may or may not be valuable as a soil amendment. Dilution increases shipping costs and can make the byproduct economically impractical if it must be transported appreciable distances or if a source of fine limestone suitable for suspensions is located nearby. Many byproducts are already in slurry form and need very little mixing before they are ready for field application. This can be a disadvantage, however, if the slurry is thick and must be removed from an inconvenient location such as a holding pond. Similar handling difficulties can be encountered in storing the slurry and in feeding it into the mix tank.

Application Equipment

Fluid lime generally is applied through conventional fluid application equipment. The only change required is the use of larger nozzles to pass the limestone. For example, one lime suspension producer changes from six KSS 60 to six KSS 120 flooding nozzles when the applicator is changed from fertilizer to limestone, even when application rate is the same.

Limestone has a hardness of about 3 (MOH hardness scale), is insoluble, and is harder than particles normally found in suspension fertilizers. Therefore, wear on nozzles, pump seals, and other equipment is greater than that encountered in fertilizer application. For that reason, some attempts have been made to decrease the amount of equipment in contact with limestone suspension. One approach is to decrease the number of nozzles used to one or two. This decreases the number of lines and fittings required and allows use of nozzles with very large openings that are less likely to become plugged. For example, a 60 flooding nozzle has an orifice opening diameter of 0.266 inches or a cross section of 0.056 square inches. Six 60 nozzles have a total cross section of 0.056 x 6 = 0.336 square inches. A single 450 nozzle has a cross section of 0.388 square inches and an orifice diameter of 0.703 inches. The similarity of cross section preserves the approximate back pressure required for a good pattern, but the larger orifice diameter decreases likelihood of plugging. An applicator which accomplishes this is shown in figure 5. This applicator uses air pressure to apply limestone. By using air pressure as a motive force, contact between the limestone and any moving parts in the equipment can be eliminated. Although there are some problems with single nozzle application due to uneven patterns and difficulty in overlapping properly, fertilizer containing pesticides is successfully applied with a single nozzle in several locations and the pattern appears to be more than adequate for limestone. A similar applicator is shown in figure 6. This applicator uses a gasoline-powered pump and can be skid mounted so farmers can apply limestone suspension using a flatbed truck.

Limestone Mixtures

Limestone has been successfully mixed and applied with urea-ammonium nitrate solution, potash, and certain herbicides. However, mixing limestone with phosphates can cause phosphate reversion and thickening, making the mixtures deficient in available phosphate and difficult to apply. Despite this, several companies are successfully mixing suspension grades containing phosphate with limestone. One company is producing and applying a 7-3-3 with 36 percent limestone. This fertilizer is made from a 10-30-0 base prepared from monoammonium phosphate, clay, and anhydrous ammonia; urea-ammonium nitrate solution and potash are added to make the final mixture.

Chemical tests of samples of 50 percent limestone suspension and 50 percent orthophosphate suspension from field mixtures show little reversion even after storage for two weeks. Physical and chemical analyses of 6.5-6.5-6.5-25% limestone suspensions made from ortho and polyphosphate bases are shown in table 5. Physical and chemical analyses were performed directly after the samples were produced and after twelve days of aging. A petrographic analysis tentatively identified the major phase in the samples, both fresh and after aging, as an optically amorphous material, $Ca(NH_4)_2P_2O_7.H_2O$, reported to be citrate soluble in the literature.

One suspension was made using an orthophosphate base (TVA 13-38-0) and the other made using a polyphosphate containing base (10-34-0, 65 percent of phosphate as polyphosphate). The analysis shows little reversion in the orthophosphate-limestone mixture immediately after mixing, but after twelve days, about 15 percent of the phosphate has reverted. Forty-four percent of the P_2O_5 in the polyphosphate containing suspension reverted after 24 hours, but very little reversion occurred after that.

Results of laboratory and field tests with limestone-phosphate suspensions are mixed. It appears that suspension made from phosphate and limestone can revert and thicken. But laboratory tests and field results show that orthophosphate-limestone suspensions can be prepared and applied successfully if they are applied soon after they are made. Further work is required on the effect of limestone suspensions on availability of ortho and polyphosphates.

Conclusion

Problems associated with proper use of limestone on the farm may be more critical than those associated with fertilizer. It appears that a substantial educational program is needed to help farmers really understand the value of lime in a fertility program. One possible solution is fluid lime. Convenience of a single application of fluid lime mixed with other materials, rather than multiple applications of lime and other straight materials, appeals to many farmers. Cost of a single application would partially offset any extra cost in preparing limestone suspension. Fluid lime is more uniform and dust free than solid limestone and the grind is usually finer. However, mixing and application costs tend to nullify these advantages. Many byproduct sources of liming material, such as excess lime from industrial processes, are suitable for use as fluid limestone but are not suitable for dry application. Basic slag, cement flue dust, and other dry industrial byproducts also have value as liming materials. Some of these products also contain other plant nutrients. Use of these products is occasionally limited by objectional physical properties, primarily dustiness which is an agronomic advantage, and regulations which restrict their sale. Development of fluid lime may be the technique required to use byproduct materials as well as conventional finely ground limestone more effectively.

References

1. "Suspensions of Limestone, Sulfur, Potash and Other Solids," New Developments in Fertilizer Technology, 8th Demonstration, Tennessee Valley Authority, National Fertilizer Development Center, Muscle Shoals, Alabama.

2. "Lime," Mineral Commodity Summaries 1980, Bureau of Mines, U. S. Department of Interior, Washington, DC.

3. Sawyer, E. W. "Lime in Suspensions, Part 1: Stable Liquid Lime Slurries Produced With Colloidal Attapulgite Clay," Solutions, Vol. 20, No. 3, May/June 1976.

4. Winter, K. T. et al. "Liming Has No Miracles," Solutions, Vol. 24, No. 2, March/April 1980.

5. Bogue, Herman. The Chemistry of Portland Cement, Reinhold Publishing Company, New York, New York, 1955, pp. 491-492.

6. Lea, F. M. The Chemistry of Cement and Concrete, Edward Arnold Publishers, Limited, London, England, 1956, p. 466.

Table 1

Formula for 10-Ton Batch of 50 Percent Limestone Suspension Using Batch Mixer

Materials[1]	Lbs/batch
Water	9,600
Attapulgite clay[2]	400
Limestone	10,000
Total	20,000

[1]Usual order of addition

[2]5-10 lbs of UAN solution added to the water aids in gelling the clay.

Table 2

Typical Analysis of Flue Dust from Two Portland Cement Plants

Analysis, % by weight	Cement Plant A		Cement Plant B
	Sample 1	Sample 2	
Al_2O_3	4.44	5.11	5
Fe_2O_3	.98	1.25	2
CaO	44.66	55.04	47
MgO	3.01	2.89	2
SO_3	9.45	5.83	3
Loss on ignition	14.18	13.48	25
Na_2O	1.0	0.8	0.3
K_2O	7.8	4.7	3.8
Density (lb/ft^3)	52		
Moisture	0.3		
$CaCO_3$ equivalent	75.6		76.3
Sieve Analysis (% by weight)			
On 50 mesh			0.3
On 100 mesh			1.0
On 200 mesh			12.0
On 325 mesh			40.0
Through 325 mesh			46.7

Table 3

Cement Flue Dust Suspensions Containing Sugar[1]

Percent flue dust	40	40	50	50
Percent sugar	0	.25	0	.25
Formulation	Lb/ton Product[2]			
Water	1,180	1,175	980	975
Sugar	0	5	0	5
Attapulgite clay	20	20	20	20
Cement flue dust	800	800	1,000	1,000
pH				
Initial	12.8	12.7	12.8	12.8
24 hours	12.9	12.8	12.8	12.9
Viscosity[3], cPs				
Initial	800	10	1,050	240
24 hours	Set up	40	Set up	1,740
Pourability (% by weight)[4]				
Initial	-	98.7	-	96.3
24 hours	-	86.5	-	76.0
Settling (% by volume)[5]				
24 hours	Set up	24	Set up	None

[1]Sucrose ($C_{12}H_{22}O_{11}$)

[2]Ingredients added in order listed

[3]Brookfield, spindle No. 2, 100 rpm. Temperature 75°F

[4]Amount poured from a quart jar tilted at 45° angle for 1 minute after indicated period of storage; temperature about 75°F.

[5]Layer free of suspension

Table 4

Cement Flue Dust Suspensions Containing Molasses[1]

Percent flue dust	40	40	40	50	50	50
Percent molasses	0	0.25	0.45	0	0.25	0.45
Formulation (Lb/ton of product)[2]						
Water	1180	1175	1171	980	975	971
Molasses	–	5	9	–	5	9
Attapulgite clay	20	20	20	20	20	20
Cement flue dust	800	800	800	1000	1000	1000
pH	12.7	12.6	12.6	12.6	12.6	12.6
Viscosity[3], cPs						
Initial	850	130	100	1580	530	380
24 hours	Set-up	710	630	Set-up	2000+	2000+
Pourability (% by weight)[4]						
Initial	75	95	97	70	90	90
24 hours	Set-up	70	85	Set-up	65	60
Settling (% by volume)[5]						
24 hours	–	10	8	–	5	7

[1]55% sucrose ($C_{12}H_{22}O_{11}$)

[2]Ingredients added in order listed

[3]Brookfield, Spindle No. 2, 100 rpm, temperature 75°F

[4]Amount poured from a quart jar tilted at 45° angle for one minute after indicated period of storage.

[5]Layer free of suspension

Figure 1

Calculation of Effective Neutralizing Value (ENV)

1. Determine total carbonate content from analysis. Percent total carbonates is the sum of % $CaCO_3$ and % $MgCO_3$ present[1].

2. Determine calcium carbonate equivalent from analysis. The calcium carbonate equivalent is the sum of the calcium carbonate equivalents of the calcium and magnesium carbonates.[2]

3. Calculate the amount of limestone in three size fractions: (Tyler Standard Sieve Series) -20 and +60; -60 and +100; and -100.

4. Calculate carbonate effectiveness of the liming material. Multiply total carbonates (as a decimal) by an arbitrary fineness factor, usually the size of the largest screen in each fraction. The factor for the -20 +60 range may be 20; for the -60 +100 ranges 60; and for the -100 range 100. The calcium carbonate equivalent rather than total carbonates is used for the -100 fraction.

5. Calculate effective neutralizing value. Multiply carbonate effectiveness for each size times the amount of material in each fraction. The sum of the carbonate effectiveness for each fraction is the effective neutralizing value (ENV).

---

[1] If values are given as the oxide, they must be converted to carbonates

$$\% \; CaO \times 1.785 = \% \; CaCO_3$$
$$\% \; MgO \times 2.092 = \% \; MgCO_3$$

[2] If values are given as the oxide, they must be converted to calcium carbonate equivalents

$$\% \; CaO \times 1.785 = \% \; CaCO_3$$
$$\% \; MgO \times 2.483 = \% \; CaCO_3 \text{ equivalent}$$

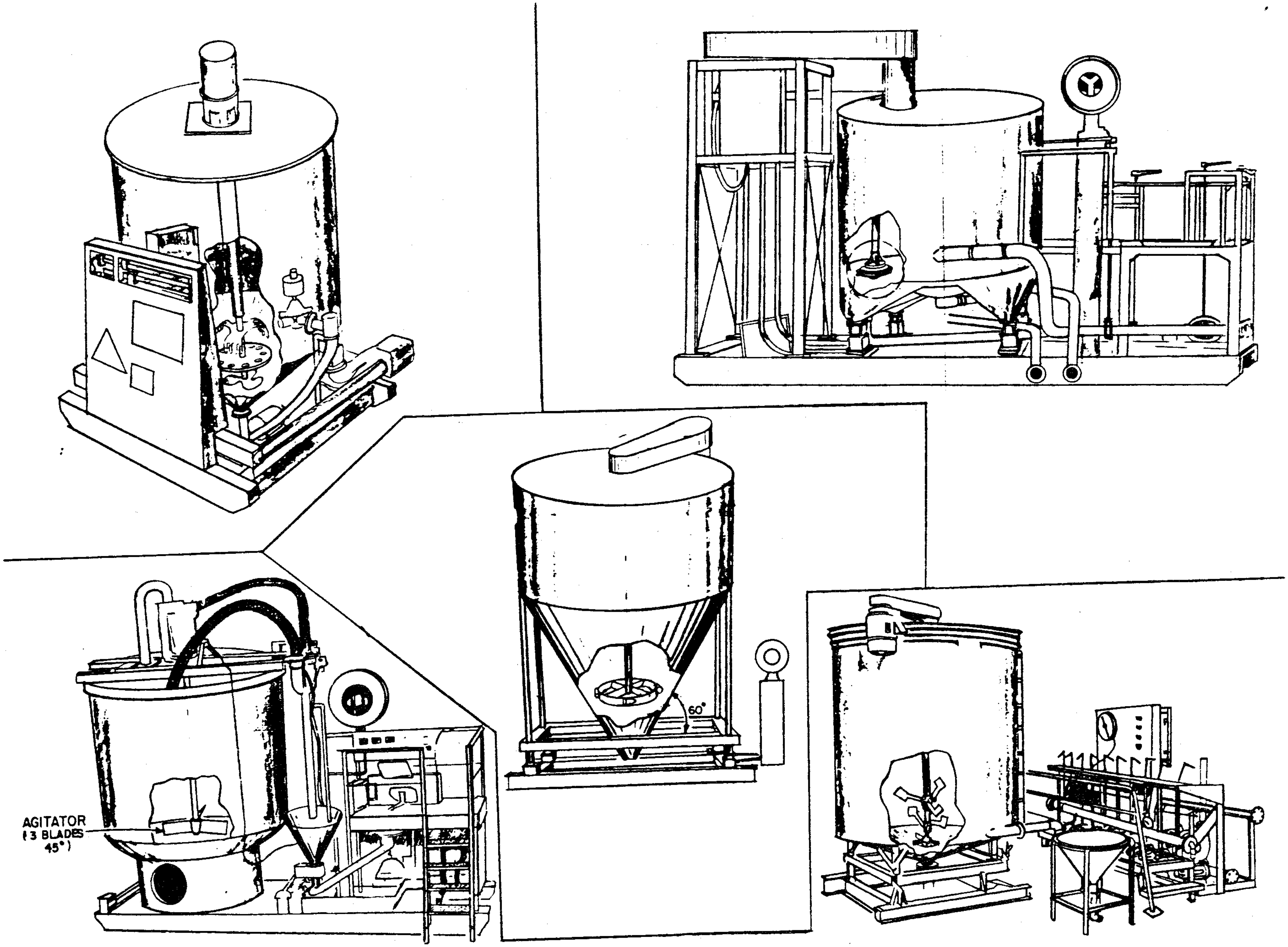

Figure 2

Typical Mix Tanks For Suspensions

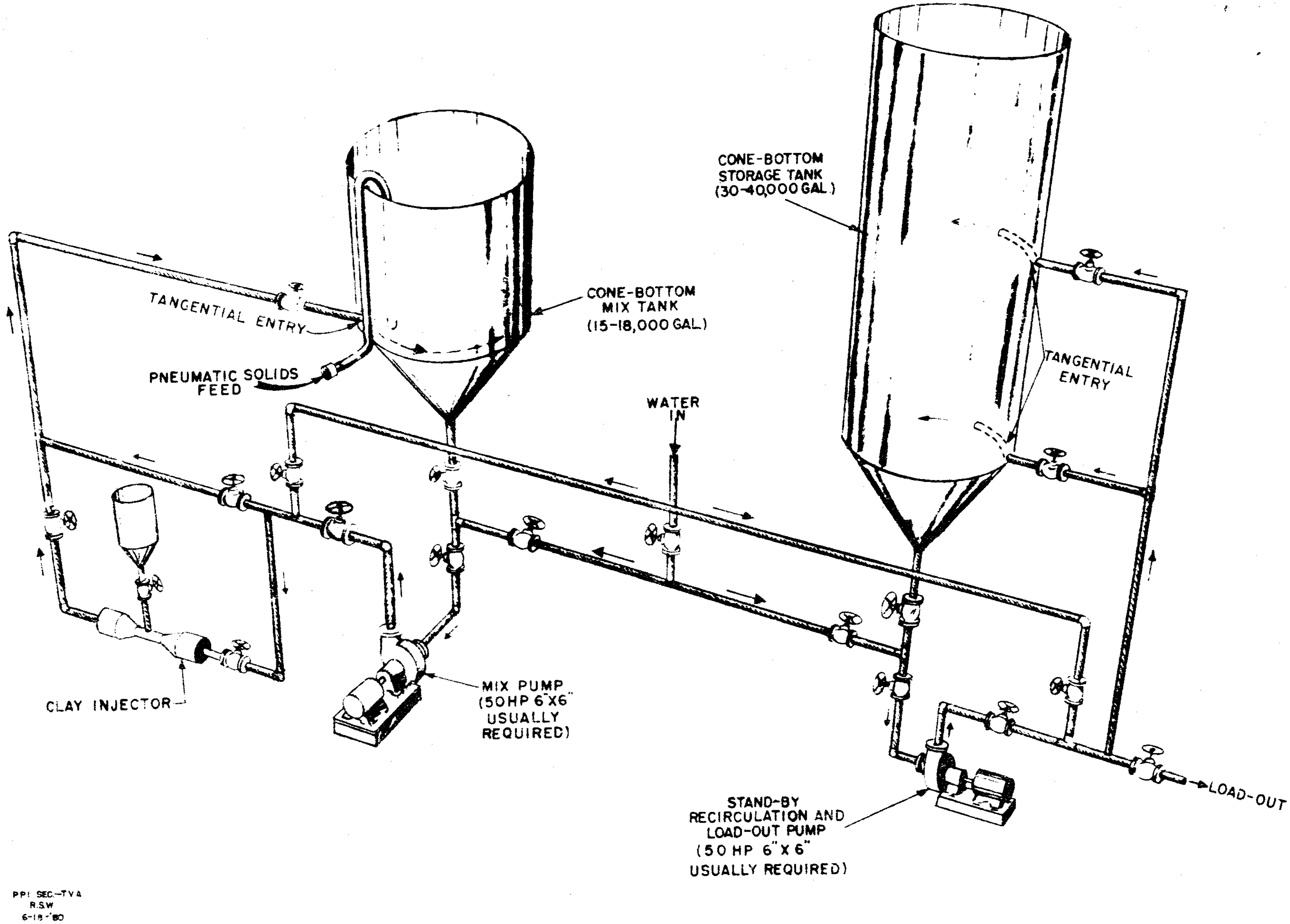

FIGURE 3

LIME SUSPENSION MIXING AND STORAGE SYSTEM

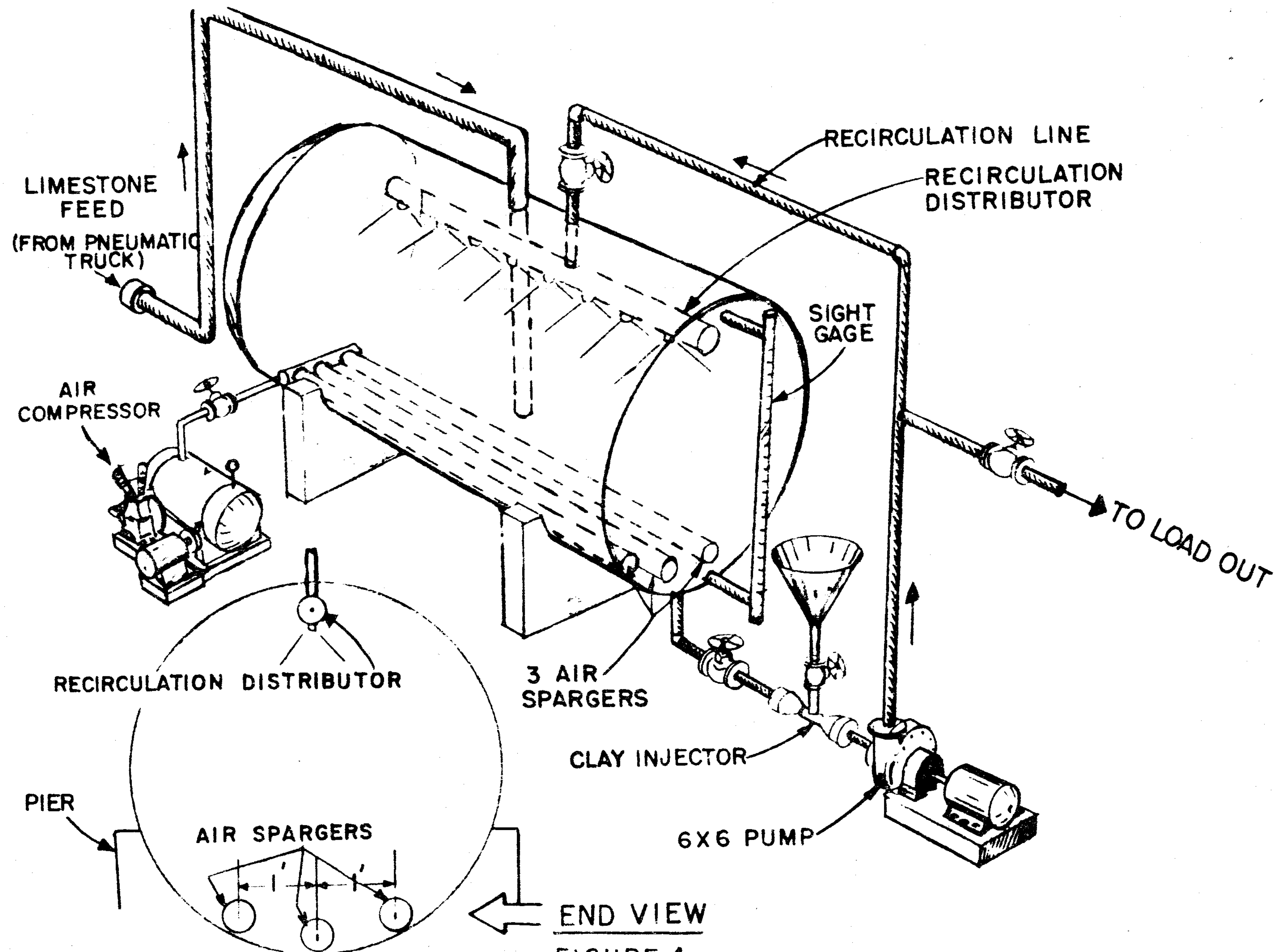

FIGURE 4

LIME SUSPENSION MIX AND STORAGE TANK

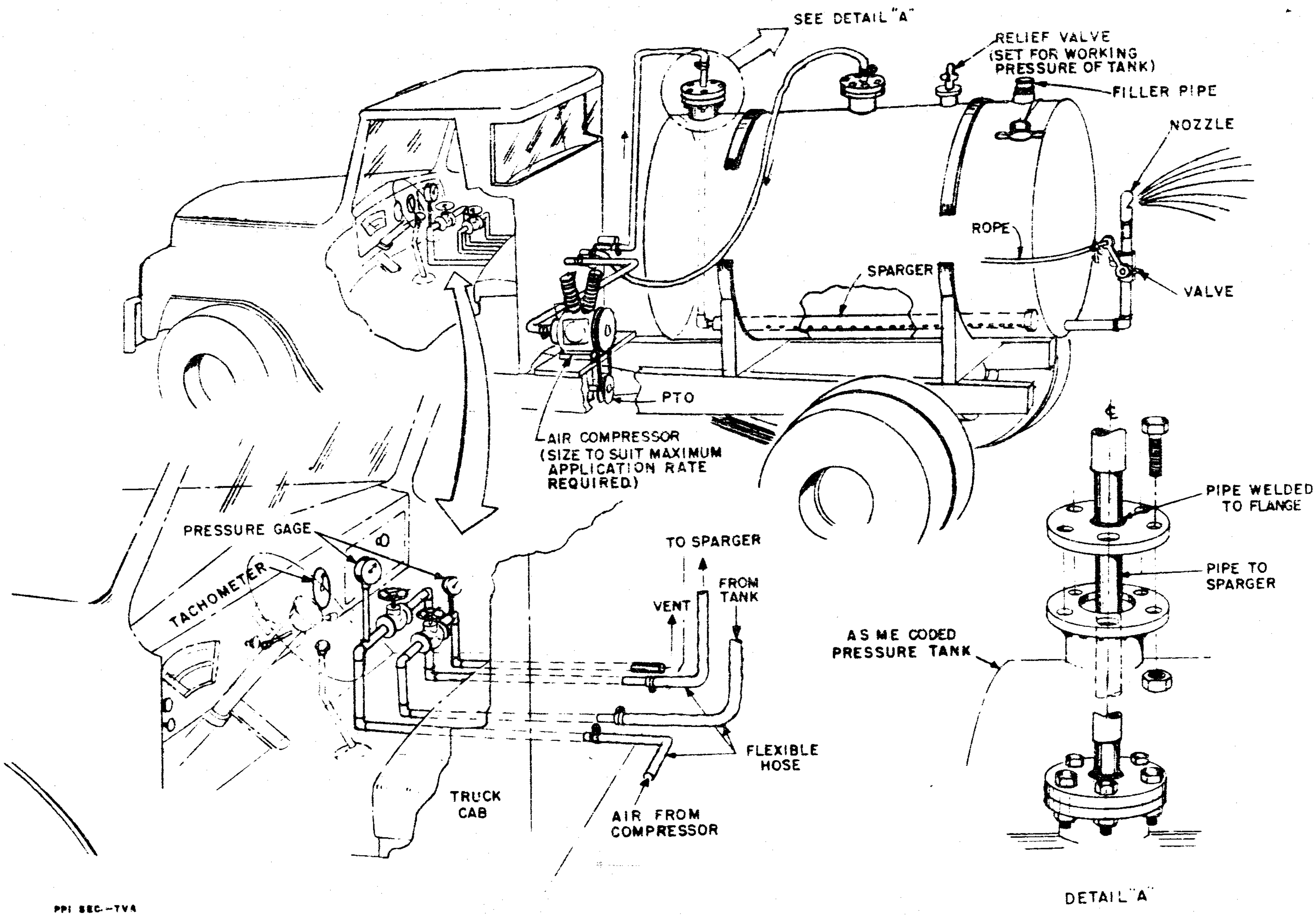

Figure 5

APPLICATOR FOR BROADCASTING SUSPENSION FERTILIZER

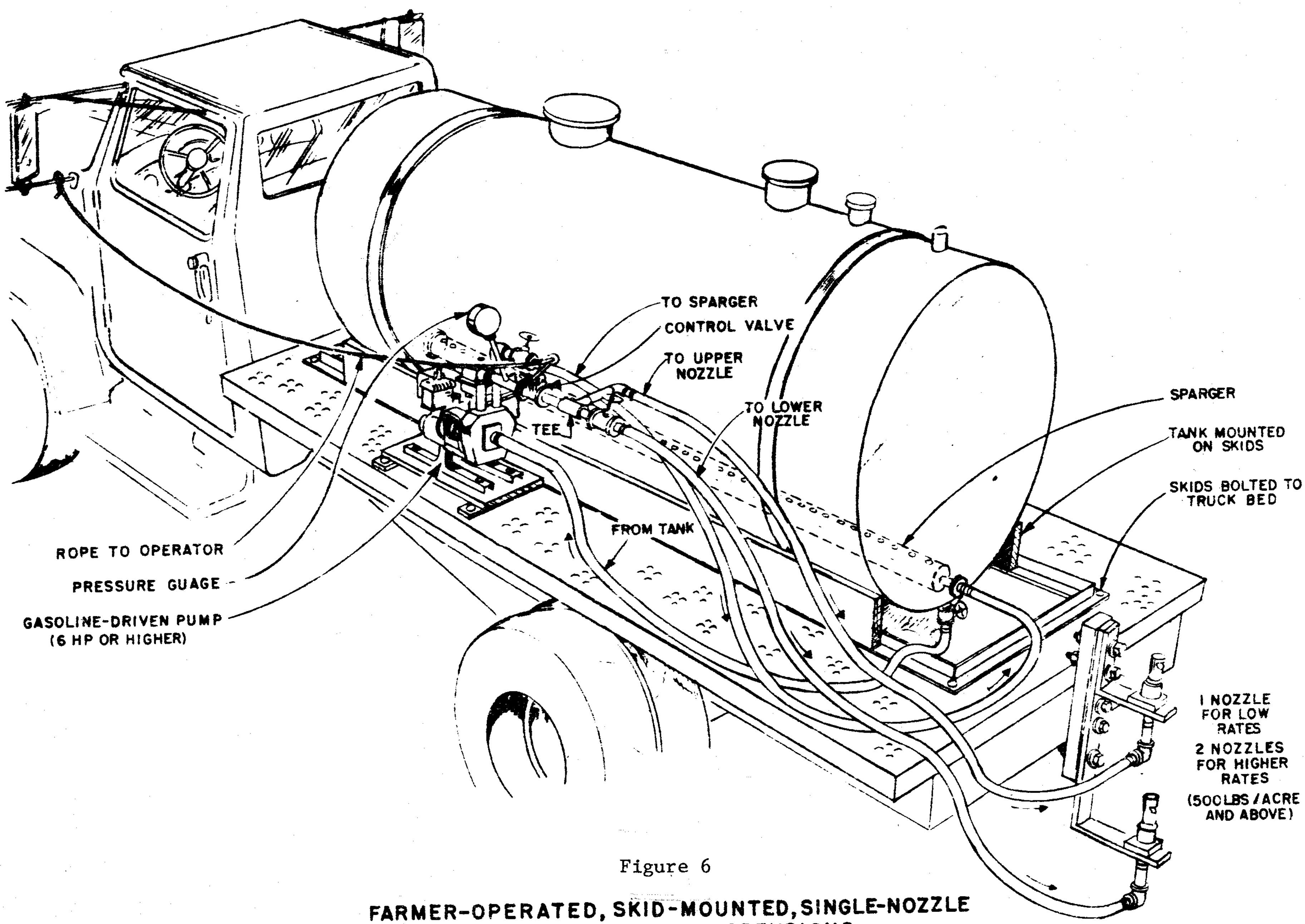

Figure 6

FARMER-OPERATED, SKID-MOUNTED, SINGLE-NOZZLE APPLICATOR FOR SUSPENSIONS