

Development of a Granular Ammonium Sulfate Process

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TVA has developed on a pilot scale a process for producing high-quality, granular ammonium sulfate in conventional equipment. The process steps are similar to those of the TVA process for granular diammonium phosphate. Sulfuric acid reacts with ammonia in a preneutralizer to an $\text{NH}_3:\text{H}_2\text{SO}_4$ mole ratio of 1.1. A brick-lined preneutralizer and suitably resistant piping are required for withstanding the corrosiveness of the solution. The highly fluid solution from the preneutralizer, containing less than 10% water, is fully ammoniated and granulated in a TVA-type drum granulator. Granulation occurs at a low pH and a recycle ratio of about 1 pound per pound

of product. Final ammoniation of the granules is enhanced by addition of water and an excess of ammonia, which is recovered in scrubbing liquid that is recycled to the preneutralizer. Chemical heat provides sufficient evaporation of water during granulation to make a drying step unnecessary. The granular product is of low free-acid content, has good physical properties, and stores well without conditioner. This process can be adapted to the use of by-product sulfuric acid and ammonium sulfate solutions. It permits easier manufacture of the larger granules desired in bulk-blending operations than the conventional crystallizer process.

For a number of years the fertilizer industry has sought to develop a feasible process for the production of granular ammonium sulfate. Demand for this material has increased rapidly as the trend toward granular fertilizers has swept the industry. The advent of bulk blending with its need for compatible, uniformly sized, and uniformly shaped materials has further increased this demand. For this use, the industry has been pressed to supply sufficiently large-sized ammonium sulfate by use of the current processes such as the crystallizer and the saturator processes that long have been standards of the industry (Holt and Farley, 1968; Laurich, 1963). Efforts to granulate or compact fine crystalline or powdered ammonium sulfate have generally had only limited success. Most of these products have somewhat poor physical strength and break up rather easily. More recently, the uncertainty of the sulfur supply has stirred interest in ammonium sulfate processes for utilization of by-product sulfuric acid and solutions of ammonium sulfate or bisulfate that are by-products in the production of steel and caprolactam.

Pilot-plant studies conducted by the Tennessee Valley Authority now indicate that granular ammonium sulfate having good physical properties and low free-acid content can be produced in the continuous ammoniator-granulator by a process very similar to that used for production of granular diammonium phosphate (Young *et al.*, 1962). ["Free acid," determined by titration to the methyl red end point (pH 5), is a measure of the proportion of ammonium bisulfate present and does not indicate actual presence of unreacted H_2SO_4 .] The corrosiveness of the hot, partially neutralized solution of ammonium sulfate does require, however, special materials of construction for the preneutralizer and the solution-handling system. The process is adaptable to the use of concentrated sulfuric acid, by-product sulfuric acids, and solutions of ammonium sulfate or bi-

sulfate if ammonia and sulfuric acid are added. Granulation of ammonium sulfate crystals should also be possible by the use of supplemental sulfuric acid and ammonia.

PROCESS

TVA's early developmental work on a process for the production of granular ammonium sulfate was first shown to the fertilizer industry in 1966 during TVA's Sixth Demonstration (Tennessee Valley Authority, 1966). A flowsheet of the process is shown in Figure 1. Sulfuric acid and about half of the total ammonia requirement are fed to the preneutralizer, where reaction occurs at a temperature which is controlled within the range of 300° to 310° F. by addition of water. The resulting fluid solution of low water content is fed to the ammoniator-granulator, where the remaining ammonia requirement, with some excess, is introduced. Small amounts of water and/or steam are fed with the ammonia to maintain a constant granulation temperature and ensure essentially complete ammoniation of the ammonium sulfate solution. The heat of reaction in the ammoniator-granulator evaporates nearly all of the moisture; therefore, no drying step is necessary following granulation. After being cooled, the granular product is screened to remove the product-size material. The

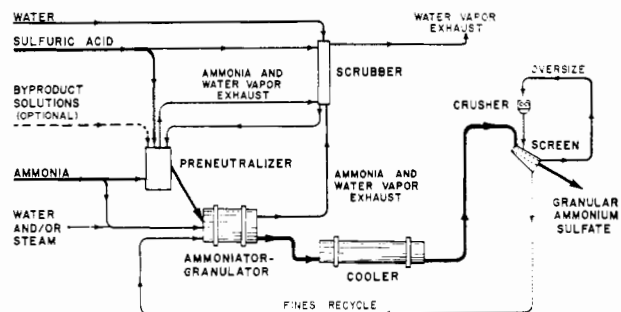


Figure 1. TVA process for production of granular ammonium sulfate

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oversize is crushed and recycled to the rotary drum together with the fines for control of granulation. Exhaust gases from the preneutralizer and the ammoniator-granulator are passed through a water scrubber, where the excess ammonia is recovered. A small amount of sulfuric acid is fed to the scrubber to maintain the pH of the scrubbing liquor between 2 and 4. This dilute scrubbing liquor is recycled to the preneutralizer, where it is used to control the temperature of the partially neutralized solution by direct evaporative cooling.

PILOT PLANT

The pilot-plant studies of this process were conducted in the equipment used for development of the TVA process for production of granular diammonium phosphate (Young *et al.*, 1962). In these current studies, however, the dryer was not operated and served only to convey the granular product from the ammoniator-granulator to the rotary cooler. Crystallization occurred rapidly and was essentially complete in the granulator; therefore, the additional time of retention in the dryer probably had no effect on the physical properties of the product.

The preneutralizer is an open-top tank, 20 inches in diameter and 5 feet high. During normal operation in this process, a 3-foot liquid level is maintained in the preneutralizer. Sulfuric acid is fed through an open-end pipe that discharges under the solution level. Ammonia and cooling water are introduced together near the bottom through two drilled pipe spargers. Although the preneutralizer is equipped with an agitator, it is not used in this process. The vigorous boiling resulting from the chemical reaction generates sufficient mixing. The solution is fed from the preneutralizer to the ammoniator-granulator by gravity flow through a steam-jacketed pipe.

The ammoniator-granulator drum is 3 feet in diameter by 6 feet long with a 9-inch retaining ring mounted 4 feet from the feed end. It is equipped with a variable-speed drive. The hot ammonium sulfate solution is sprayed onto the rolling bed of solids near the feed end of the drum through two spray nozzles, producing a hollow cone pattern. Anhydrous liquid ammonia is fed under the bed together with the water and/or steam through a drilled pipe sparger extending from the feed end of the drum to a point located about half the length of the ammoniator-granulator. A reciprocating, tooth-type scraper keeps the walls of the drum free of buildup.

The water scrubber is 2 feet in diameter by 10 feet high, and contains about 8 feet of ceramic packing. Scrubbing liquor is recirculated to the top of the tower through a distributing cone. Make-up water and sulfuric acid are added to the seal tank at the base of the tower.

To facilitate and simplify the pilot-plant work during these tests, the preneutralizer exhaust gases were not scrubbed; nor was the scrubbing liquor from the tower returned to the preneutralizer as cooling water. Instead, fresh water was fed to both the preneutralizer and the scrubbing tower at about the same rates to simulate a balanced system.

Hot granular material from the ammoniator-granu-

Table I. Pilot-Plant Production of Granular Ammonium Sulfate

Typical data from operation of preneutralizer	
Feed rate, lb./ton product	
Ammonia (gas)	287
Sulfuric acid (93%)	1514
Water	726
Preneutralized solution	
Temperature, °F.	306
pH of 10% solution in water	0.60
Equivalent acid concentration, % H ₂ SO ₄	63
Chemical composition ^a	
Ammonia	14.8
Sulfuric acid	77.1
Water	8.1
NH ₃ :H ₂ SO ₄ mole ratio	1.10
Viscosity, centipoises	60
Evaporation	
Lb./ton	682
Lb./(hr.)(sq. ft.)	95
Lb./lb. ammonia fed	2.4

^a Calculated from NH₃-N and free acid equivalent determined by laboratory titration.

lator is cooled in a rotary cooler 21 feet long and 2.5 feet in diameter equipped with lifting flights. Air is pulled through the cooler countercurrently to the flow of solids. After cooling, the granular product is screened on double-deck vibrating screens to remove product-size material. Oversize is crushed in a chain mill, combined with the undersize, and recycled to the ammoniator-granulator for control of granulation.

PILOT-PLANT TESTS

Preneutralization. Pilot-plant tests of the direct production of granular ammonium sulfate from concentrated sulfuric acid and ammonia were conducted at the rate of 0.3 ton per hour of granular product. Typical data from operation of the preneutralizer are presented in Table I. Sulfuric acid containing 93% H₂SO₄ and anhydrous gaseous ammonia were metered to the preneutralizer to maintain the NH₃:H₂SO₄ mole ratio at 1.10. Water was fed with the ammonia at a rate of about 730 pounds per ton of granular product to maintain the temperature of the solution near 310° F. by evaporation of the water. About 680 pounds of water was evaporated from the preneutralizer per ton of granular product. This corresponded to an evaporation rate of 95 pounds of water per hour per square foot of surface area, or about 2.4 pounds of water per pound of ammonia fed to the preneutralizer. Under these conditions, the hot, fluid, acidic preneutralizer solution contained about 8% water and had a viscosity of about 60 cp. When diluted with about 10 parts of water, its pH was about 0.6.

The relationship between the boiling temperature and the moisture content of the partially neutralized ammonium sulfate solution is shown in Table II for a solution with an NH₃:H₂SO₄ mole ratio within the range of 1.00 to 1.10. An increase in the amount of water fed to the preneutralizer from 715 to 760 pounds

Table II. Pilot-Plant Production of Granular Ammonium Sulfate

Effect of water feed rate on evaporation rate, boiling temperature, and moisture content of preneutralizer solution

Water Added to Preneutralizer, Lb./Ton of Granular Product	Preneutralizer Solution		Water Evaporation Rate from Preneutralizer	
	Temp., °F.	Moisture content, % H ₂ O	Lb./ton of granular product	Lb./(hr.)(sq. ft.) of surface area
715	300	9	660	90
719	290	10	630	86
760	285	14	600	81

per ton of granular product decreased the solution temperature from 300° to 285° F. and increased the moisture content from 9 to 14% with a corresponding decrease in the evaporation rate from 660 to 600 pounds per ton of granular product. Even at the high water evaporation rate there were no foaming and no boilovers from the preneutralizer.

Measurements indicate that the ammonia loss from the preneutralizer was only 0.1 to 0.3% of the total ammonia fed to the process. Under most conditions, this loss would be considered negligible and may not warrant recovery in a scrubbing system.

The NH₃:H₂SO₄ mole ratio of 1.10 was chosen for operation of the preneutralizer to take advantage of a high point in solubility for the system NH₃-H₂SO₄-H₂O. A typical curve for this system is shown in Figure 2. Control of the mole ratio in the preneutralizer is most important because a slight increase in ammonia flow can result in formation of an ammonium sulfate slurry too viscous to flow. The change in pH of the solution resulting from changes in the mole ratio is too small to use pH for control measurement of the mole ratio. Field titration of the free acid in samples of the preneutralizer solution is a very reliable control procedure.

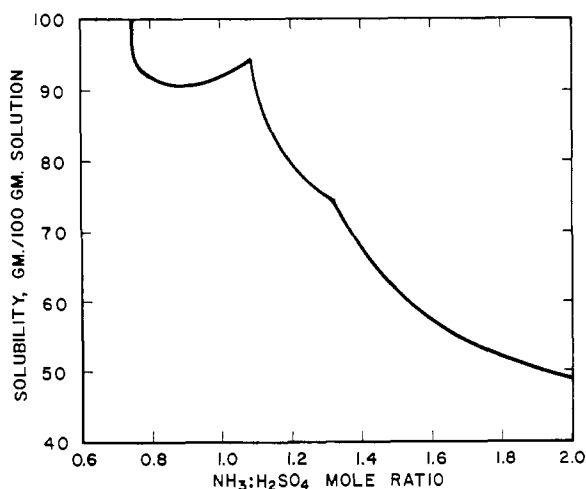


Figure 2. Effect of mole ratio on solubility at 209° F.

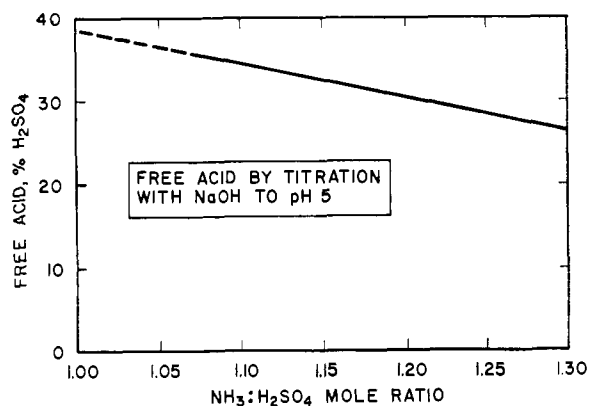


Figure 3. Mole ratio by free acid measurement

The NH₃:H₂SO₄ mole ratio may be closely maintained by comparing the calculated percentage free acid (% H₂SO₄) determined in the field with prepared plots of free acid vs. the mole ratio as determined by chemical analysis. A curve depicting this relationship for the operating temperature range of 300° to 310° F. is shown in Figure 3. The relationship changes considerably with changes in temperature of the preneutralizer solution because of concentration changes; however, the exact relationship can be determined rather easily during operation. The success of this method for determining the mole ratio depends primarily on the accuracy in weighing the sample that is titrated. A good platform beam balance capable of weighing to the nearest 0.01 gram is recommended for the field titrations.

The preneutralizer operation was studied on a bench scale using ammonium bisulfate solution containing about 65% ammonium bisulfate, 30% water, and 5% free sulfuric acid. This solution is similar to by-product solutions now available. When about 53% of the total sulfuric acid requirement was supplied by this solution, operation of the preneutralizer was good at the NH₃:H₂SO₄ mole ratio of 1.10. No addition of fresh water was required to maintain the solution temperature at 305° F.; sufficient water for cooling was present in the ammonium bisulfate solution that was added. The moisture content of the preneutralizer solution averaged 9.3% and its physical properties were identical to those of solution made with only concentrated sulfuric acid and ammonia.

Granulation. In pilot-plant operation, the hot, fluid preneutralizer solution was fed by gravity through the steam-jacketed pipe to the ammoniator-granulator where ammoniation was completed with simultaneous granulation. Although this method was satisfactory in the pilot plant, it may be preferable in a different plant to locate the preneutralizer at ground level, which necessitates pumping this solution to the preneutralizer. It was necessary to control the heat applied to the steam-jacketed pipe closely to keep the temperature in the jacket equal to or a few degrees lower than that of the solution. When excess heat was applied, evaporation occurred in the line and caused steam pockets and dehydration of the

solution. Back pressure from the steam pockets stopped the gravity flow of solution and the dehydration caused deposits that plugged the pipe. Close control was easily obtained by regulation of the steam pressure in the jackets around the piping.

During early pilot-plant studies, no water was added to the ammoniator-granulator. Although granulation was good, the $\text{NH}_3:\text{H}_2\text{SO}_4$ mole ratio of the product was only 1.7 to 1.9. The products contained only about 19% nitrogen and their physical and storage properties were poor. The addition of water together with the liquid ammonia improved reaction between the pre-neutralizer solution and the ammonia. To obtain the maximum benefit of the water addition, the temperature of the bed should be about 200° F. During pilot-plant operation it was necessary at times to add a small unmetereed amount of steam with the water and ammonia to maintain this bed temperature. Because of the low production rate in the pilot plant, the temperature of the recycle was only about 80° F., compared with about 120° F. in plant-scale operation of granulation processes; consequently, steam addition probably will not be needed in a production-scale plant.

Changes in the amount of water fed to the drum apparently do not affect granulation as significantly in this process as in most conventional fertilizer processes based on the more soluble salts. An almost threefold increase in the amount of water added produced no significant change in the size distribution of the granular product. Because of the rapid evaporation of water from the drum, it appears that the liquid phase does not persist.

In this process the rotational speed of the drum granulator is normally 10 to 15 r.p.m. for best granulation. This speed range is 39 to 59% of the critical speed.

The relationship of variables that affect ammonia retention and granulation is shown in Table III. When the proportion of water fed to the drum was increased from 0.26 to 0.75 pound per pound of ammonia, the evolution of ammonia from the ammoniator-granulator was decreased from 11 to 6% of the total ammonia fed. Correspondingly, the free-acid content of the granular product was decreased from 4 to 0.6%. With the highest rate of water addition, an increase in the ammonia rate above 290 pounds per ton of product

Table III. Pilot-Plant Production of Granular Ammonium Sulfate

Variables affecting ammonia retention and granulation					
Feed Rates to Ammoniator-Granulator			Granulator Product		
Lb. $\text{H}_2\text{O}/$ lb. NH_3	NH_3 , lb./ton product	Recycle, lb./lb. product	Temp., °F.	Free acid equivalent, %	Loss of NH_3 , %
0.26	290	1.3	225	2.7-4.0	11
0.52	290	1.3	218	2.2-2.4	9
0.75	289	1.7	205	0.6-1.1	6
0.70	306	1.6	200	0.5-0.6	7
0.66	323	2.9	196	0.3	10

Table IV. Pilot-Plant Production of Granular Ammonium Sulfate

Typical data from granulation system

Granulation conditions	
Feed rate, lb./ton	
Ammonia	306
Water	214 ^a
Solution	1851
Recycle	3128
Ammonia loss, % of total feed	7.2
Evaporation, lb./ton product	369
Ammoniator-granulator product	
Temperature, °F.	201 ^a
Chemical composition, %	
$\text{NH}_3\text{-N}$	20.9
SO_3	59.3
H_2O	0.1
Free acid equivalent as H_2SO_4	0.8
$\text{NH}_3:\text{H}_2\text{SO}_4$ mole ratio	1.98
Screen analysis (Tyler mesh), %	
+6	5.0
-6 +10	22.6
-10 +16	59.7
-16	12.7
Recycle	
Ratio, lb./lb. product	1.6
Temperature as fed, °F.	79
Onsize product	
Chemical composition, %	
$\text{NH}_3\text{-N}$	20.9
SO_3	59.4
H_2O	Nil
Free acid equivalent	0.8
$\text{NH}_3:\text{H}_2\text{SO}_4$ mole ratio	1.98
pH of 10% solution	2.9

^a A small unmetereed amount of steam added to maintain bed temperature.

resulted in slightly lower free acid but higher evolution of ammonia. When 10% excess ammonia was fed, free acid was 0.3% compared with 0.5% for 7% excess. Even with the highest water rate, the moisture content of the granulator product did not exceed 0.1%. Good granulation was obtained with a recycle ratio of only 1.0 to 1.5 pounds per pound of product when the temperature in the ammoniator-granulator was maintained at 200° F. Higher recycle ratios resulted in smaller product and excessive undersize particles. In this process, granulation is of the slurry type in which granule growth occurs by deposition and solidification of successive layers of slurry onto the surface of the recycled particles.

Granulation data from a typical pilot-plant test using the recommended operating conditions are shown in Table IV. In this test the water evaporation rate from the granulator was about 370 pounds per ton of product. More than 82% of the material was contained in the minus 6- plus 16-mesh screen fraction. The granular product leaving the drum contained only 5% oversize. The screened product contained 20.9% nitrogen and 0.8% free acid; the $\text{NH}_3:\text{H}_2\text{SO}_4$ mole ratio was 1.98. A 10% aqueous solution of the product had a pH of 2.9.

AMMONIA RECOVERY

During pilot-plant tests, the exhaust gases from the ammoniator-granulator were scrubbed in the packed tower with 580 to 670 pounds of water per ton of product to recover the ammonia evolved. When sufficient sulfuric acid was added to the scrubbing liquor to maintain the pH between 2 and 4, ammonia recovery was 92 to 94% of that entering the scrubber. With a typical evolution in the ammoniator-granulator of 7% of the ammonia fed, the loss from the scrubber would be 0.5%. At the lower water rate there was no condensation in the system, but at the higher rate there was considerable condensation of water.

PHYSICAL AND STORAGE PROPERTIES OF PRODUCTS

Ammonium sulfate products made in the pilot plant consist of hard, well-shaped granules normally containing 0.5 to 1.0% free acid and about 0.1% moisture. The bulk density of the sized product (-6 +10 mesh) averages about 50 pounds per cubic foot. Granules containing up to 1.2% free acid retain their shape and are fairly firm under finger pressure after being exposed to 80% relative humidity at 86° F. for 96 hours. Under these conditions moisture penetrates the exposed surface of the material to a depth of about 4.0 cm. This penetration is only one fourth that usually encountered with ammonium nitrate, but slightly greater than that for diammonium phosphate (18-46-0). The critical relative humidity of the same granular ammonium sulfate product containing 1.2% free acid is 65 to 70% at 86° F. This means that at 86° F. the ammonium sulfate granules will absorb moisture from the surrounding atmosphere if the relative humidity is above 65 to 70%; conversely, if the relative humidity is below that point, the granular ammonium sulfate will lose water or crystallize. In comparison, the critical relative humidity of ammonium nitrate is 59.4%; urea, 75.2%; and diammonium phosphate, 82.5% (Silverberg, 1966).

The bag-storage properties of granular ammonium sulfate produced in the pilot plant were determined by tests conducted in both 3- and 50-pound bags having moisture barriers. Test bags were stored under weight equivalent to 20 bags of fertilizer. After 1, 3, 6, and 9 months of storage, the bags were inspected to determine the degree of bag set and caking. These data indicated that the unconditioned granular ammonium sulfate stores well in bags having a moisture barrier for 9 months or more. Only a very light bag set occurred and there were no lumps after one drop of the bags from a height of 3 feet. Unconditioned products having free-acid contents as high as 3.6% have been stored without caking or breakdown of the granules or deterioration of the bags.

Petrographic examination indicates that the unconditioned granular ammonium sulfate products consist of a bulk phase of ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ and a minor phase of triammonium bisulfate $[(\text{NH}_4)_3\text{H}(\text{SO}_4)_2]$ that is produced by incomplete ammoniation. The amount of the triammonium salt is generally proportional to the equivalent free acid content.

During early pilot-plant tests, several granular ammonium sulfate products containing 3 to 6% free acid, for some unknown reason, contained large crystals (up to 1000-micron length) of ammonium sulfate. These products caked severely in storage because of intergrowth of triammonium bisulfate crystals which were concentrated in the interstices and on the surface of the large crystals of the ammonium sulfate. In products made later, the ammonium sulfate crystals were relatively small (about 40 microns) and the triammonium bisulfate crystals were intimately mixed throughout the granule. This dispersion evidently prevented development of strong caking bonds as shown by the good storage properties of these products.

MATERIALS OF CONSTRUCTION

Although an existing preneutralizer and steam-jacketed solution line used in these pilot-plant studies were constructed of Type 316 stainless steel, this metal is not a satisfactory material of construction for equipment that comes in contact with the hot, acidic ammonium bisulfate-ammonium sulfate solution (pH 0.6). Throughout the pilot-plant work, corrosion specimens were exposed in the preneutralizer to evaluate various materials of construction. Exposure time of the specimens was limited to 3 to 22 hours per test because of the short duration of the pilot-plant tests. Thus, long-term corrosion rates extrapolated from these data are not absolute but provide a good indication of the resistance of the materials tested.

Typical corrosion data are summarized in Table V. Of the metals tested, only Duriron and tantalum satisfactorily withstood the corrosive attack. The corrosion rate for Duriron ranged from 1 to 29 mils per year, while that for tantalum was only 1 mil per year. For Type 316 stainless steel welded with Type 316 electrode, the corrosion rate ranged from 755 to 2765 mils per

Table V. Pilot-Plant Production of Granular Ammonium Sulfate

Corrosion of metal specimens in preneutralizer^a

Metals Tested	Corrosion Rate, Mils/Yr.
A.I.S.I. stainless steel	
Type 304 welded with Type 316 electrode	260-1262
Type 316 welded with Type 316 electrode	755-2765
Carpenter 20 Cb-3	178-749
Chemical lead	240-444
Durimet 20	125-207
Duriron	< 1-29
Hastelloy D	45-108
Incoloy	1395-2338
Incoloy 825 welded with Incoloy 825 rod	109-417
Monel 400	79-1126
Monel 400 welded with 140 Monel rod	105-788
Tantalum	1
Titanium	81
Worthite	187-945

^a Data based on pilot-plant tests of short duration—3 to 22 hours' total exposure time of specimens.

year and averaged about 1700. Several nonmetallic materials were also exposed in the preneutralizer. Two graphite-based materials, Polybloc and Karbate No. 2, withstood the corrosive solution without apparent attack. Viton also appears promising as a tank and pipe lining material.

Duriron or similar high-silicon alloys appear to be suitable for construction of the preneutralizer, solution pump, and pipelines. Although tantalum is a high-cost metal, it may be economical to construct a preneutralizer of tantalum-clad mild steel. It seems, however, that the best construction for the preneutralizer is a mild steel vessel coated with rubber and lined with acidproof or carbon brick.

CONCLUSIONS

This process for the production of granular ammonium sulfate is of special interest to the fertilizer industry because of its relative simplicity and its adaptability to

existing granular fertilizer plants. Although the corrosiveness of the preneutralizer solution presents special construction problems, the advantages of producing the granular product would seem to outweigh this disadvantage.

LITERATURE CITED

- Holt, J. F., Farley, P. J., *Chem. Eng. Progr.* **64** (5), 54-8 (1968).
Laurich, S. A., *Agr. Chem.* **18** (9), 54-5, 175, 177 (1963).
Silverberg, J., "Storage Properties and Conditioning Requirements of Various Fertilizers," 16th Annual Meeting, Fertilizer Industry Round Table, Washington, D. C., 1966, pp. 3-5.
Tennessee Valley Authority, Muscle Shoals, Ala., "New Developments in Fertilizer Technology. 6th Demonstration," Oct. 4-5, 1966, pp. 36-8.
Young, R. D., Hicks, G. C., Davis, C. H., *J. AGR. FOOD CHEM.* **10**, 442-7 (1962).

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