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ADVANTAGES OF PRODUCING AND USING MONOAMMONIUM PHOSPHATE

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Ammonium phosphate production has increased faster than production of other kinds of fertilizer since about 1960 when a practical and versatile process for production of economical high-quality granular products was introduced. The production increase has been mostly in granular diammonium phosphate (18-46-0 grade) made from wet-process phosphoric acid and ammonia. Recently, however, monoammonium phosphate has increased in popularity mainly because of its usefulness as a fluid fertilizer base.

Production of ammonium phosphates started in the early 1930's, and most of the early plants produced mainly straight monoammonium phosphate and mixtures of monoammonium phosphate with ammonium sulfate. Once again, large tonnages of monoammonium phosphate and monoammonium phosphate containing ammonium sulfate are being marketed. However, the predominant form of ammonium phosphate continues to be diammonium phosphate (18-46-0). Tonnage reporting services do not distinguish between diammonium phosphate and monoammonium phosphate except for direct application. Therefore, it is impossible to determine just how many tons of monoammonium phosphate are produced. It is known, however, that tonnages sold of monoammonium phosphate and monoammonium phosphate containing ammonium sulfate are increasing and are expected to continue to increase. This is because monoammonium phosphate has advantages over diammonium phosphate in every branch of production and use including ammonium phosphate production plants, regional granulation plants, bulk blend plants, fluid fertilizer plants, transportation, storage, and agronomics.

Advantages in Ammonium Phosphate Production

Most granular diammonium phosphate is produced by the slurry process developed by TVA. In this process phosphoric acid is ammoniated to an $NH_3:H_3PO_4$

mole ratio of 1.45:1 in a preneutralizer. This ratio is chosen because it corresponds to the high solubility point between the monoammonium and diammonium phosphate and allows a slurry with only about 20 percent water to be pumped to the granulator. Solubility of ammonium phosphate at various ammoniation rates is shown in figure 1. An excess of ammonia is then added in the granulator to raise the NH_3:H_3PO_4 mole ratio of the product to about 2:1. A flow diagram of the TVA diammonium phosphate process is shown in figure 2. One of the major problems in operating such a plant is capturing ammonia escaping from the granulator. This is generally done by scrubbing the ammoniator off-gases with the incoming weak acid (30% P_2O_5) in a corrosion resistant scrubber. The scrubber solution is then added to a preneutralizer where it is mixed with stronger acid, ammoniated, and added back to the granulator as a slurry. The product produced is then dried, cooled, sized, and transported to storage.

The same equipment can be used to make monoammonium phosphate by merely operating the preneutralizer at an NH_3:H_3PO_4 mole ratio of 0.5:1 to 0.6:1, which produces a slurry similar in solubility (as shown in figure 1) to that at the 1.45:1 mole ratio, pumping the slurry to the granulator, and adding enough ammonia to bring the NH_3:H_3PO_4 mole ratio to 1.0:1 (1). The major advantage of using this system to produce monoammonium phosphate over production of diammonium phosphate is in scrubbing. Operating at the NH_3:H_3PO_4 mole ratio of 0.5:1 to 0.6:1 results in less steam generation from the preneutralizer because less chemical heat is liberated. Also, only the first hydrogen on the phosphoric acid molecule is replaced resulting in a reaction that more easily goes to completion in the granulator. This produces a more stable compound with less ammonia loss. It also simplifies removal of ammonia from the ammoniator off-gases. These gases can be scrubbed with conventional scrubbing equipment rather than with phosphoric acid. This also allows more flexibility in the concentration of the phosphoric acid used; high strength acid can be used if desired.

Nongranular monoammonium phosphate, which is valuable as an ingredient in granulation and fluid fertilizer plants, can be made in comparably simple plants (2). In general, nongranular processes are simplified by eliminating granulation, recycling, crushing, drying, and cooling steps. These systems produce a product which, although nongranular, has sufficiently good physical properties to permit storage, handling, and transportation without excessive caking or dusting. Four processes, Swift, Scottish Agricultural Industries, Fison, and Nissan are used to produce most nongranular monoammonium phosphate.

In the Swift process phosphoric acid containing 50 percent P_2O_5 is reacted with liquid ammonia in a two-fluid nozzle which discharges into a reactor pipe. The mixture is ejected into a cooling tower where a countercurrent air stream removes water vapor and cools the product. A product containing 3 to 5 percent moisture is produced (3,4).

The Scottish Agricultural Industries process consists of a vessel where phosphoric acid containing 50 percent P_2O_5 is neutralized with ammonia to an $NH_3:H_3PO_4$ mole ratio of about 1.35:1. The resulting slurry is mixed with more phosphoric acid in a blunger-like reactor which breaks the mass into small granules. The product usually contains 6 percent moisture (3,5).

The Fison process reacts phosphoric acid containing 50 percent P_2O_5 with gaseous ammonia under pressure. Reaction heat drives off part of the water as superheated steam. The slurry containing 9 to 10 percent water is released into a spray tower through a special nozzle where water is flashed. The particles then solidify by falling through a rising air stream (3).

The Nissan process reacts droplets of phosphoric acid in an ascending stream of air and ammonia (3).

Other advantages in the production of monoammonium phosphate over diammonium phosphate are: less ammonia must be shipped from areas where ammonia is produced to areas where phosphoric acid is produced; grades with plant food contents equal to or higher than 18-46-0 can be produced if reasonably pure acid is used; and finally, no fixed grade (such as with 18-46-0) has been established, leaving manufacturers free to make the grade which best suits their phosphate source and manufacturing method.

Advantages in Regional Granulation Plants

Until recently phosphoric acid has been used only in relatively small quantities in ammoniation-granulation plants because addition of a preneutralizer was expensive and its operation was often beyond the technical capabilities of the operating personnel. To use as much ammonia as possible when the acid was added directly to the granulator, the phosphoric acid was usually ammoniated to an NH_3:H_3PO_4 mole ratio of 1.5:1. This tended to limit the amount of phosphoric acid that could be used because, as shown in figure 1, the solubility of the ammonium phosphates at this mole ratio is high. This increased the solubility of ammonium phosphate in the mixture and the liquid phase of the mass being granulated. Also the critical relative humidity of the mixture was increased and storability of the product impaired.

During the last few years, however, operators of regional granulation plants have discovered that more phosphoric acid and sometimes more ammonia can be used if the acid is ammoniated to a mole ratio of 1.0:1 (monoammonium phosphate) rather than 1.5:1. The decreased solubility in going from a 1.5:1 to a 1.0:1 mole ratio assists granulation because the lower solubility of the monoammonium phosphate in the mixture allows more phosphoric acid to be used, reduces the recycle ratio, and produces a product which stores better.

Recently, development of the pipe-cross reactor which replaces the preneutralizer in regional granulation plants has allowed even more phosphoric acid to be used (6). The NH_3:H_3PO_4 mole ratio in the pipe-cross usually is held at 1:1 to prevent ammonia loss, to aid granulation, to decrease recycle rates, and to produce a product with a lower solubility and higher critical relative humidity. This can be done with the pipe-cross because most of the water added to the pipe-cross with the raw materials is flashed and a melt with only about 3 percent water is produced. Despite the low solubility of the melt at an NH_3:H_3PO_4 mole ratio of 1:1, the pipe-cross melt does not need additional water because it discharges immediately after completion of the reaction onto the rolling bed of solids in the granulator. This is in contrast to a preneutralizer where the ammonium phosphate slurry has to be kept at a minimum of 16 percent water so that it can be pumped to the granulator. Use of the pipe-cross melt process rather than a slurry process decreases equipment cost, simplifies operation, and allows drying of the final product to be eliminated or greatly reduced.

With the pipe-cross, monoammonium phosphate grades containing small amounts of sulfur have been produced in regional granulation plants; 12-48-0-3.8S and 11-53-0-2S grades have been produced in some quantity. These products have been found to be useful in bulk blends and as bases for fluid fertilizers.

Nongranular monoammonium phosphate from processes described previously can be used as an intermediate in granulation (7). Nongranular monoammonium phosphate is especially useful in high nitrogen grades. The amount of ammonia that can be used as a nitrogen source in high nitrogen grades is limited because when large quantities of ammonia are used, the heat and liquid phase generated are excessive. Usually as much nitrogen as possible is obtained from ammonia and the balance is obtained from ammonium nitrate or ammonium sulfate. Both of these materials, if used in quantity, degrade handling and storage properties of the product, and the nitrogen in these compounds is usually more expensive than the ammonia in monoammonium phosphate. If monoammonium phosphate is used as a phosphate source, ammonium nitrate and ammonium sulfate requirements are reduced because of nitrogen in the monoammonium phosphate.

Nongranular monoammonium phosphate is also useful as a phosphate source in high-analysis grades that cannot be formulated with triple and normal superphosphates because there is not enough room in the formula. Usually granular diammonium phosphate is used in these grades, but the granules of diammonium phosphate often are not covered during the granulation process. This causes segregation and poor appearance of the product. Nongranular monoammonium phosphate is sold as a substitute for powdered normal and triple superphosphates and can be useful as a substitute for these raw materials if the delivered cost is attractive. This is especially true in independent regional granulation plants that do not have access to supplies of normal or triple superphosphate or phosphate rock.

Advantages in Bulk Blends

Granular monoammonium phosphate is especially useful in bulk blending. Monoammonium phosphate has the advantage over diammonium phosphate (18-46-0) in that all of the popular ratios, even the 1:4:X and 1:3:X ratios, can be blended without an additional phosphate material (2). If ratios below 1:2.56 are blended from 18-46-0, granular triple superphosphate or some other phosphate material must be available. Additional nitrogen is sometimes required with monoammonium phosphate, but bulk blending plants usually have nitrogen available to blend the higher nitrogen ratios. This eliminates the need to ship and store one material. All of the ratios that can be blended from monoammonium phosphate can be blended from triple superphosphate and nitrogen; however, monoammonium phosphate has an advantage over triple superphosphate in that it contains 60-66 units of plant food per ton rather than 42-46 for triple superphosphate. This results in lower freight rates and less storage space requirements.

The 12-48-0 grade mixture of monoammonium phosphate and ammonium sulfate produced in pipe-cross reactor plants is especially useful for blending the popular 1:4:X ratios. This cuts down the number of materials required in the formula and helps alleviate segregation problems that still worry blenders.

Monoammonium phosphate is compatible with all fertilizer ingredients used in bulk blending. This is not true of diammonium phosphate. Diammonium phosphate as shown in figure 3 has limited compatibility with normal and triple superphosphates (8). When diammonium phosphate is mixed with superphosphate, a reaction can occur in which ammonia is released from the diammonium phosphate and absorbed by the superphosphate. This releases the water of hydration from monocalcium phosphate monohydrate (superphosphate). This reaction wets the blend and helps form monoammonium phosphate crystals which can cause pile and bag set by creating bonds between the pellets. P_2O_5 water solubility can also be reduced because of conversion of monocalcium phosphate to dicalcium phosphate. These are normally slow reactions that usually do not interfere with bulk spreading; however, it can ruin bagged bulk blends.

The 1:5 and 1:4 ratios are natural ratios for monoammonium phosphate and monoammonium phosphate combined with ammonium sulfate and are also natural starter ratios when combined with potash. This allows monoammonium phosphate and monoammonium phosphate mixed with potash to be applied in the row as starter fertilizer and followed later with anhydrous ammonia. This can be done with diammonium phosphate; however, again either an excess of nitrogen usually must be applied in the starter or triple superphosphate must be shipped and stored to mix with the 18-46-0 grade. Also, as discussed later, placing diammonium phosphate near the seed can cause germination problems.

Advantages in Suspension Fertilizers

Use of monoammonium phosphate in manufacturing suspension fertilizers has done more to spur the return of monoammonium phosphate as a major fertilizer ingredient than any other factor. There are many reasons for this. A major reason is the low shipping cost of monoammonium phosphate as compared to fluid bases. Not only is monoammonium phosphate higher in analysis than any fluid base, but higher per ton shipping rates generally are charged by the railroads for fluids than for solids.

Monoammonium phosphate presents no cold weather storage problems. Storage of most fluid bases containing phosphate can be a problem in cold weather because they solidify or salt-out. Fluid bases that store well are expensive, and even these bases sometimes precipitate impurities which cause problems. This makes it difficult to buy fluid bases during discount periods and successfully store them until they are required in the spring.

The recent appearance on the market of high-horsepower, high-shear mixing equipment has made it possible to disintegrate granular monoammonium phosphate efficiently to produce suitable suspensions (9). Reaction of ammonia with the monoammonium phosphate to provide heat and increase solubility of the phosphate is required for this process. This is an additional advantage since the cost of nitrogen from anhydrous ammonia is usually lower than the cost of nitrogen in fluid bases and always lower than the cost of nitrogen in supplemental nitrogen sources such as urea or urea-ammonium nitrate solution.

Monoammonium phosphate alone is comparatively insoluble. As shown in figure 1 only about 25 pounds will dissolve in 100 pounds of water at 32^{o}F. If ammonia is added to raise the NH_3:H_3PO_4 mole ratio from 1:1 to 1.45:1, about 110 pounds will dissolve in 100 pounds of water at 32^{o}F. Since the amount of solid that can be suspended is roughly the same regardless of how much material may have been dissolved, ammoniating to a mole ratio of 1.45:1 maximizes the total amount of plant food in a given amount of fluid fertilizer. Some producers sacrifice solubility slightly by ammoniating past the maximum solubility point to a mole ratio of 1.65:1 because the usual crystallizing phase at that mole ratio is diammonium phosphate. Diammonium phosphate crystals are less dense and better shaped for suspensions than monoammonium phosphate crystals. This also slightly decreases the cost of nitrogen in the fluid.

When the impurity content of nongranular monoammonium phosphate is kept low by using quality acid, the product is especially suited for fluids because the fine material will ammoniate more easily than granules, and less power is required to produce a suspension because granules do not have to be disintegrated. Because of the economics in its production, nongranular monoammonium phosphate should become an important fluid base.

Suspensions also can be produced by adding phosphoric acid to diammonium phosphate to reduce the NH_3:H_3PO_4 mole ratio from 2:1 to 1.45:1 (or 1.65:1); however, high-shear equipment and additional phosphoric acid alone are usually not sufficient to break down the diammonium phosphate pellets. A little extra acid and some ammonia must be added to provide enough heat and liquid phase to disintegrate the diammonium phosphate. This requires that both phosphoric acid and ammonia be stored.

Advantages in Transportation and Storage

Many of the advantages mentioned before are also advantages in storage and transportation. When P_2O_5 is required in a bulk blend or a granulation process, the high P_2O_5 content of monoammonium phosphate is an advantage over diammonium phosphate because 4 to 9 units more of P_2O_5 are shipped per ton of product. Monoammonium phosphate also has the same advantage over triple superphosphate because it not only contains 4 to 9 more units of P_2O_5, but 10 to 11 units of nitrogen are included.

The savings in shipping monoammonium phosphate over shipping a fluid base are even greater than the advantage over solid diammonium phosphate and triple superphosphate because the analyses of fluid bases are lower. Also, in the fluid plant a solid material which does not solidify, freeze, or salt-out, can be purchased during the discount period, and is available in quantity at the start of the fertilizer season is a definite advantage.

Monoammonium phosphate stores physically better than diammonium phosphate because it has a higher critical relative humidity (8). As shown in figure 4, monoammonium phosphate has a critical relative humidity of 91.6 while diammonium phosphate has a critical relative humidity of 82.5.

When nongranular monoammonium phosphate is used in granulation plants to replace phosphoric acid, it can be stored in bulk in ordinary bins. This eliminates the special fiberglass tanks, the type 316 stainless steel tanks, or the rubberlined tanks required for phosphoric acid. Also nongranular monoammonium phosphate can be shipped in ordinary steel barges, rail cars, and ships which can then backhaul other materials.

Advantages in Agronomics

Monoammonium phosphate is superior to diammonium phosphate for both surface and row application. Agronomic studies show that loss of nitrogen after surface application on calcareous soil is less with monoammonium phosphate than with diammonium phosphate (10). Also, numerous studies show that diammonium phosphate placed in the row as a starter fertilizer can cause seed germination damage, probably as a result of the release of free ammonia from the secondary ammonia radical. This effect can be exaggerated when the starter fertilizer is poorly placed, as is too often the case. In addition (as mentioned previously) the lower nitrogen content of monoammonium phosphate can be beneficial because often less nitrogen is required in starter fertilizers than in blends made from diammonium phosphate alone and more ammonia can be used for side dressing.

Conclusion

Many of the advantages of monoammonium phosphate are significant enough to cause one to wonder why monoammonium phosphate has not been a more popular fertilizer material. Among these advantages are ease and simplicity of production; superiority as an ingredient in starter fertilizer; usefulness as a base in fluid fertilizer; high critical relative humidity; high P_2O_5 analysis; high total plant food content; superior storability of fertilizers made from monoammonium phosphate and other fertilizer ingredients; and its availability in two forms, granular and nongranular. Presently, the tonnage of monoammonium phosphate used in manufacturing processes cannot be separated from those reported for diammonium phosphate; however, it is thought that significant tonnage of monoammonium phosphate is being used. An indication might be the increase in the amount of monoammonium phosphate used for direct application. It has been reported that the amount of direct application material which was primarily monoammonium phosphate increased from 86,000 tons in 1975 to almost 264,000 tons in 1979 (11). Presumably, a similar increase has occurred in the amount of monoammonium phosphate used in granulation, blends, and fluids and the amount used will continue to increase as the advantages of using monoammonium phosphate become better known throughout the fertilizer industry.

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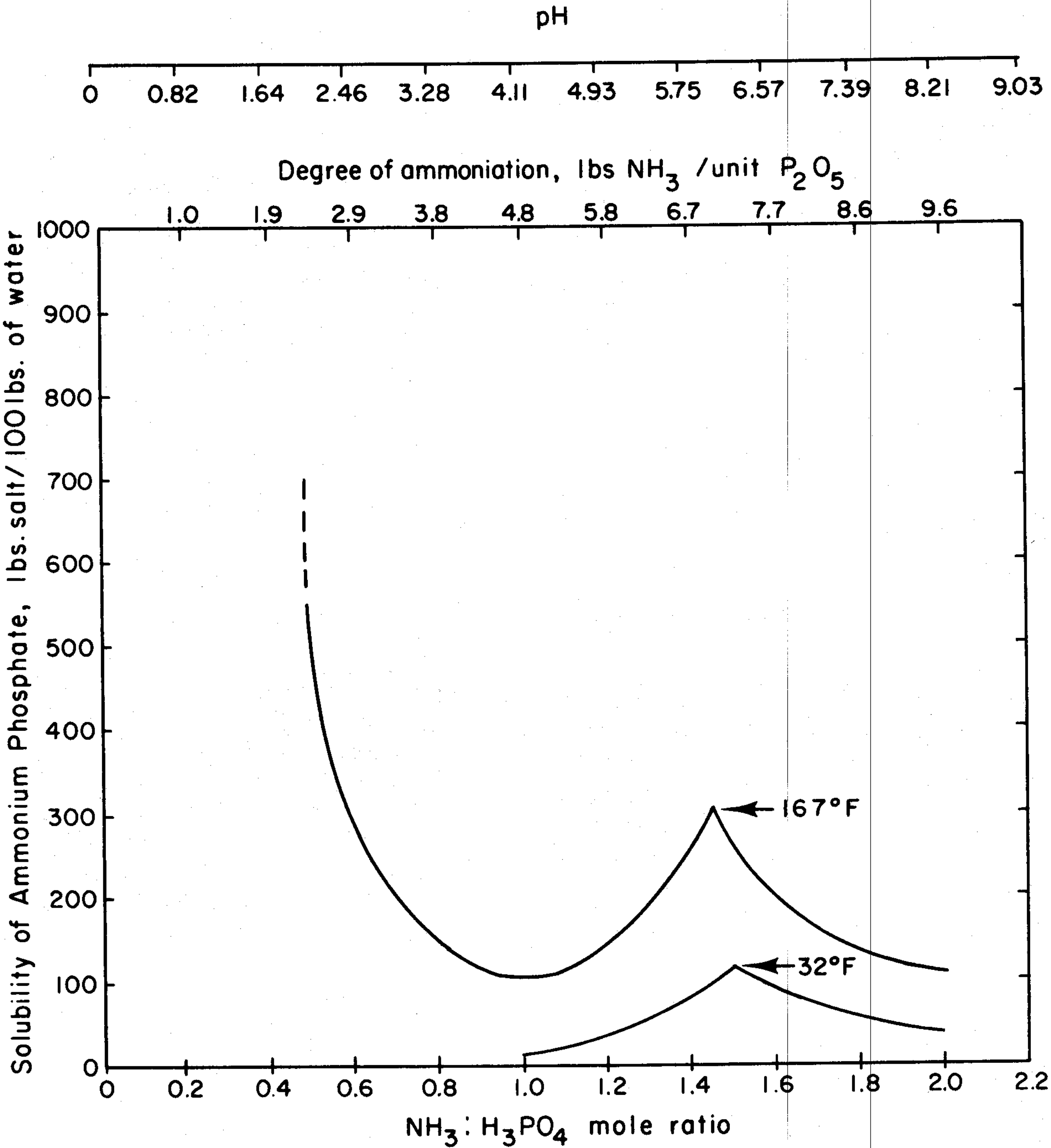


Effect of $NH_3 : H_3PO_4$ Mole Ratio on Solubility of Ammonium Phosphate

Fig. 1

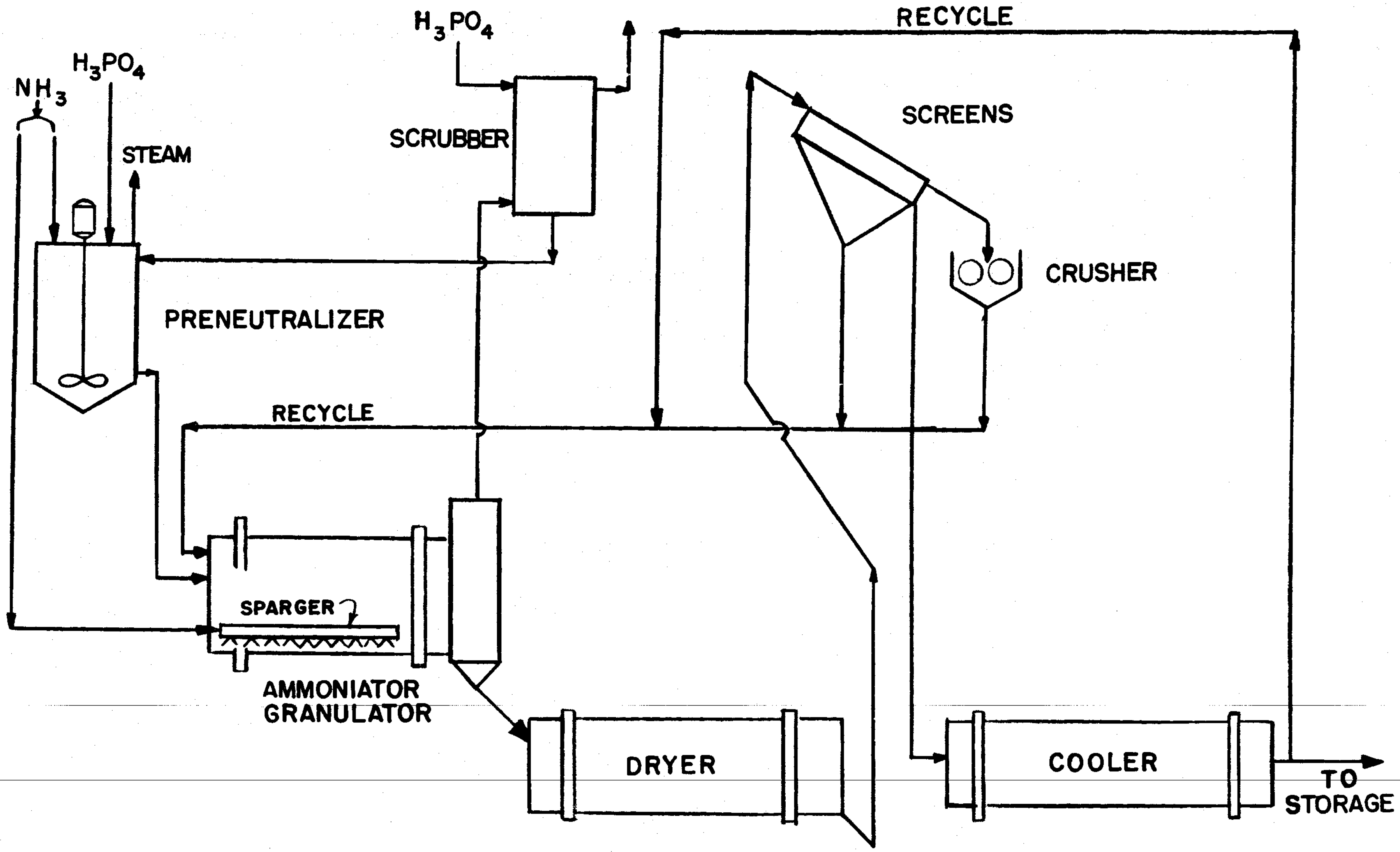
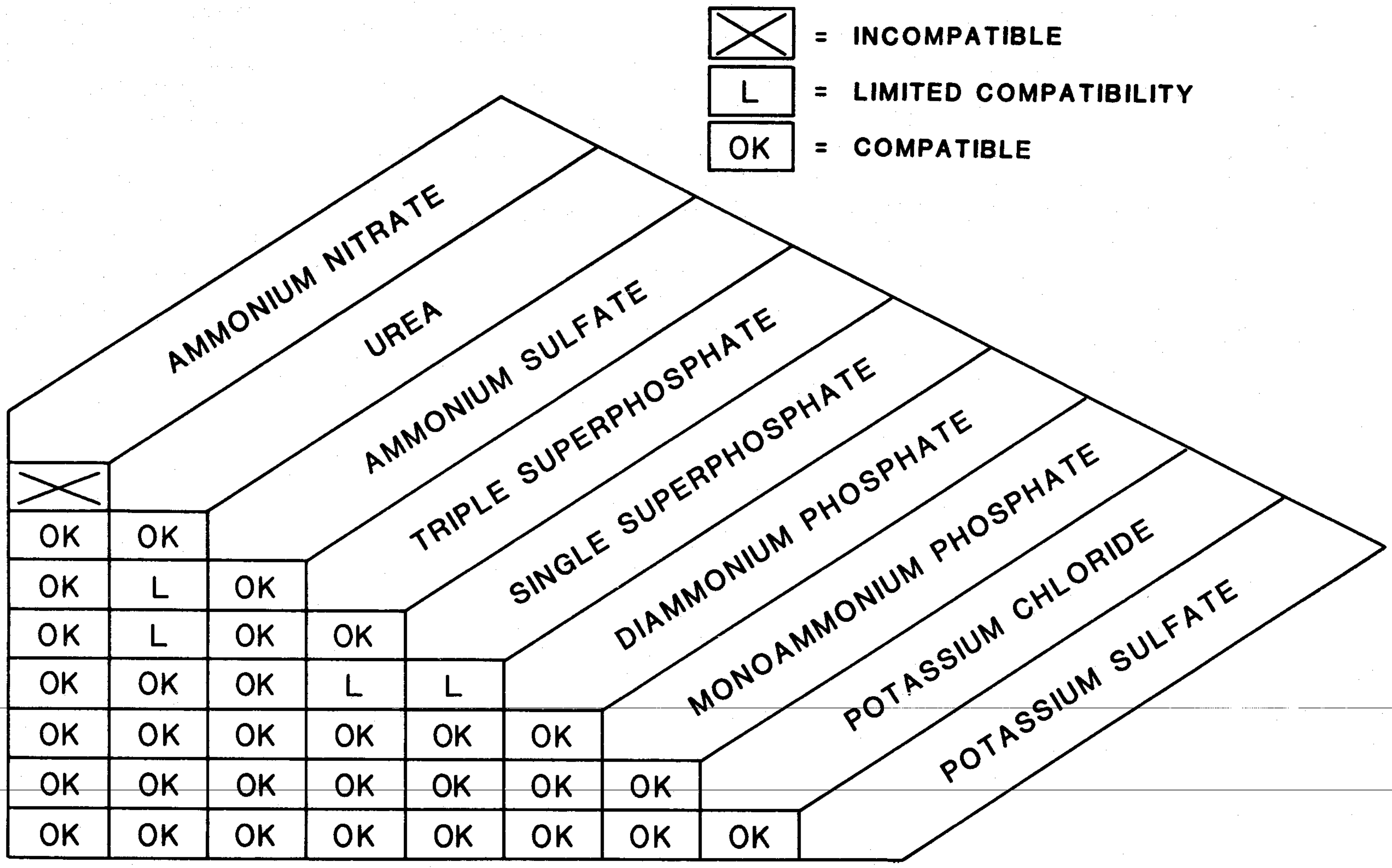


FIGURE 2

PROCESS FOR PRODUCTION OF GRANULAR DIAMMONIUM OR MONOAMMONIUM PHOSPHATE



☒ = INCOMPATIBLE
L = LIMITED COMPATIBILITY
OK = COMPATIBLE

	AMMONIUM NITRATE	UREA	AMMONIUM SULFATE	TRIPLE SUPERPHOSPHATE	SINGLE SUPERPHOSPHATE	DIAMMONIUM PHOSPHATE	MONOAMMONIUM PHOSPHATE	POTASSIUM CHLORIDE
UREA	☒							
AMMONIUM SULFATE	OK	OK						
TRIPLE SUPERPHOSPHATE	OK	L	OK					
SINGLE SUPERPHOSPHATE	OK	L	OK	OK				
DIAMMONIUM PHOSPHATE	OK	OK	OK	L	L			
MONOAMMONIUM PHOSPHATE	OK	OK	OK	OK	OK	OK		
POTASSIUM CHLORIDE	OK	OK	OK	OK	OK	OK	OK	
POTASSIUM SULFATE	OK	OK	OK	OK	OK	OK	OK	OK

Figure 3. Chemical compatibility of blend materials.