CONF-930802--17

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WASTES AND BY-PRODUCTS -- ALTERNATIVES FOR AGRICULTURAL USE

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Talk presented at the 206th National
Meeting of the American Chemical Society
in Chicago, Illinois, August 22-27, 1993

DISCLAIMER

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Abstract

To address a growing national problem with generation of wastes and by-products, TVA has been involved for several years with developing and commercializing environmentally responsible practices for eliminating, minimizing, or utilizing various wastes/by-products. In many cases, reducing waste generation is impractical, but the wastes/by-products can be converted into other environmentally sound products. In some instances, conversion to safe, value-added agricultural products is the best or only practical alternative. TVA is currently involved with a diversity of projects converting wastes/by-products into safe, economical, and agriculturally beneficial products. Environmental improvement projects have involved poultry litter, cellulosic wastes, used battery acid, ammonium sulfate fines, lead smelting effluents, deep-welled sulfuric acid/ammonium bisulfate solutions, wood ash, waste magnesium ammonium sulfate slurry from recording tape production, and ammunition plant waste sodium nitrate/ammonium nitrate streams.

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Introduction

To address a growing national problem with generation and discharge of wastes and by-products, TVA's National Fertilizer and Environmental Research Center (NFERC) has for several years been involved with developing and commercializing environmentally responsible practices for eliminating, minimizing, or utilizing various wastes/by-products. Although avoidance of waste generation might be ideal, this often is impractical or impossible. In such cases, the practical solution may be to convert the wastes/by-products to other environmentally sound, useful products or to environmentally sound forms for disposal. In some instances, conversion to safe, value-added agricultural products is the most cost effective or the only practical alternative. NFERC is involved in several projects for converting wastes/by-products into safe, economical, and agriculturally beneficial products. Although NFERC's motivation is to resolve Tennessee Valley problems, much of the developed technology has national applications.

NFERC conducts chemical and engineering laboratory studies to evaluate initial process concepts, and designs and operates bench- and pilot-scale equipment to further refine and develop processes and to obtain data for scale-up to the commercial level. Demonstrations or introduction activities at customer sites are a vital part of NFERC's technology development program. Efforts are made to involve potential customers in every step of the development cycle to ensure a clear focus on technical and economic feasibility issues and to help guide development efforts toward technology that is needed and will actually be implemented.

Waste/by-product projects are not new at NFERC. Over the years, NFERC has been involved in a number of waste/by-product utilization projects. However, in the past, the dominant motivation behind such projects was often to develop methods for utilizing low-cost wastes/by-products as substitutes for higher-priced pure raw materials in fertilizer operations, thereby lowering raw material costs for the fertilizer producer or dealer in hopes of lowering the cost of growing food. In later years, the rationale had shifted to developing methods for utilizing wastes/by-products in fertilizer operations as an environmentally sound waste management practice compared with some of the environmentally unsound practices that were and are still being used. NFERC's environmental improvement projects have involved poultry litter, cellulosic wastes, waste battery acid, low-quality by-product ammonium sulfate fines, lead recycling smelter effluents, deep-welled sulfuric acid/ammonium bisulfate solutions, wood ash, waste magnesium ammonium sulfate slurry from recording tape production, and nitrate-laden ammunition plant waste streams.

Waste Nitrate Streams from Ammunition Production

For example, in the mid 1980's, under contract with the Holston Army Ammunition Plant (HSAAP), NFERC developed optimum chemical compositions and procedures for utilization of waste sodium nitrate/ammonium nitrate slurry in production of nitrogen solution and suspension fertilizers. At that time, the nitrate-laden waste streams were being stored in an open pond with potential for surface and ground water contamination; utilization of the waste in production of conventional nitrogen fluid fertilizers stored in properly contained storage tanks would greatly decrease the potential for water pollution. Schematic diagrams depicting the existing pond-storage and two of the several alternatives NFERC developed for environmentally sound management of the nitrate-laden waste are shown in Figures 1 and 2. These diagrams as well as the following discussion are only an overview of the actual comprehensive development program conducted on the nitrate waste at NFERC.

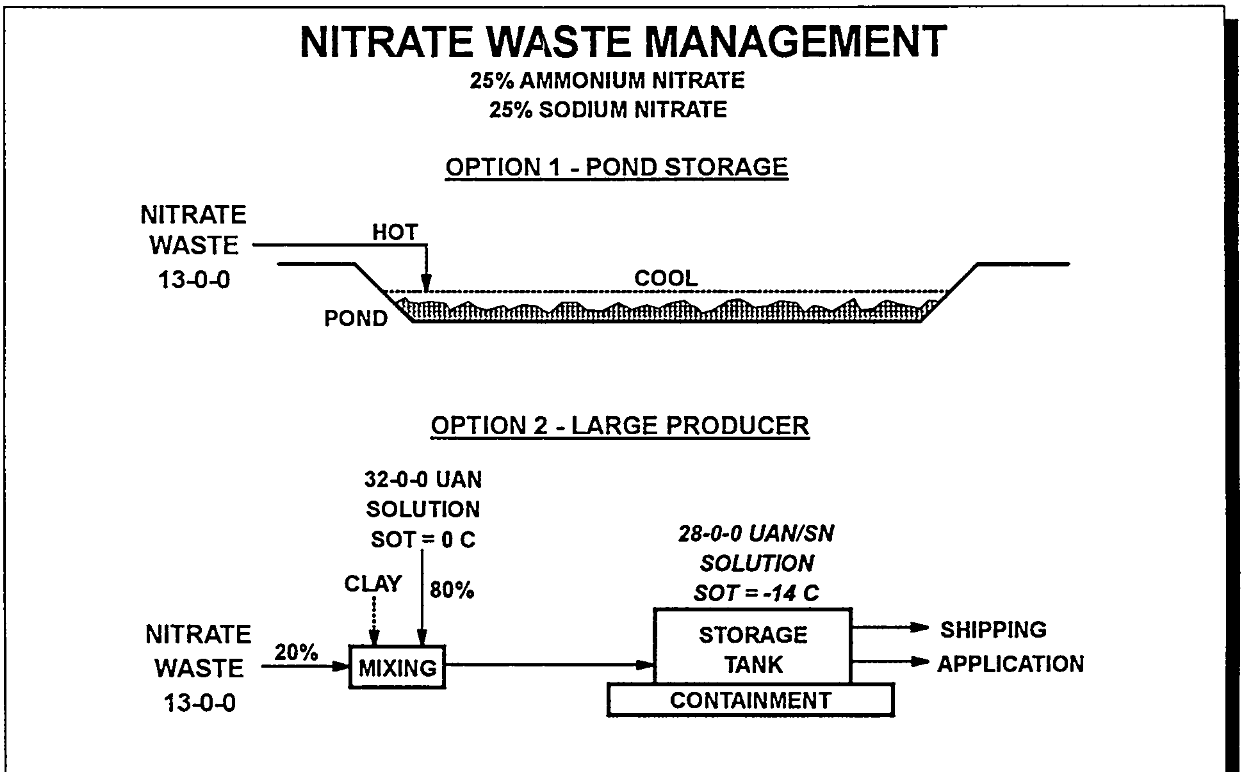

FIGURE 1

With pond storage, there is obviously the potential for contamination of surface and ground water. In option 1 (Figure 1), 1 part of nitrate waste is blended with 4 parts of common 32-0-0 urea-ammonium nitrate (UAN) solution to produce a 28-0-0 nitrogen solution which is pumped to storage tanks equipped with sound containment to prevent pollution in the event of tank/pump failure. This was one of several formulation/procedure options developed but was chosen as perhaps the most favorable option for the large producer because of the widespread availability and use of 32-0-0 and 28-0-0 UAN solutions, thereby expediting sale of the end product and thus use of larger tonnages of the waste nitrate stream. Also, the -14 °C salt-out temperature (SOT) of the 28-0-0 solution from sludge is not appreciably higher than the -18 °C (0 °F) SOT of normal 28-0-0 solution, so storage through winter would not be a problem except in the very coldest regions.

Other formulations/procedures were developed which utilize a higher proportion of the nitrate waste but which yield less than the conventional 28% nitrogen in the end product, as shown in Figure 2 and Table I. Such options might be more favorable for the small dealer, since shipping distances are much shorter and the low nitrogen content would not be as significant a factor; also, product volumes are much lower than the large producer, so the extra profit margin through use of a higher proportion of sludge would play a bigger role. Procedures and compositions were also developed for production of suspension products for cases in which the nitrate waste was too low in clarity or too high in insoluble solids to be marketed easily as a nitrogen solution; with these options, gelling clay is employed to keep the insoluble solids suspended. Examples of some of these options are shown in Table II. In later work with HSAAP, procedures and compositions were developed to produce similar products from a 50% sodium nitrate waste stream.

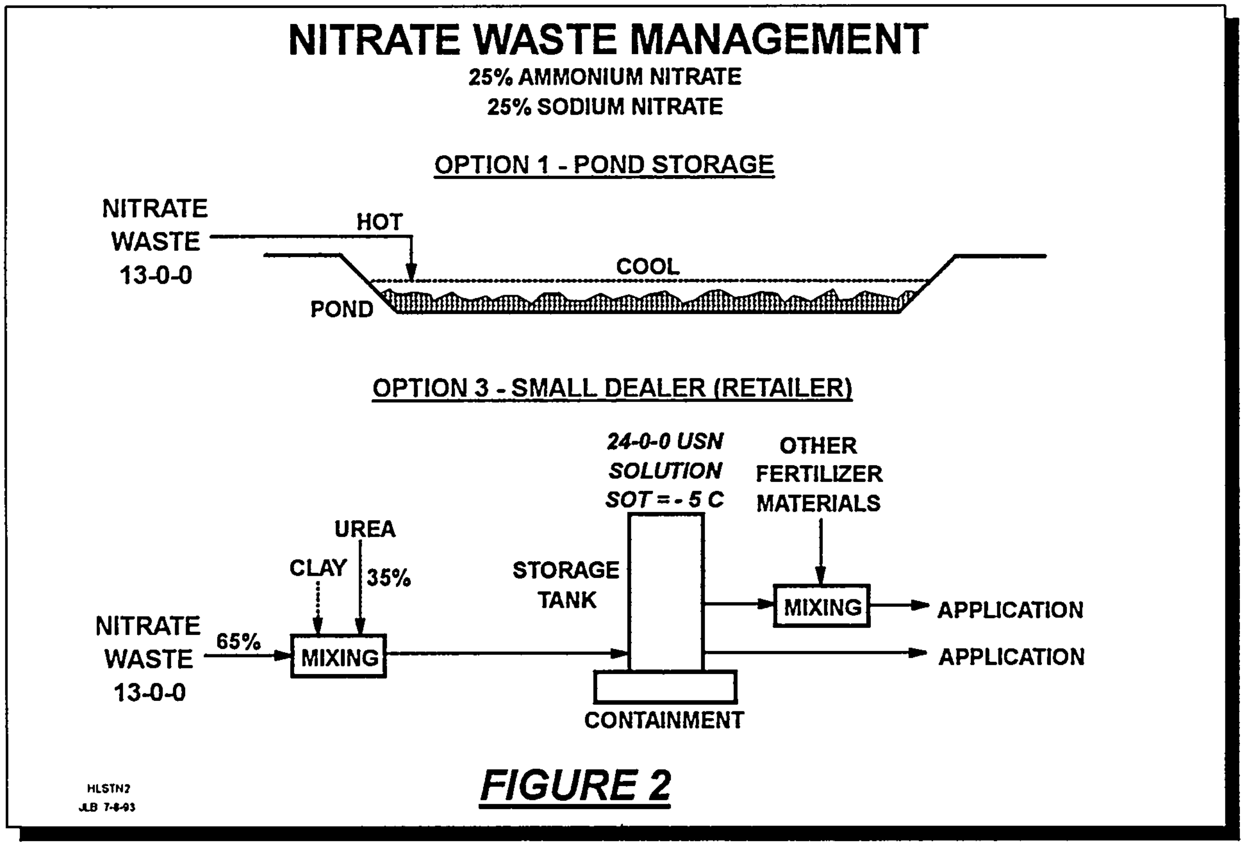

FIGURE 2

TABLE I

FAVORABLE PROCESS OPTIONS FOR UTILIZATION OF AMMUNITION NITRATE WASTE IN NITROGEN SOLUTIONS

OPTION NUMBER	PRODUCT NITROGEN, WEIGHT %	NITRATE WASTE, WEIGHT %	SALT-OUT TEMP, C
WASTE, UREA, AND AMMONIUM NITRATE (UREA:NITRATE = 1)			
1	32	20	-5
2	28	47	-5
3	28	37	-14
WASTE, 75% UREA SOLUTION, 75% AMMONIUM NITRATE SOLUTION (UREA:NITRATE = 1)			
4	28	12	-14
WASTE AND EUTECTIC 32-0-0 UAN SOLUTION (UREA:AMMONIUM NITRATE = 1)			
5	28	20	-14
WASTE AND UREA			
6	24	65	-5
7	19	80	<-18

HLSTN3
JLB 7-8-93

TABLE II

FAVORABLE PROCESS OPTIONS FOR UTILIZATION OF AMMUNITION NITRATE WASTE IN NITROGEN SUSPENSIONS

OPTION NUMBER	PRODUCT NITROGEN, WEIGHT %	NITRATE WASTE, WEIGHT %	SALT-OUT TEMP, C
WASTE, UREA, A/N, AND 16-0-0-30C FLUID CLAY (UREA:NITRATE = 1)			
1	31	10	-5
2	28	30	-14
3	22	60	-5
WASTE, UREA, AND 0-0-0-25C FLUID CLAY)			
4	23	57	-14

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Waste Magnesium Ammonium Sulfate from Recording Tape Production

In 1990, a project funded by a recording tape industry involved a waste magnesium ammonium sulfate/ammonium sulfate/iron oxide stream being generated by the process and stored in a leaky plastic-lined pond. NFERC developed optimum compositions, process operating conditions, and plant designs for conversion of this waste into a good quality suspension fertilizer capable of being stored in properly contained tanks and used in established fluid fertilizer operations, preventing possible surface and ground water contamination. Schematic diagrams depicting the existing pond storage as well as the more environmentally sound methods for managing this waste are shown in Figures 3 and 4. This waste stream contains appreciable magnesium ammonium sulfate (MAS) solids at ambient temperatures but was pumped into the pond hot, so, as the waste cooled, large mounds of MAS crystals formed on the bottom of the pond and grew toward the surface. Eventually, the solids had to be removed from the pond by payloader, and this resulted in tears in the plastic liner, thus increasing the likelihood of surface and ground water contamination.

Through laboratory, bench, and pilot tests, NFERC developed several environmentally sound alternatives for managing this waste. In the first and simplest option (Figure 3), the hot waste is pumped to an evaporative spray tower cooler to cool the material very quickly to near ambient temperature to bring about formation of many small MAS crystals which can be easily suspended. The warm slurry from the spray tower is then fed to a mixing vessel, and suspending clay is added to produce the finished suspension. The finished suspension is then pumped to a storage tank equipped with sound containment and shipped to fertilizer dealers. Other options, Figure 4,

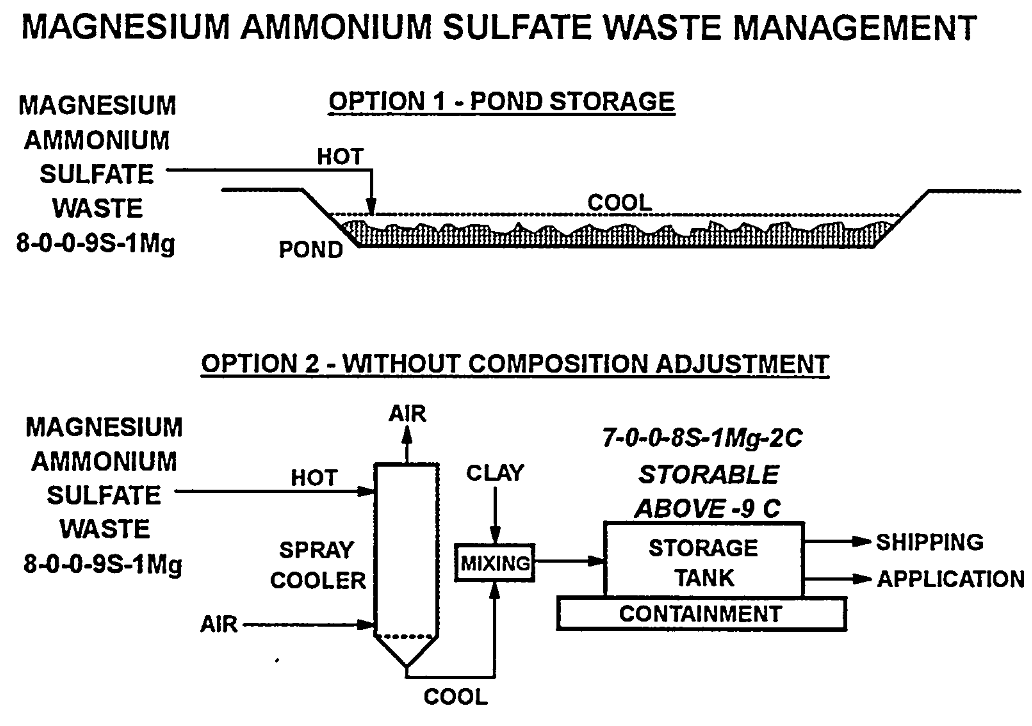


FIGURE 3

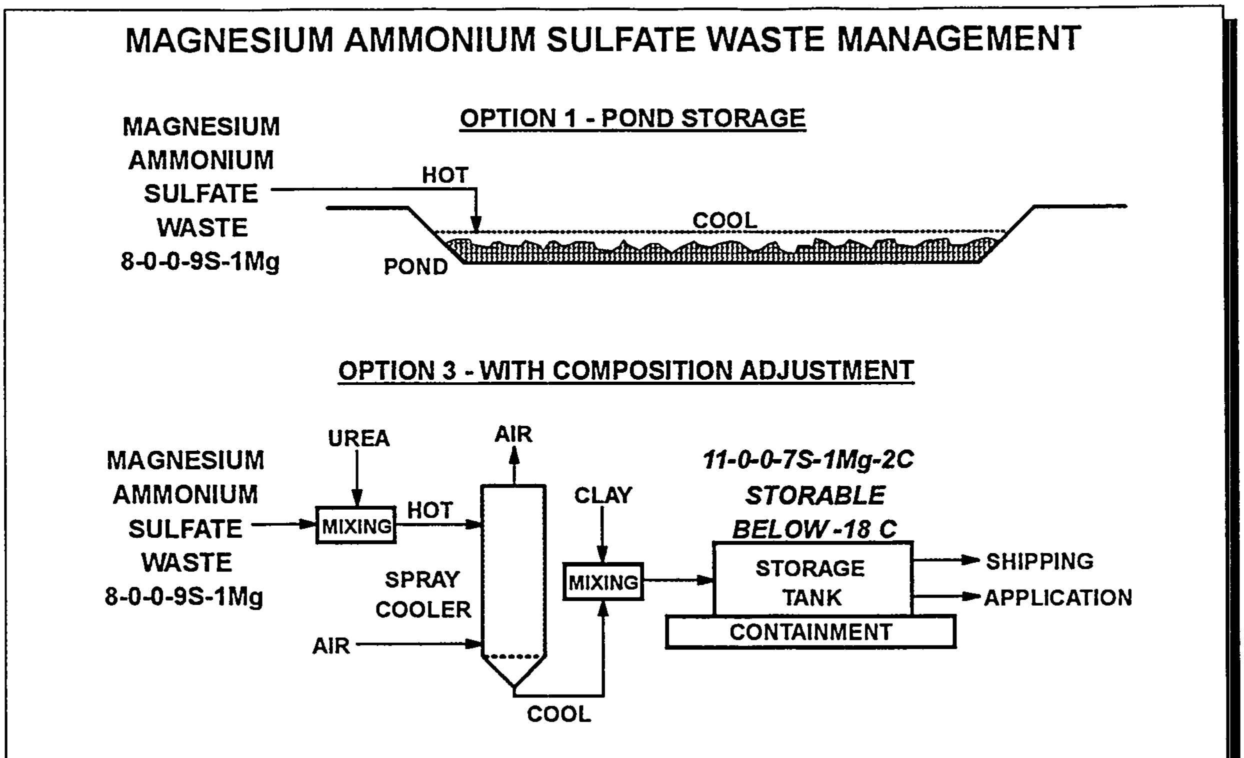
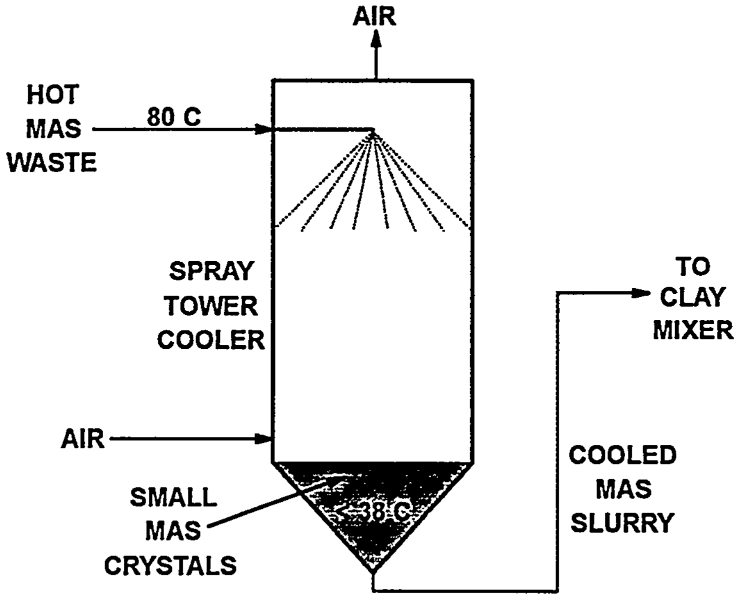


FIGURE 4

consisted of this same basic process but also involved adjustment of the waste concentration or the chemical composition with small amounts of urea to improve the low-temperature storage properties of the finished suspension, which would be required for satisfactory storage through winter.

A critical factor in this process is the relationship between product composition and the spray tower pool temperature, as depicted in Figure 5. It is necessary that the spray tower be operated at a pool temperature of at least several degrees below the saturation temperature of the MAS to yield an abundance of small crystals of this phase. Complicating control of the pool temperature, the MAS concentration, and thus the MAS saturation temperature, can vary in the normal course of operation of the process which generates the waste. If the pool temperature is not operated sufficiently below the MAS salt out temperature, very little or no crystals will be formed in the pool, and slow cooling during the clay addition step and later in storage results in formation of vary large MAS crystals which cannot be supported by the suspending clay, Figure 6. This occurs because slow cooling results in more crystal growth, rather than nucleation of new crystals. With little or no MAS crystals present in the slurry exiting the spray tower, further slow cooling results in nucleation of only a few crystals, and subsequent precipitation occurs in the form of growth on the few existing crystals, which eventually become very large in size. This is why the hot waste pumped into the pond resulted in formation of large crystal masses at the bottom, requiring that the material eventually be scooped out. To avoid formation of large MAS crystals in storage, it was determined that the spray tower pool should be operated below the lowest MAS saturation temperature encountered during normal operation of the waste generating process. Otherwise, it

CONVERSION OF MAGNESIUM AMMONIUM SULFATE WASTE TO SUSPENSIONS - QUALITY CONTROL



MASSPRAY
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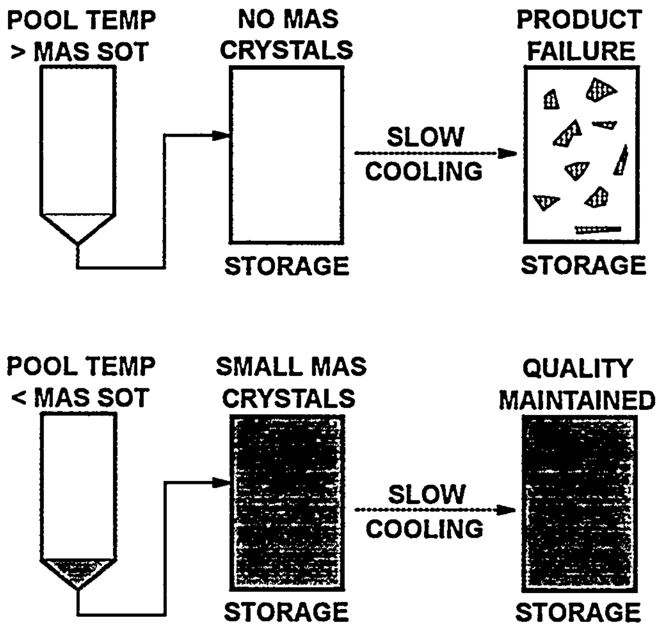
FIGURE 5

EFFECT OF POOL TEMPERATURE ON PRODUCT QUALITY



POOLTEMP
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FIGURE 6

would be necessary to control the pool temperature by online measurement of the MAS concentration.

Without adjustment of the concentration or adjustment of the composition with small amounts of urea, the finished suspension containing small MAS crystal stores well at most temperatures but begins to fail in storage at temperatures below about -9 °C (15 °F) due to formation of large ice and/or ammonium sulfate (AS) crystals, as shown in Figure 7. This is because neither AS nor ice was formed as small crystals during the spray cooling step (which would require refrigeration and would obviously be impractical). By adjusting the concentration or the composition with urea addition, Figure 7, compositions were developed with substantially lower AS and ice crystallization temperatures (< -18 °C, 0 °F), allowing stable storage of the material in colder weather. In some parts of the country, storage capability at -18 °C and lower is a requirement. The cost incurred with addition of urea would be recovered at sale of the material because the product would contain extra nitrogen, and the product price would be based on the plant nutrient content.

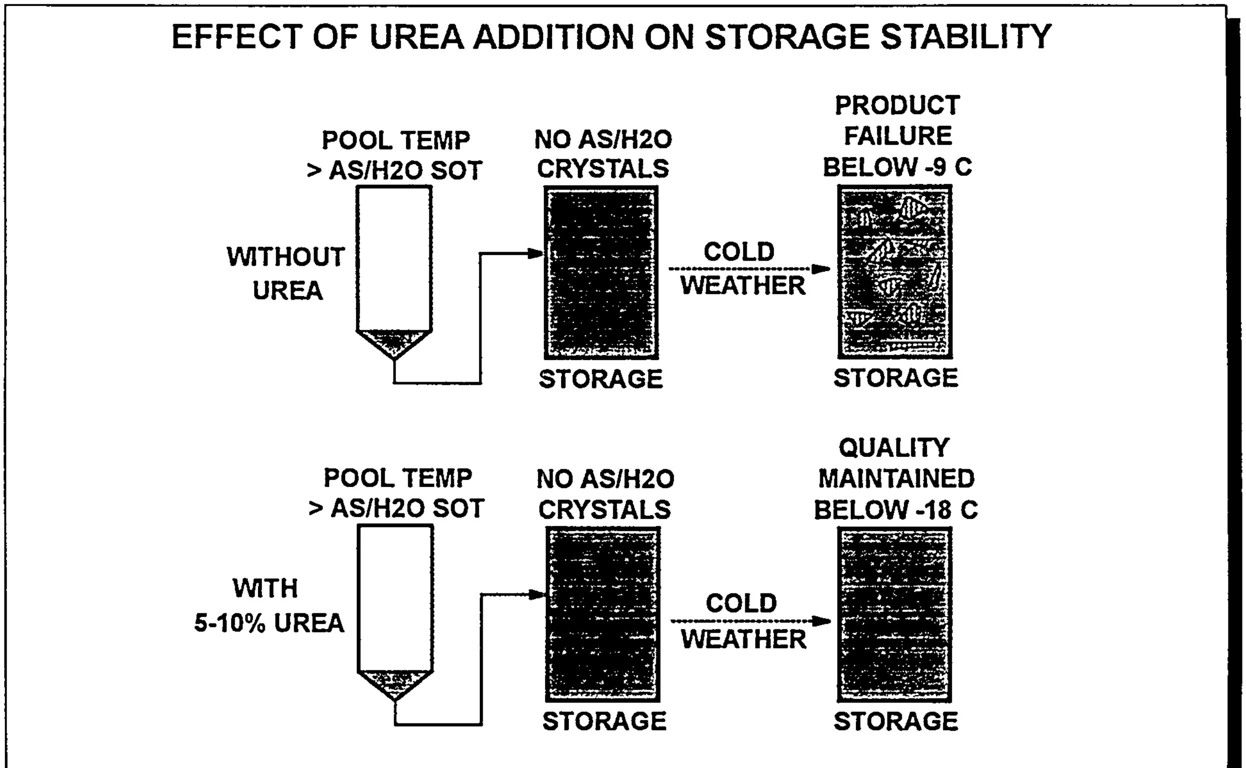
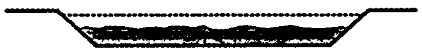


FIGURE 7

Another project in early 1990 involved conversion of clay-like calcium carbonate pond settlings from a steel industry into a free-flowing, fluid soil liming agent, Figure 8. This material had the consistency of molding clay and was grayish-white in appearance. Employing small quantities of a surfactant reduced the material to a completely fluid state. This material could then be blended with other dolomitic limestone, water, and clay to produce a good quality fluid lime. In the envisioned batch process shown in Figure 9, the clay-like pond settlings would be fed by belt or

FLUID LIME FROM CALCIUM CARBONATE POND SETTLINGS



CALCIUM CARBONATE POND SETTLINGS (FROM STEEL INDUSTRY) + **SURFACTANT + LIMESTONE + CLAY** → **FLUID LIME**

FIGURE 8

PONDLIME
JLB 7-13-93

FLUID LIME FROM CALCIUM CARBONATE POND SETTLINGS

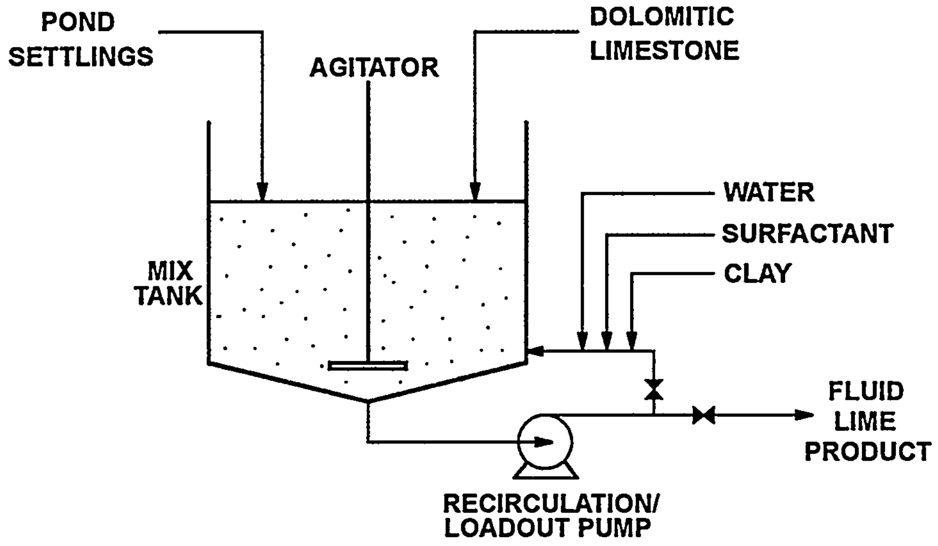


FIGURE 9

LIMEBAT
JLB 7-13-93

payloader to a mixing vessel which had been precharged with the appropriate quantity of surfactant, dolomitic limestone, water, and suspending agent; if a product with lower liming value per unit weight could be tolerated, the dolomitic limestone feed could be eliminated from the process.

By-Product Ammonium Sulfate and Waste Sulfuric Acid

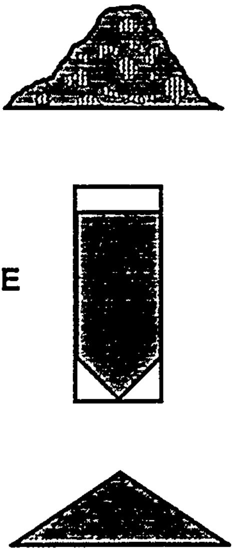
More than three million metric tons of crystalline ammonium sulfate (AS) is produced in the United States each year as by-products of caprolactam and coke production, SO_2 recovery, and neutralization of spent sulfuric acids. New generators of by-product AS are on the increase; industries with processes under development will recover lactic acid in cheese whey with generation of large quantities of AS as a by-product, and, as power and other industries begin recovering SO_2 with ammonia, much larger tonnages of by-product AS will be generated.

Much of the by-product AS on the market today is of poor physical quality due to small particle size and high moisture content, which results in rapid, severe caking. This caking makes the by-product AS very difficult or impossible to store, ship, handle, and use in conventional applications. It has been reported that seasonal low demand and high inventories have necessitated storage outdoors where rainfall could result in contamination of surface and/or ground water. A substantial portion of the total AS produced in the United States cannot be tracked to specific applications, and some have speculated that by-product AS is still being dumped, as it was in the past due to its low value. Proposed legislation would impose a stiff tax on any AS (solution or dry) discharged to water or any publicly owned treatment works.

NFERC is currently introducing its two patented processes developed for converting poor-quality AS or waste sulfuric acid into fluid suspensions, Figure 10, which can be stored for long periods and shipped, handled, and used in established operations without the difficulties associated with small by-product AS crystals. This by-product suspension can be substituted for more expensive fluid fertilizers on the market, resulting in substantial savings to the agricultural industry while making use of an often unwanted by-product.

Another method developed at NFERC for improving by-product AS involves treating the material to keep it free flowing in storage for long periods of time, Figure 10. Currently, use of stored, caked by-product AS results in extreme difficulties in handling, as depicted in Figure 11. Several inexpensive treatments, some utilizing waste materials, have been successfully used in a simple process to convert the caking-type by-product AS into a dry, free-flowing, long-storing product facilitating its use in a diversity of applications; a patent application covering these treatments is being processed. The improved AS could be purchased from the producer in the off season, when its price is generally lower, because it has the capability of being stored at retailer locations until needed in the growing season. Storage capability at retailer locations could reduce the seasonal glut of by-product AS at producer locations and thereby reduce the risk of surface and ground water contamination.

OPTIONS FOR USE OF B-P AMMONIUM SULFATE



STORE AS IS

- SEVERE CAKING
- UNSATISFACTORY FOR FLUIDS OR SOLIDS

PRODUCE/STORE SUSPENSION

+ SATISFACTORY STORAGE
+ SATISFACTORY HANDLING/USE
- MORE EXPENSIVE STORAGE
- MORE DILUTE (65-75% AS)
- FLUIDS USE ONLY

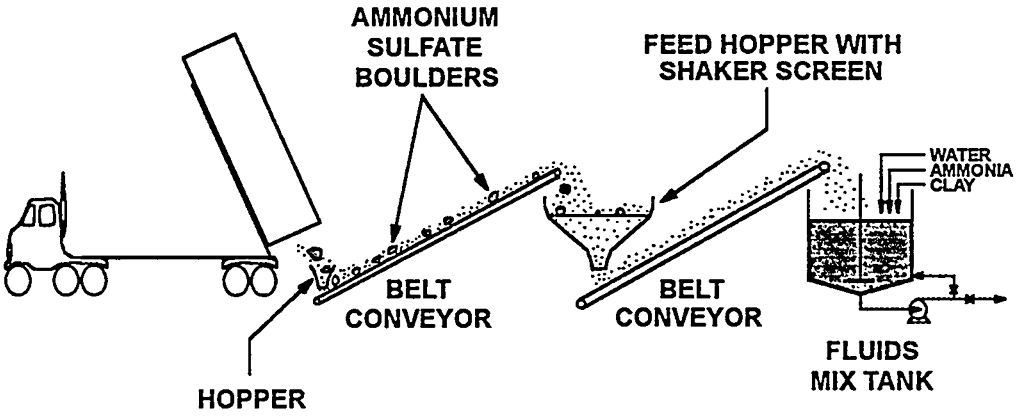
TREAT/STORE IN DRY FORM

+ SATISFACTORY STORAGE
+ SATISFACTORY HANDLING/USE
+ USE IN FLUIDS OR SOLIDS
+ LESS EXPENSIVE THAN FLUIDS STORAGE

ASOPTS
JLB 7-13-93

FIGURE 10

PROBLEMS WITH CAKED BY-PRODUCT AMMONIUM SULFATE



FEEDPROB
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FIGURE 11

Economic Advantage With By-Product Ammonium Sulfate

Whether in suspension or solid form, by-product AS fines generally enjoy a remarkable economic advantage over other common fertilizer sources of nitrogen (N) and sulfur (S), especially those used in fluid fertilizers. By-product AS can be used to replace ammonium thiosulfate solution (ATS) or elemental sulfur (ES) in production of fluid fertilizers with substantial savings in raw materials costs. When by-product AS is used to replace either ES or ATS, less urea-ammonium nitrate solution (UAN) is required to produce the same grade of fluid fertilizer. This adds to the raw material cost savings when using by-product AS.

Several cost savings equations were developed to enable dealers to determine the savings that can be achieved with by-product AS as functions of raw material costs and usage rates. Equations 1 and 2 below determine the savings achieved when ATS or 95% S (a commercial grade of ES), respectively, are replaced with by-product AS in production of fluid fertilizers, expressed in terms of dollars saved per ton of ATS or 95% S replaced. Equations 3 and 4 determine the savings achieved when ATS or 95% S, respectively, are replaced with AS suspension intermediates, expressed in terms of dollars saved per ton of ATS or 95% S replaced. Equations 3 and 4 differ from equations 1 and 2 only in that they take into account the cost of the clay to produce the AS suspension intermediates. Equations 5-8 are simplified versions of equations 1-4, respectively, and give very close approximations of savings. For any equation, the calculated savings per ton of ATS or 95% S replaced can be multiplied by the annual usage rate of ATS or 95% S, respectively, to determine the annual savings on either raw material. The annual savings on each raw material (ATS and 95% S) can then be added to determine the total annual savings by replacing all ATS and 95% S with AS.

ATS = Price of ATS, $/ton
AS = Price of AS, $/ton
S = Price of 95% S, $/ton
U = Price of UAN-32, $/ton
Sa = Savings on ATS, $/ton ATS replaced with AS
Ss = Savings on 95% S, $/ton es replaced with AS

Use of AS With No Extra Clay

(1) $ATS + 0.336U - 1.08AS = Sa$ (Savings on ATS)
(2) $S + 2.6U - 3.96AS = Ss$ (Savings on 95% S)

Production of AS Suspension Intermediates for Later Use

(3) $ATS + 0.336U - 1.08AS - 3.5 = Sa$
(4) $S + 2.6U - 3.96AS - 13 = Ss$

For Close Estimates, Equations 1-4 Can Be Simplified to:

(5) $ATS + 0.34U - 1.1AS = Sa$
(6) $S + 2.6U - 4AS = Ss$
(7) $ATS + 0.34U - 1.1AS - 3 = Sa$
(8) $S + 2.6U - 4AS - 13 = Ss$

EXAMPLE

A dealer uses 650 tons per year of ATS and 185 tons per year of 95% S. How much can be saved by supplying these sulfur needs with by-product AS? Basis: raw material costs are: ATS, \$115/ton; 95% S, \$270/ton; UAN-32, \$100/ton; AS, \$60/ton.

Eq 1 115 + 0.336x100 - 1.08x60 = **\$83.80** **saved per ton ATS** replaced with AS

Eq 2 270 + 2.6x100 - 3.96x60 = **\$292.40** **saved per ton es** replaced with AS

83.80x650 = **\$54 470** **saved annually on ATS** replaced with AS

292.40x185 = **\$54 094** **saved annually on es** replaced with AS

54 470 + 54 094 = **\$108 564** **total saved annually on both ATS and es** replaced with AS

Equation 1 above was used to generate the information in Figures 12-14, which illustrate the savings achieved by replacing ATS with by-product AS as functions of UAN, ATS, and AS costs. Surprisingly, Figure 13 indicates that with UAN-32 at \$100/ton and by-product AS at \$40/ton, the cost of ATS solution must fall below \$10/ton for by-product AS to loose its economic advantage over ATS. Shown below are some example scenarios for savings with by-product AS calculated from equations 1 and 2 above.

Raw Material Costs, $/ton				Savings, $/ton replaced	
AS	ATS	ES	UAN	ATS	ES
60	80	-	80	42	-
40	80	-	80	64	-
60	115	-	100	83	-
60	125	-	120	101	-
60	-	200	80	-	170
60	-	200	96	-	212
60	-	270	120	-	344

COST SAVINGS WITH BY-PRODUCT AMMONIUM SULFATE

AS VERSUS ATS SOLUTION UAN-32 = $80/TON

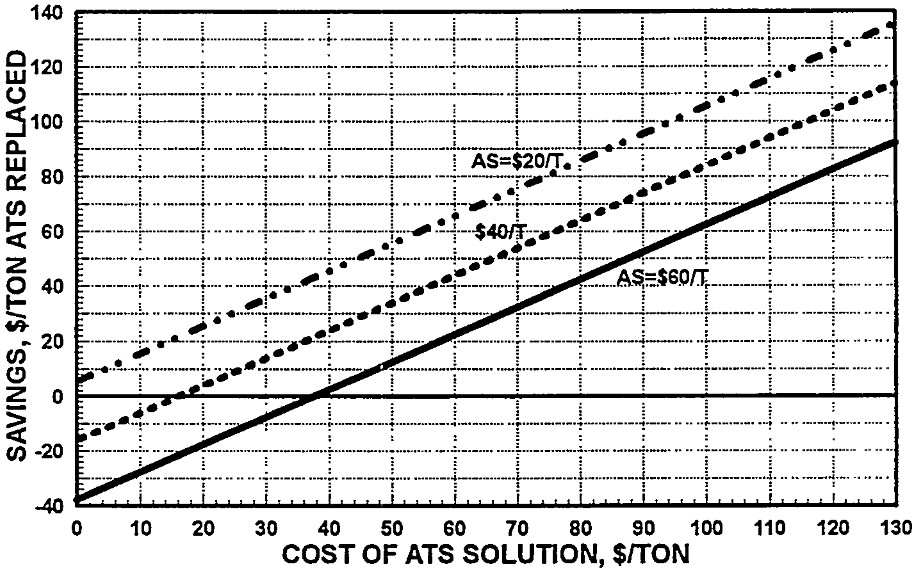


FIGURE 12

S-SAVE1
9-24-92 JLB

COST SAVINGS WITH BY-PRODUCT AMMONIUM SULFATE

AS VERSUS ATS SOLUTION UAN-32 = $100/TON

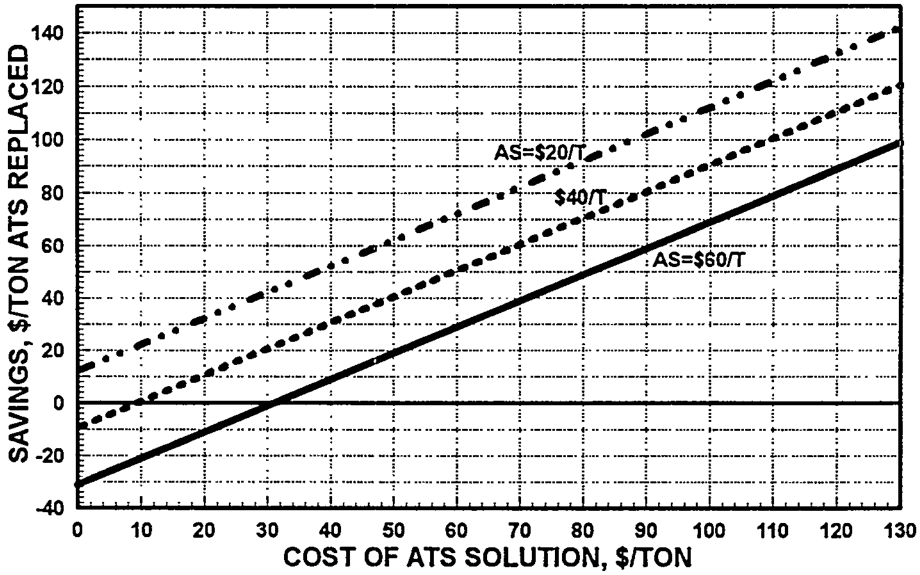


FIGURE 13

S-SAVE2
-24-92 JLB

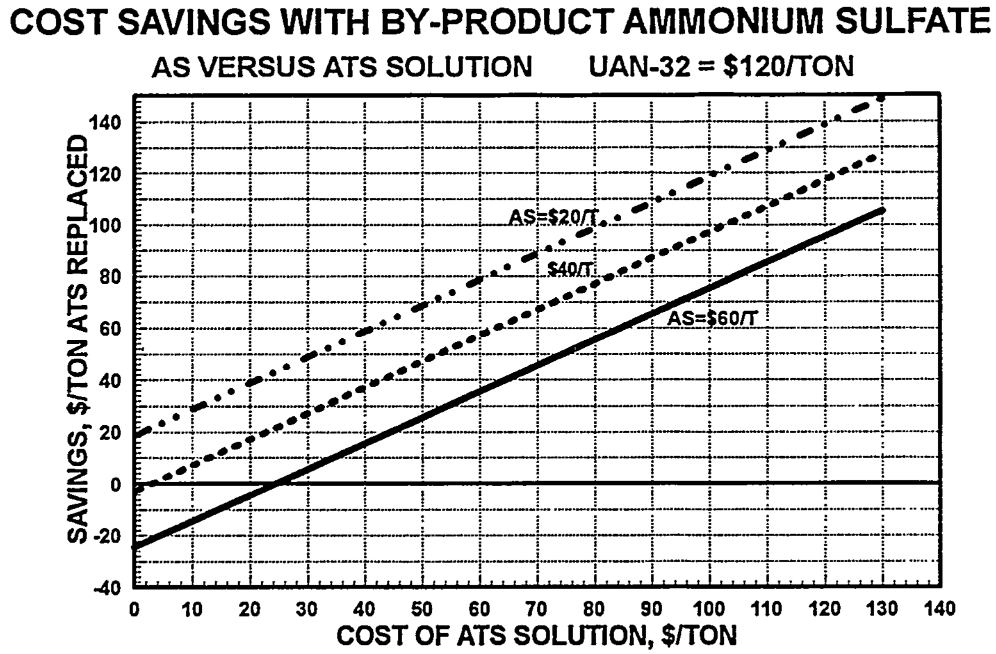


FIGURE 14

S-SAVE3
9-24-92 JLB

In the vast majority of the cases with application of sulfur in fluid fertilizer form, nitrogen is applied in quantities greater than the amount of sulfur, so the assumption to credit the UAN value of nitrogen in AS is almost always valid and the above equations and cost savings apply in most cases. Obviously, savings would be lower for finished grades with N:S ratios substantially less than 1, since the extra N in AS for such grades would not be required.

AS Suspension Intermediates

There are distinct advantages in producing, storing, and using low-quality AS fines in suspension form. Although AS fines are often unsuitable for shipping, storage, handling, blending, or application in solid form, they are ideal for use in suspension fertilizers because they are easier to suspend, require less clay, and allow production of higher grades. Larger crystals or granules are more difficult to suspend, require the addition of extra clay which reduces grade, and can plug screens and application equipment. Simply put, AS which is of the lowest quality for use as a solid can often be of the highest quality for use in suspensions. Production of AS suspensions provides a good means for stable storage of small and/or wet by-product AS crystals, providing the dealer with a good, inexpensive fluid sulfur source ready immediately when needed for application or blending with other fertilizer fluids and solids. Storage of poor-quality AS in dry form until needed for use results in extreme handling problems, production difficulties, and delays in filling orders as shown in Figure 11; operation under such conditions cannot be tolerated during heavy business seasons, so dealers often resort to higher-priced, pure raw materials, such as ATS.

Furthermore, a by-product AS producer would not have to dry or even centrifuge the AS crystals and could simply blend wet crystals or slurry with clay and water, lowering production costs and at the same time upgrading a low-quality AS into a more usable form. In addition, efforts to obtain large crystals with long retention times in crystallizers would be unnecessary and even detrimental if the AS is intended for fluid fertilizer use. Small crystals are easier to produce with shorter crystallizer retention times and less elaborate, expensive equipment. Disadvantages to production and storage of AS suspension intermediates are (1) the suspensions are more dilute than the AS solid (2/3 to 3/4 the concentration of the solid) and (2) storage for fluids is generally more expensive and labor intensive than storage for solids.

Production of AS suspension intermediates and storage for later use in fluid fertilizer blends is a dramatically better alternative to the severe caking encountered when low-quality AS fines are shipped and stored as produced. Furthermore, the solubility characteristics of AS lend it to production of high-quality, long-storing suspensions. As shown in Figure 15, the solubility of AS does not vary appreciably with temperature. This is a distinct advantage for the solid phase(s) present in a suspension. In some suspensions, temperature fluctuations during storage result in appreciable dissolution of small crystals and then precipitation on existing crystals, which results in substantial crystal growth over time, as illustrated in Figure 16. With AS, temperature fluctuations normally encountered in storage dissolve and precipitate only very small amounts of AS, so crystal size remains relatively constant over long periods of time.

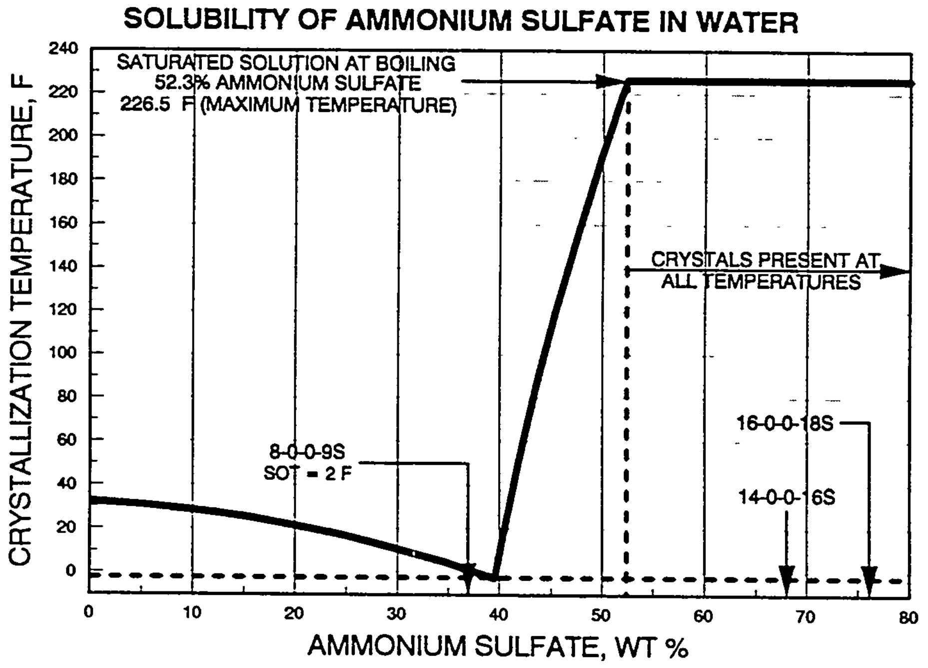


FIGURE 15

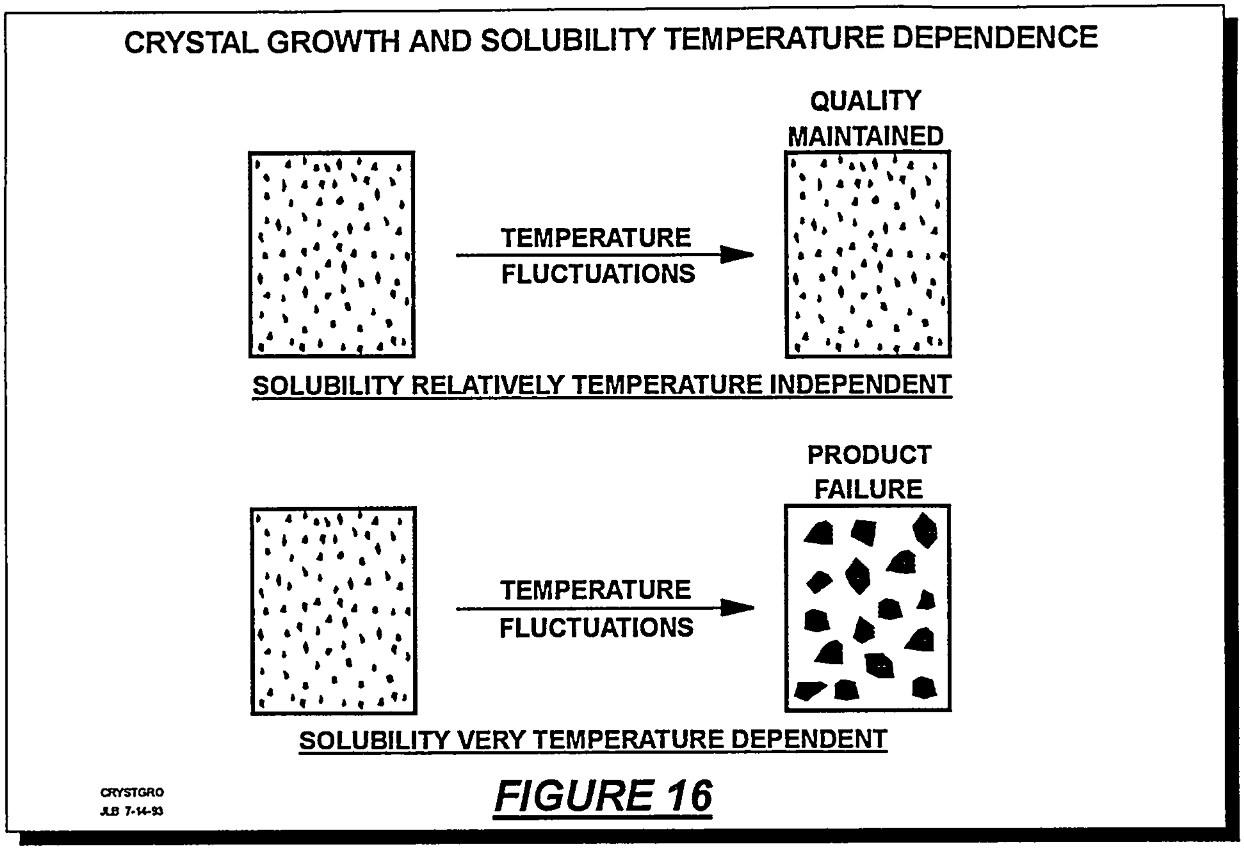
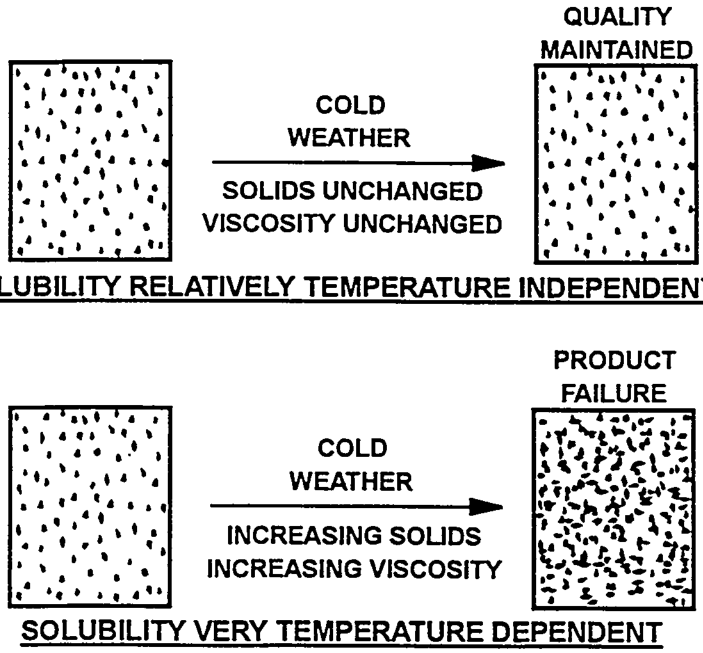


FIGURE 16

Another advantage associated with AS's relatively temperature-insensitive solubility is the viscosity of AS suspensions remains practically constant over the entire range of temperatures normally encountered in field storage (-18 to 38 °C, 0 to 100 °F). This is because the solids content of the AS suspensions changes only very little over this temperature range, as depicted in Figure 17.

AS suspensions such as 14-0-0-16S and 16-0-0-18S can be produced with up to twice the nutrient content and with as little as 38% of the water contained in 8-0-0-9S AS solution, as illustrated in Figure 15. As shown in Figure 18, AS solutions must be limited to a about 8-0-0-9S grade; above about 9.5%, the salt-out temperature of AS solutions increases very rapidly with increase in concentration, and care must be taken to avoid crystallization and settling out in storage tanks. With 8-0-0-9S, containing 63% water, many blends cannot be formulated to contain the desired sulfur content. With the AS suspensions, containing 30-34% plant food and only 24-32% water, storage volume requirements are lower, shipping costs are lower, and much more flexibility is available in formulating fluid blends than with AS solutions. Furthermore, the AS suspensions can be blended with UAN solution and water with only mild mixing to produce true N-S solutions such as 20-0-0-5S, 22-0-0-4S, and 25-0-0-3S, as illustrated in the solubility diagram in Figure 19. The resulting solutions are slightly cloudy due to the clay in the AS suspensions, but the clay content is only 0.7% or less. The clay particles, which are only 1 micrometer in size, resist settling but yet do not impart any thickness to the solutions as might be expected. The clay apparently resists settling because of first being gelled in the AS suspension intermediate. The resulting solutions have viscosities and flow properties that are typical of

VISCOSITY AND SOLUBILITY TEMPERATURE DEPENDENCE



QUALITY MAINTAINED

COLD WEATHER

SOLIDS UNCHANGED
VISCOSITY UNCHANGED

SOLUBILITY RELATIVELY TEMPERATURE INDEPENDENT

PRODUCT FAILURE

COLD WEATHER

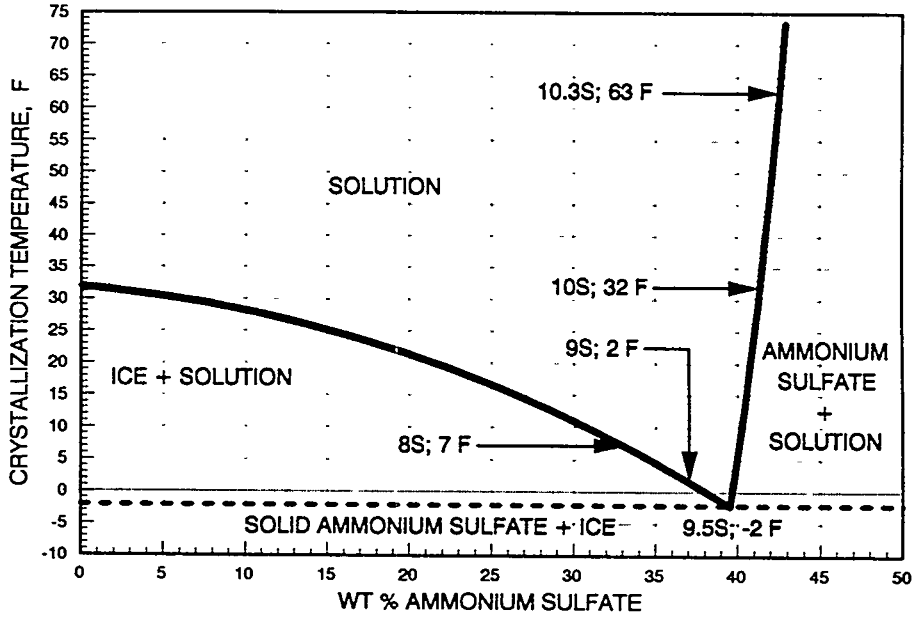
INCREASING SOLIDS
INCREASING VISCOSITY

SOLUBILITY VERY TEMPERATURE DEPENDENT

VISCTEMP
JLB 7-14-93

FIGURE 17

SOLUBILIITY OF AMMONIUM SULFATE IN WATER



S-SOLS
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FIGURE 18

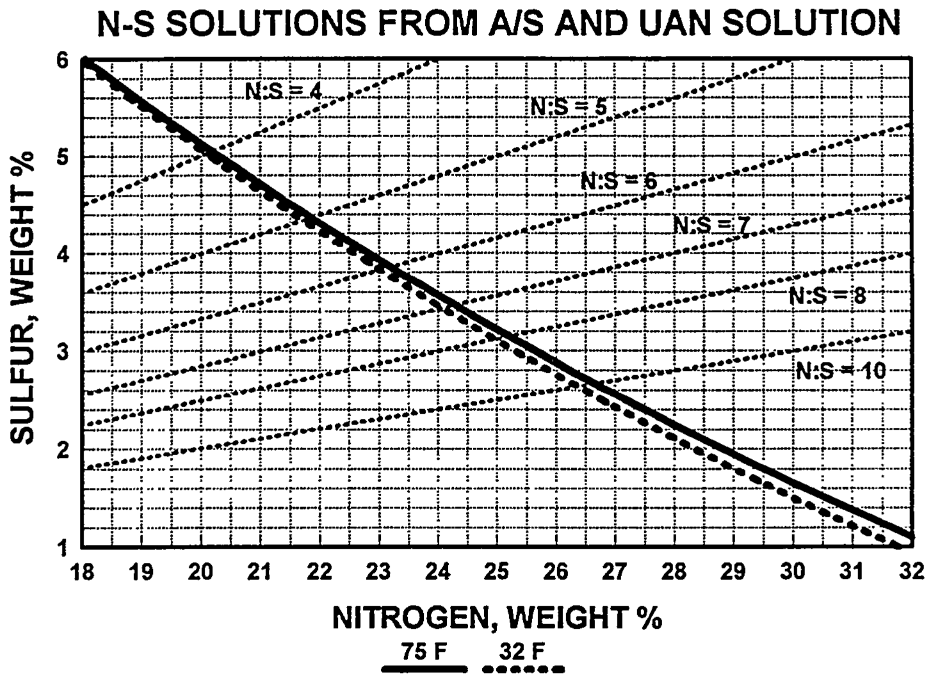


FIGURE 19

solution fertilizers. A 22-0-0-4S solution from AS suspension and UAN, for example, has the same N:S ratio as 28-0-0-5S solution from ATS and UAN and handles and applies as a true solution, but it is substantially lower in cost to produce than the 28-0-0-5S from ATS. Physical properties of AS suspensions are shown below.

	14-0-0-16S	15-0-0-17S	16-0-0-18S
Clay, wt %	2.8	2.3	1.8
Viscosity, mPa s (cP)			
at 38 °C (100 °F)	1150	1140	1130
at 27 °C (80 °F)	1160	1160	1170
at 7 °C (45 °F)	1190	1190	1190
at 0 °C (32 °F)	1200	1240	1270
at -9 °C (15 °F)	1210	1260	1320
at -18 °C (0 °F)	1120	1280	1340
Preferred crystal size range, mm (Tyler mesh)		99% < 1.70 (99% -10) 95% < 0.85 (95% -20) 85% < 0.60 (85% -28)	
Solidification temperature, °C (°F)	-19 (-2)	-19 (-2)	-19 (-2)
Specific gravity, g/mL (lb/gal)	1.39 (11.6)	1.44 (12.0)	1.47 (12.3)
pH	7	7	7

AS suspension could well be considered the "sulfur version" of a high-potash suspension such as 4-10-30, or a sulfur base suspension, analogous to a phosphate base suspension such as 10-30-0 from MAP.

Production of AS Suspensions from By-Product AS Crystals

AS suspensions are very easy to produce in common batch suspension fertilizer equipment, as illustrated in Figure 20. The procedure consists of simply adding the water of formulation to the mix tank, starting agitation and recirculation, and then adding the dry clay with continued recirculation and agitation for a few minutes. Next, the AS fines are fed into the mix tank with continued recirculation and agitation. When addition of the AS is complete, the mixture is further recirculated and agitated for a few minutes if desired to ensure a homogeneous mixture. The suspension is then ready for direct application, production of fluid blends, or storage for later use. The higher-grade, lower-clay-content suspensions such as the 16-0-0-18S grade are most suitable for short term storage up to one month, and grades such as 14-0-0-16S with 3% clay are suitable

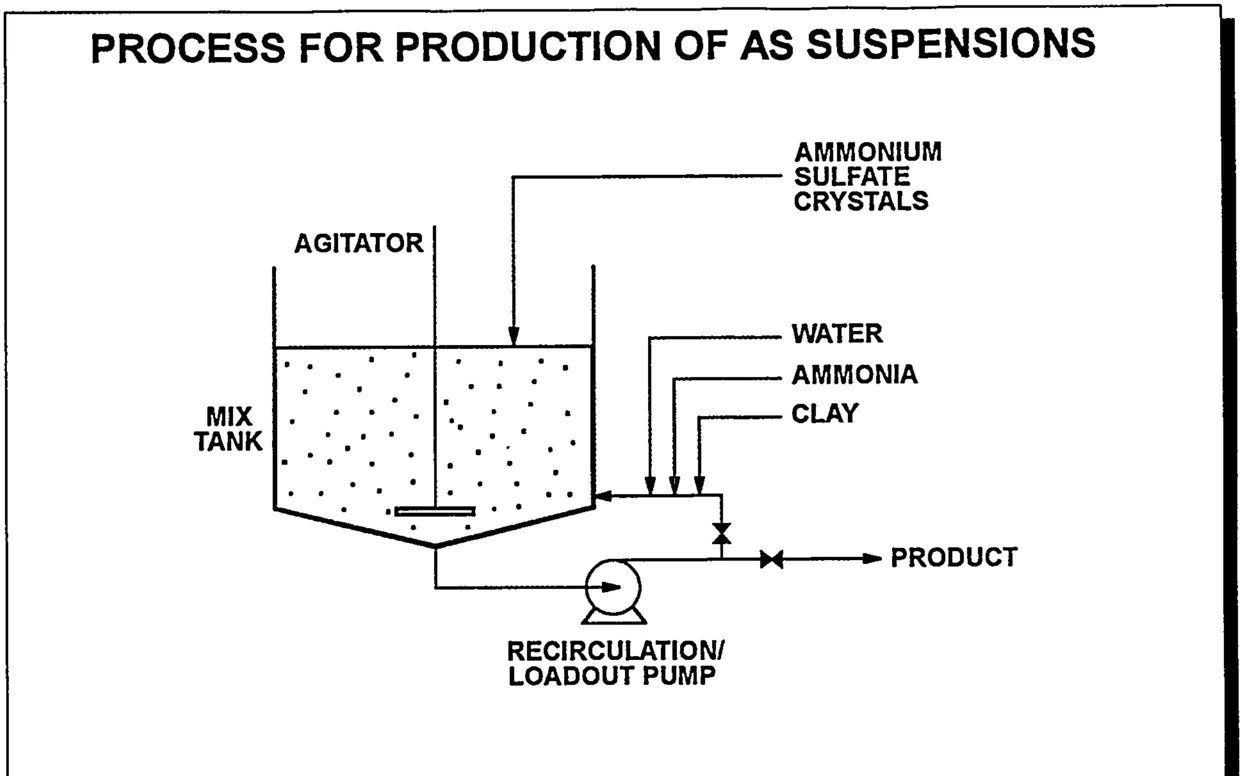
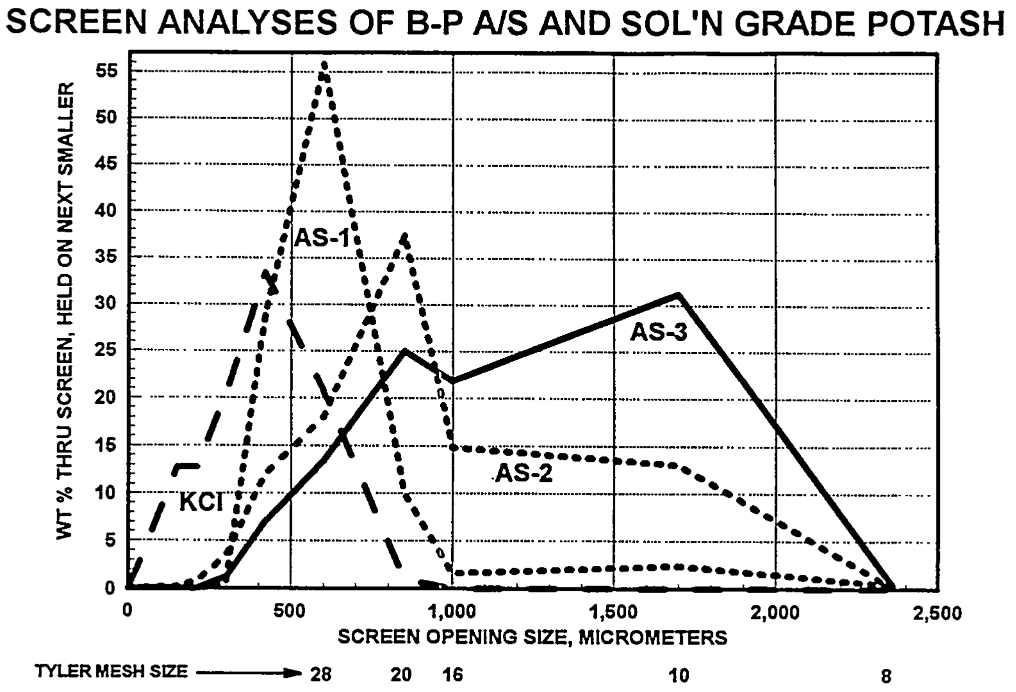


FIGURE 20

for long-term storage up to 6 months or longer. The AS suspensions should be agitated by air sparging and/or recirculating with a pump (preferably both) during storage to maintain optimum condition and homogeneity of the suspensions. The 16-0-0-18S grade should be agitated more frequently for shorter periods of time, such as a 2 or 3 minutes 3-5 times per week, whereas the 14-0-0-16S grade only needs thorough agitation 3-4 times per month. Agitation time depends on the intensity of the agitation (air pressure and volume or recirculation rate in relation to tank volume).

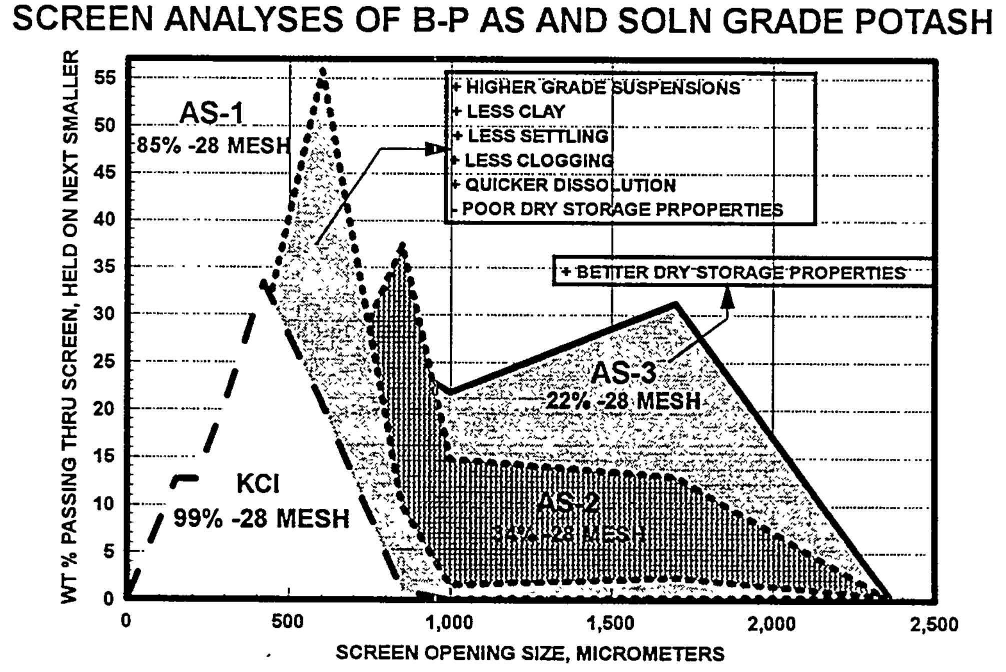
An important consideration in producing and storing AS suspensions is of course the size of the AS crystals. AS referred to as "fines" can vary dramatically in size, as shown in Figures 21 and 22. Obviously, as shown in Figure 22, the smaller crystals are more suitable for production of AS suspensions because they (1) allow production of higher grades, (2) require less clay, (3) result in less settling, and (4) result in less clogging of screens and application equipment than large AS crystals. However, the smaller AS crystals do not store as well in solid form as the larger crystals, so they must be converted to suspensions as soon as possible after shipment. If possible, it is desirable to use AS crystals with a size range similar to that of solution grade potassium chloride, such as "AS-1" in Figure 22; solution grade potassium chloride is already commonly used in production of suspension fertilizers and the specific gravity of potassium chloride crystals is even greater than that of AS (2.0 versus 1.8 for AS). If the larger-crystal AS fines are used, it is usually necessary to reduce the grade and increase the clay content to prevent settling in the suspension. Also, the larger AS crystals take longer to dissolve when making solution fertilizers



SCREEN ANALYSES OF B-P A/S AND SOL'N GRADE POTASH

SCREEN1 -25-92 JLB

FIGURE 21



SCREEN ANALYSES OF B-P AS AND SOLN GRADE POTASH

SCREEN2 -25-92 JLB

FIGURE 22

from the AS suspensions. However, the larger AS crystals generally have better storage properties in solid form.

AS Suspension Intermediates from Waste Sulfuric Acid or AS Slurry

AS suspensions can also be produced from waste sulfuric acid and ammonia by the process shown in Figure 23. This process is more suitable for continuous operation for corrosion reasons. In the continuous process, sulfuric acid and ammonia replace AS and are fed simultaneously to a reactor at rates required for maintaining the pH in the neutral range to lessen tendency for corrosion. Reaction of sulfuric acid with ammonia produces a hot slurry containing AS crystals. This hot slurry is cooled to about 38 °C (100 °F) in a spray type evaporative cooler with addition of suspending clay in the cooler or after cooling in a separate mixer.

This "hot" process would be applicable to industries which are currently generating waste/by-product sulfuric acid or otherwise generating hot AS slurry as a by-product stream, such as in production of coke. As shown in Figures 24 and 25, conversion of the hot AS slurry directly into AS suspension would eliminate the need for elaborate equipment for producing large crystals and eliminate centrifuging and drying steps in production of crystalline AS. To accomplish this, a common batch suspension fertilizer plant could be installed at the AS sulfate producer site to intercept the AS slurry before centrifuging and drying and convert the AS slurry directly into AS suspension by cooling and adding clay.

UTILIZING WASTE SULFURIC ACID OR HOT B-P A/S SLURRY

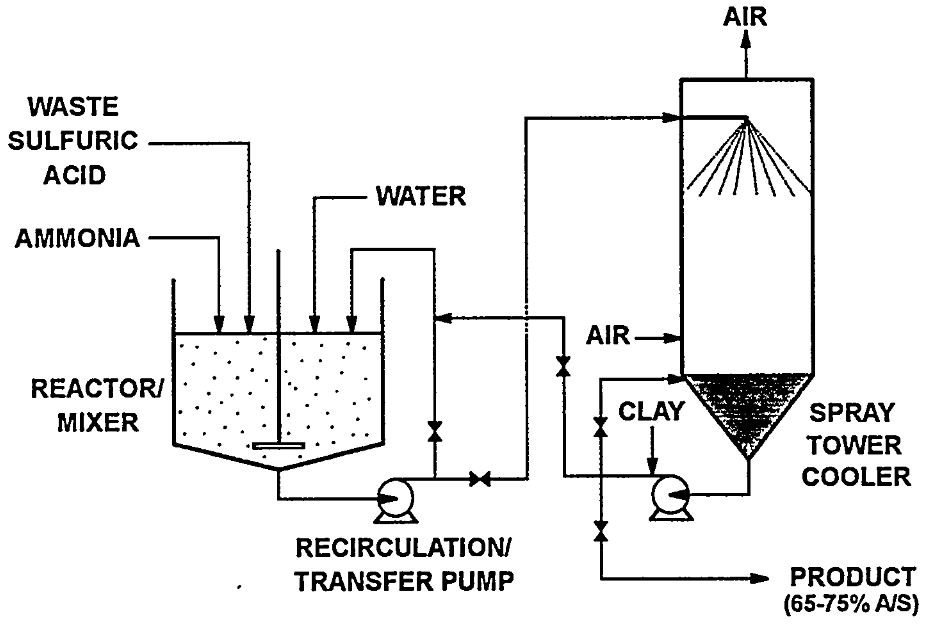
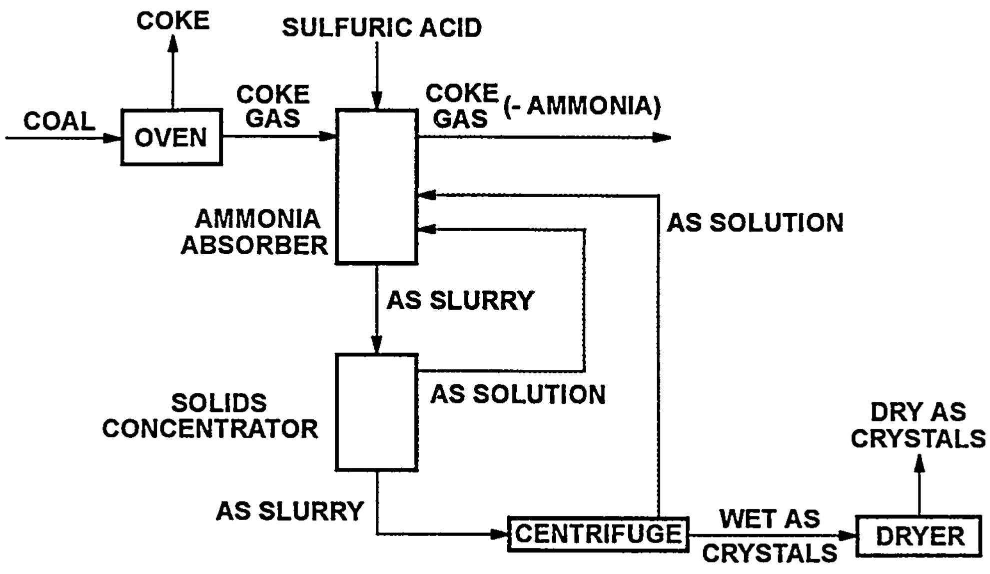


FIGURE 23

PRODUCTION OF AMMONIUM SULFATE FROM COKE GAS

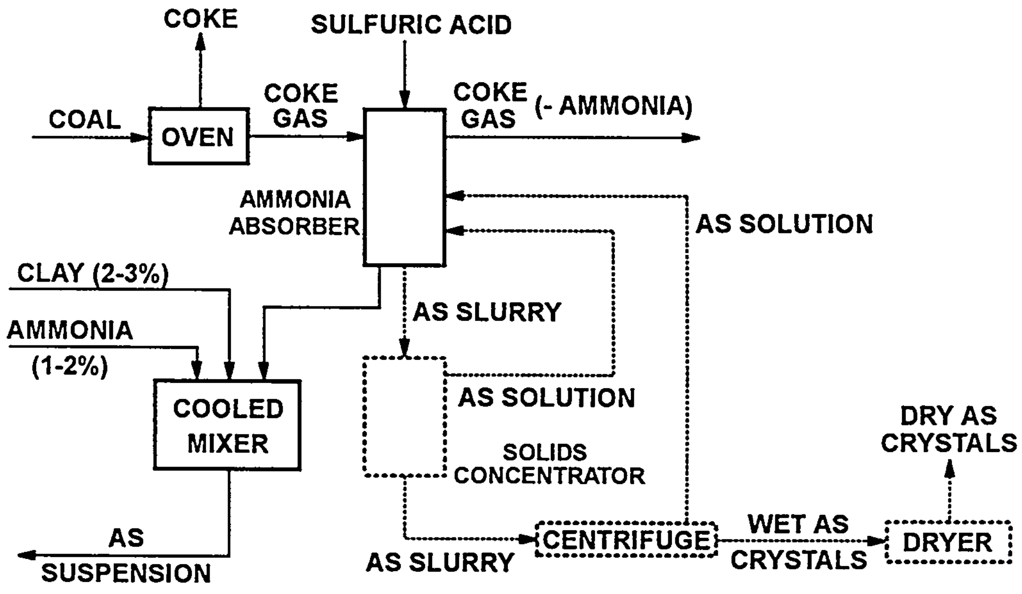


COKE
SULFURIC ACID
COAL
OVEN
COKE GAS
COKE GAS (- AMMONIA)
AMMONIA ABSORBER
AS SOLUTION
AS SLURRY
SOLIDS CONCENTRATOR
AS SOLUTION
DRY AS CRYSTALS
AS SLURRY
CENTRIFUGE
WET AS CRYSTALS
DRYER

COKEPRO
JLB 7-7-93

FIGURE 24

PRODUCTION OF AMMONIUM SULFATE FROM COKE GAS



COKE
SULFURIC ACID
COAL
OVEN
COKE GAS
COKE GAS (- AMMONIA)
AMMONIA ABSORBER
AS SOLUTION
CLAY (2-3%)
AMMONIA (1-2%)
AS SLURRY
COOLED MIXER
AS SOLUTION
SOLIDS CONCENTRATOR
DRY AS CRYSTALS
AS SUSPENSION
AS SLURRY
CENTRIFUGE
WET AS CRYSTALS
DRYER

COKEPRO2
JLB 7-7-93

FIGURE 25

Treating Low-Quality AS to Improve Dry Storage Properties

Simple and economical methods have been developed for treatment of AS fines which provide for satisfactory storage for at least 6 months and excellent after-storage flowability, facilitating ease of use in direct application of the fines, solid and fluid fertilizer programs, granulation, or other applications; a patent application covering these treatments is currently being processed. If AS fines are relatively dry as produced or can be dried after production, methods for treating the fines to obtain good long-term storage properties and after-storage free-flowability are simple and inexpensive. However, methods for treating AS fines which are relatively wet (e.g. > 1% moisture) have so far been economically prohibitive because excessively high quantities of additives or relatively expensive additives are required to achieve the desired anticaking/free-flowing properties. Results so far indicate that it would probably be less expensive to first dry the AS fines to less than 1% moisture and then to use the far less expensive treatments.

Figure 26 illustrates the relative flowability of untreated AS fines as a function of moisture content. The relative flowability of the AS fines is represented by the angle of repose, which has proven to be a useful and predictable measure of flowability in our work with AS fines. The angle of repose, however, indicates only flowability and yields no information on the caking tendency of the fines, for which measurements other than actual storage have been used. Generally, AS fines with angles of repose (AOR) less than about 40 degrees have demonstrated good flowability, whereas AS fines with angles of repose much in excess of 40 degrees have poor flow properties.

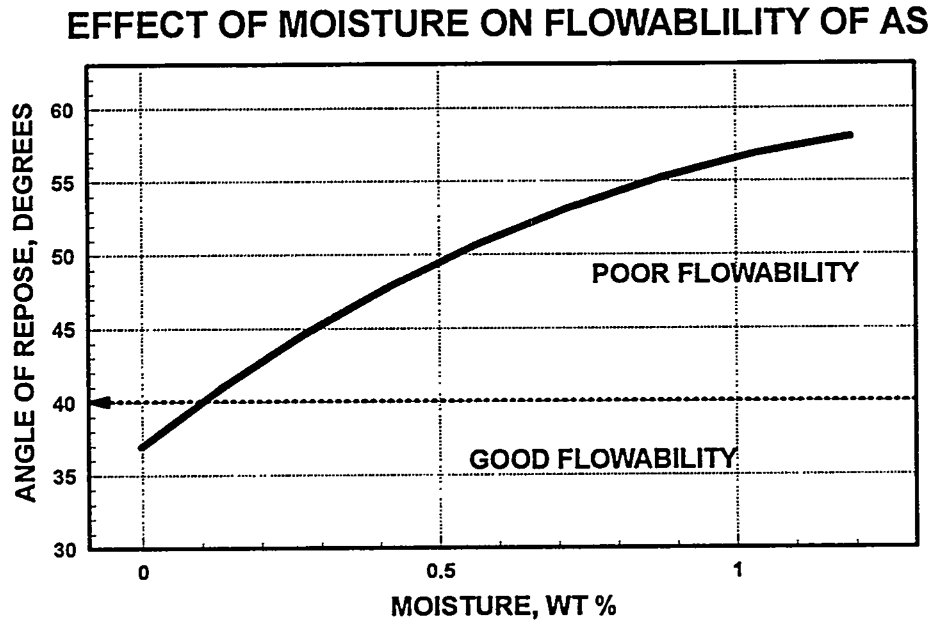


FIGURE 26

MOIST1
3-28-92 JLB

Figure 27 shows that, even when considering two different sources of AS fines with significantly different crystal size distributions, the relationship between flowability and moisture content is practically the same. With moisture contents much in excess of 0.1 to 0.2%, the flow properties of AS fines are generally poor.

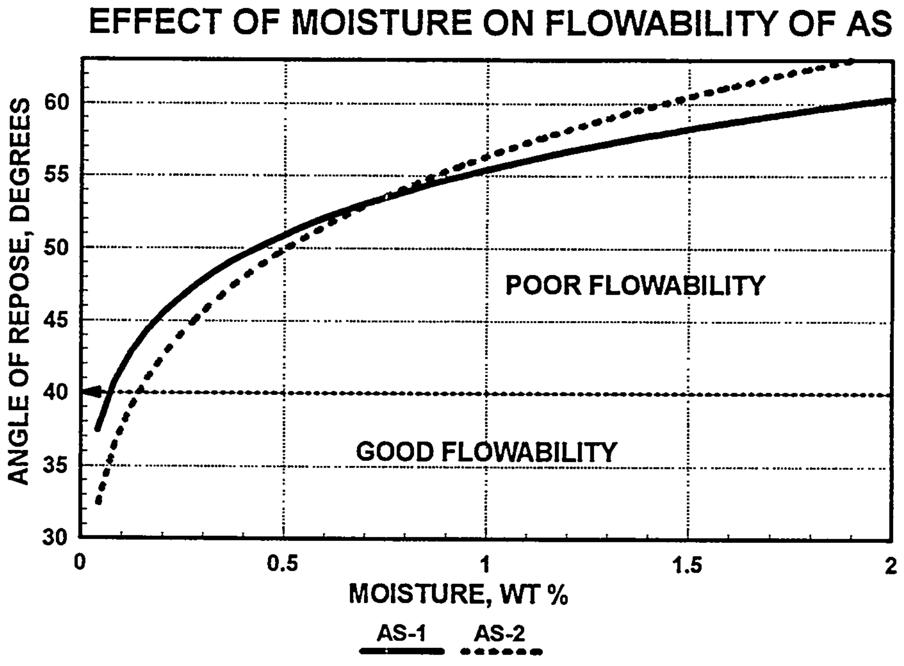
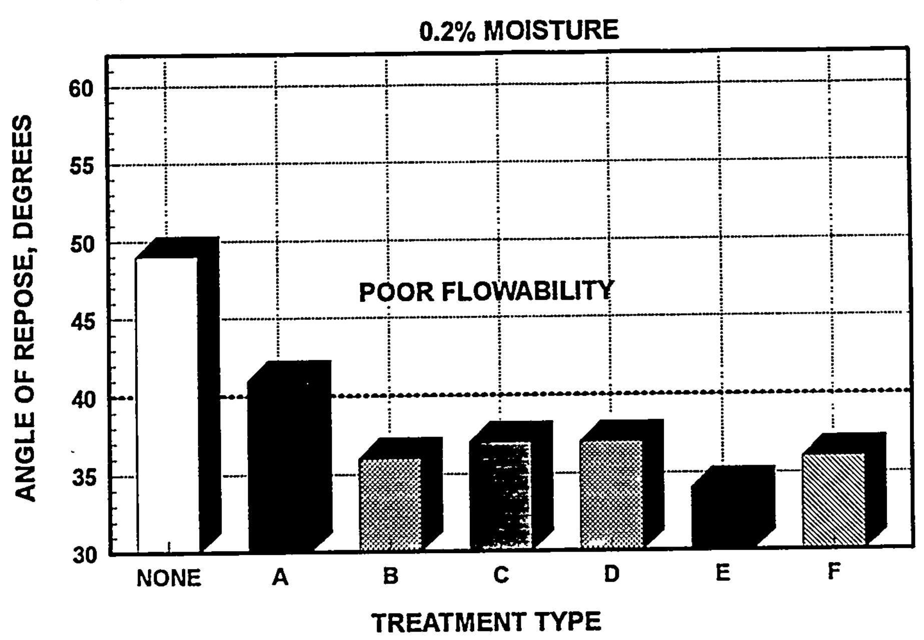


FIGURE 27

MOIST2
-24-92 JLB

However, several inexpensive treatment methods for relatively dry AS (0.2% moisture), Figure 28, have been successful in reducing the AOR to satisfactory flowability levels. Furthermore, these treatments have resulted in good storage and after-storage flow properties in 6-month storage tests of 25-kg quantities, as illustrated in Figure 29. The 25-kg sample of untreated AS as well as a 25-t pile of the same untreated AS exhibited severe caking throughout during the 6 months of storage. The untreated AS fines exhibited caking throughout the volume of the material, but the treated AS fines generally formed 10- to 25-mm crusts on top of the material, with the material underneath being as free flowing as dry sand. The hardness of the thin crust on the treated AS fines varied from very soft and crumbly to hard depending on the method of treatment.

The cost for treating by-product AS to achieve good flowability and storage properties has generally been in the range of $1 to $4 per metric ton of AS; however, using some of the successful treatments involving waste materials, the added cost to the AS would consist of only the cost to ship the waste material to the AS treatment site. Some of the successful treatment methods shown in Figures 28 and 29 are currently being tested in 200-kg bins and 1.5-kg weighted bags at NFERC. One- and three-month storage results of these tests appear in Tables III-VI. These results show that both the open bin and the weighted bag type tests are needed to

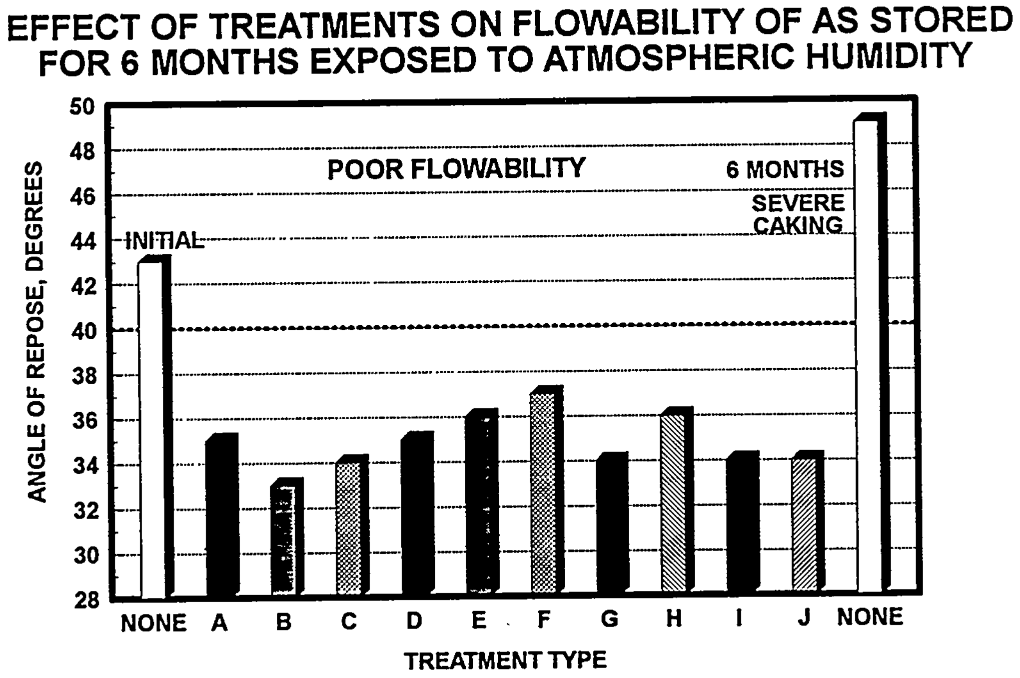


EFFECT OF TREATMENT ON FLOWABILITY OF AS

0.2% MOISTURE

FIGURE 28

TREAT1
9-24-92 JLB



EFFECT OF TREATMENTS ON FLOWABILITY OF AS STORED FOR 6 MONTHS EXPOSED TO ATMOSPHERIC HUMIDITY

FIGURE 29

TREAT2
9-28-92 JLB

ADDTAB1
JLB 7-15-93

TABLE III

IMPROVING STORAGE/HANDLING OF B-P A/S - 400-LB BIN TESTS

1-MONTH STORAGE

SAMPLE	CRUST THICKNESS (mm)	CRUST HARDNESS (0-5)	SUBCRUST HARDNESS (0-5)	SUBCRUST FLOWABILITY (1-5)
BLANK	9	4	3	1
BLANK/N	9	3.5	0	2.5
1% A	4	5	0	4.5
1% A/N	13	5	1	4
4% A	6	5	1	5
4% A/N	5	4	1	5
4% B	5	4	2	4
4% B/N	4	4	3	3.5
4% W	6	1	0	5
4% W/N	10	5	1	5
1% C	11	4	2	5

ADDTAB3
JLB 7-15-93

TABLE IV

IMPROVING STORAGE/HANDLING OF B-P A/S - 400-LB BIN TESTS

3-MONTH STORAGE

SAMPLE	CRUST THICKNESS (mm)	CRUST HARDNESS (0-5)	SUBCRUST HARDNESS (0-5)	SUBCRUST FLOWABILITY (1-5)
BLANK	187	3	3	1
BLANK/N	17	4	0	3.5
1% A	10	3	0	4
1% A/N	14	5	0	4
4% A	7	4	0	4.5
4% A/N	6	4	0	5
4% B	3	3	0	4.5
4% B/N	4	3	0	4.5
4% W	3	2	0	5
4% W/N	12	5	0	5
1% C	18	5	0	5

TABLE V

IMPROVING STORAGE OF B-P A/S - WEIGHTED BAG TESTS

1-MONTH STORAGE

SAMPLE	BAG CAKE HARDNESS (L,M,H)	+13 mm LUMPS AFTER BAG DROP (WEIGHT %)	LUMP HARDNESS (L,M,H)
BLANK	H	23	L
BLANK/N	H	65	L
1% A	M	4	L
1% A/N	H	27	M
4% A	H	24	L
4% A/N	M	7	L
4% B	L	2	L
4% B/N	H	26	L
4% W	0	0	0
4% W/N	H	47	M
1% C	M	7	L

ADDTAB4
JLB 7-15-93

TABLE VI

IMPROVING STORAGE OF B-P A/S - WEIGHTED BAG TESTS

3-MONTH STORAGE

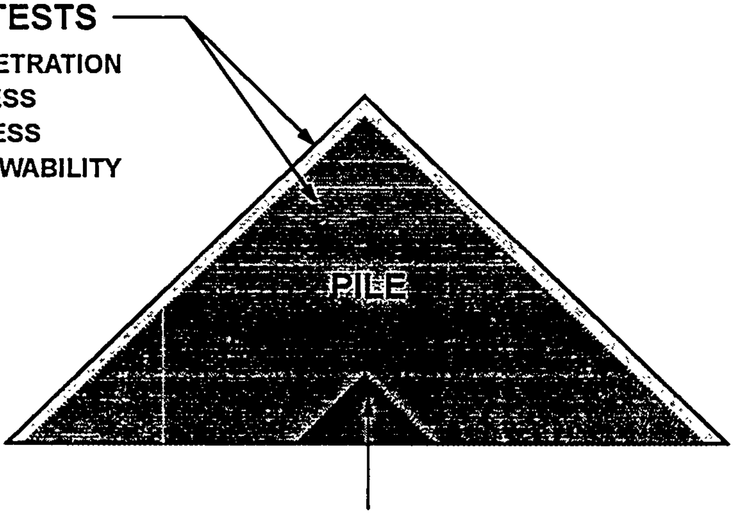
SAMPLE	BAG CAKE HARDNESS (L,M,H)	+13 mm LUMPS AFTER BAG DROP (WEIGHT %)	LUMP HARDNESS (L,M,H)
BLANK	H	50	L
BLANK/N	H	76	H
1% A	H	6	L
1% A/N	H	36	H
4% A	H	24	M
4% A/N	H	11	H
4% B	L	3	L
4% B/N	H	31	M
4% W	0	0	0
4% W/N	H	47	H
1% C	H	15	L

ADDTAB2
JLB 7-15-93

fully evaluate the performance of a particular treatment, since results from these two procedures can differ dramatically. The open bin storage method, Tables III and IV, predicts storage performance with respect to surface moisture penetration, crust hardness and thickness, and subcrust flowability, as shown in Figure 30. The weighted bag storage method, Tables V and VI, predicts storage performance deep within a pile, where the material is essentially sealed from outside moisture penetration but yet is exposed to high pressures due to the pile weight (Figure 30). Storage performance of a solid under these two conditions can vary dramatically, as indicated by the results in Tables III-VI. Therefore, it is necessary to test storage performance under both conditions to develop treatments which will maintain satisfactory storage properties throughout an entire pile of material.

The treatments in Tables III-VI consist of 1 to 4% by weight of various additives with differing physical properties and chemical compositions. Successful treatments have included conventional conditioning agents, non-conventional conditioning agents, and waste materials. The additives in Tables III-VI were each tested with and without a neutralizing agent; without a neutralizing agent, coke oven AS generally has a pH of about 3. The costs of these treatments ranged from about \$1-\$4 per metric ton of AS or about \$1 per percent of additive.

B-P A/S PROPERTY IMPROVEMENT STORAGE TESTS



OPEN BIN TESTS

✓ MOISTURE PENETRATION
✓ CRUST HARDNESS
✓ CRUST THICKNESS
✓ SUBCRUST FLOWABILITY

WEIGHTED BAG TESTS

✓ DEEP-PILE CAKING TENDENCY

PILESTOR
JLB 7-23-93

FIGURE 30

Conversion of Low-Quality AS Fines to Storable Granular AS

NFERC has also developed and patented a process for converting poor-quality by-product AS fines into a large granular form with storage and use capabilities on par with other conventional granular fertilizers on the market. The process, Figure 31 consists essentially of reacting sulfuric acid with ammonia and simultaneously adding by-product AS fines; the hot reaction mixture formed by the fresh sulfuric acid and ammonia binds the AS fines together to produce granules. Approximately 30% by weight of the final granular AS product is supplied by the addition of sulfuric acid and ammonia to agglomerate the by-product AS fines. The AS fines are fed to a rotary drum granulator along with product recycle. The sulfuric acid along with an alum solution (binding agent) is sprayed on the rolling granulator bed, and ammonia is introduced under the bed. The granules exiting the granulator are fed to a countercurrent rotary drum dryer to remove excess water and then to a countercurrent rotary drum cooler to reduce product temperature sufficiently for satisfactory storage. This process has been successfully tested on both bench- and pilot-scale facilities.

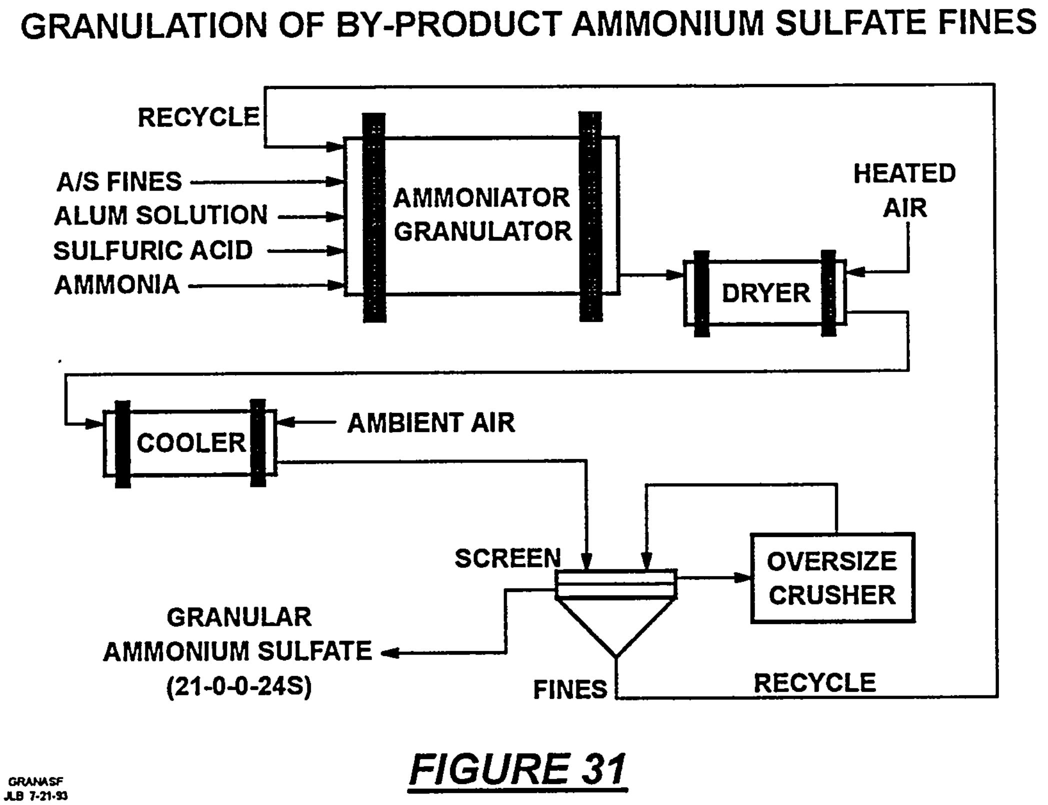


FIGURE 31

Deep-Welled Waste Ammonium Bisulfate Solutions - Conversion to Granular AS

NFERC developed a process to convert ammonium bisulfate solution, a highly acidic waste from synthetic fiber production that is normally disposed of by deep-well injection, to a satisfactory granular plant nutrient product, as illustrated in Figure 32. This process is an adaptation of the process for granulating AS fines using sulfuric acid-and ammonia to agglomerate the fines (Figure

31). The process consists of essentially the same steps as the AS fines granulation process except that the ammonium bisulfite solution is substituted for the sulfuric acid and ammonia. This process was successfully tested with a small-scale granulation unit to show the feasibility of the process; no further scale-up testing was done.

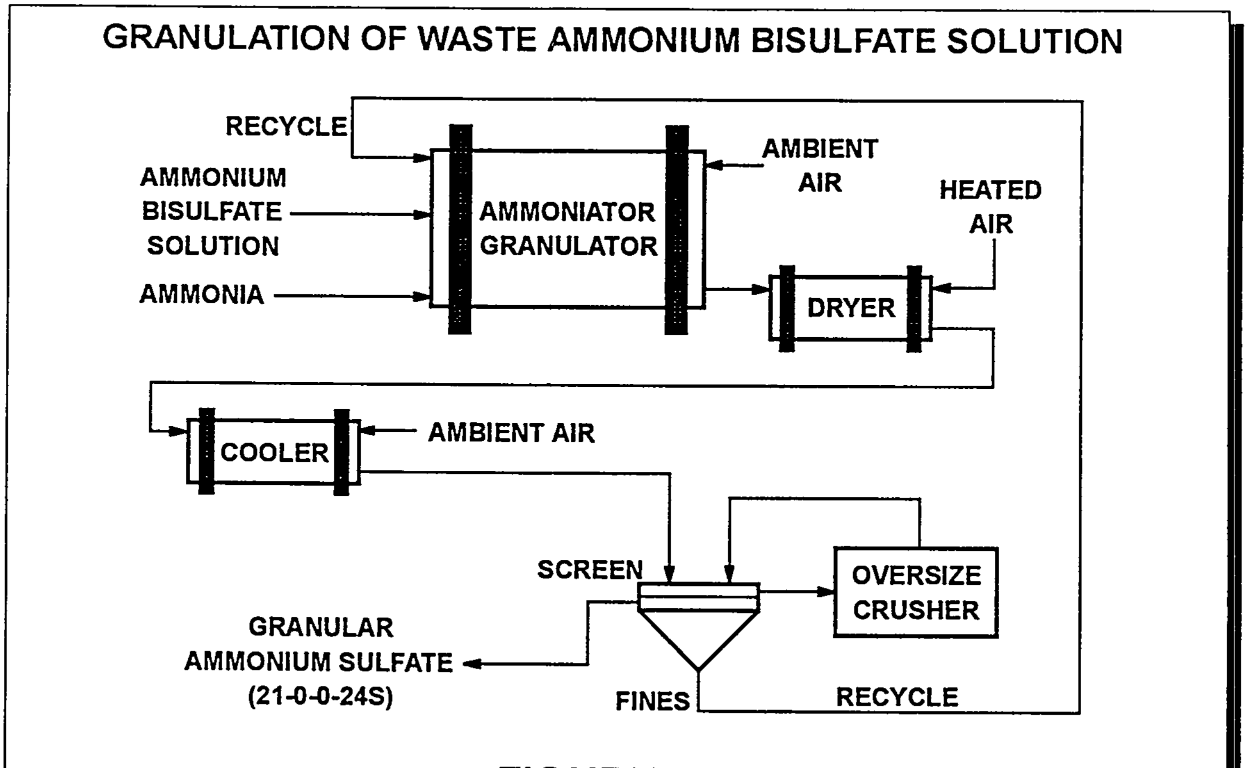


FIGURE 32

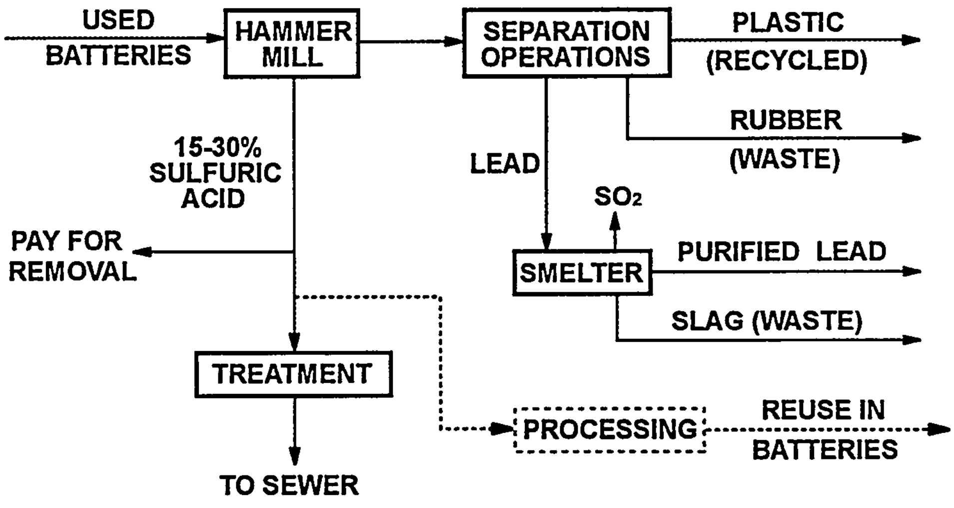
Wastes from Lead-Acid Battery Recycling/Secondary Lead Smelting

Of the 1.3 million metric tons of lead produced annually in this country, 900,000 metric tons are produced by secondary smelting from scrap, consisting mostly of used lead-acid batteries, Figure 33. Generally, only the lead and plastic (polypropylene) from the batteries is recycled. Reportedly, a satisfactory/economical process for recycling the used battery acid in new batteries has yet to be developed for widespread use; typically, the used battery acid is neutralized and disposed of in sewers. A typical secondary lead smelter generates several waste streams: aqueous waste from acid drained from crushed batteries, SO_2 emitted in smelting operations, hard rubber from old batteries (contaminated with lead), and slag (produced in smelter from iron addition to remove sulfide). There are 22 secondary lead smelters in this country and three primary smelters (from ore). Secondary smelters are located in Tennessee (3), Alabama (2), Georgia (1), Florida (1), Louisiana (1), Texas (2), Missouri (3), and Indiana (3). Nearly two thirds of 1990 lead production (approximately 800,000 metric tons) was destined for lead-acid battery production; this translates into 72,000,000 new car batteries for 1990. Since 80 to 90% of lead-acid batteries are recycled and a typical battery contains about 5 kilograms of sulfuric acid, it is estimated that

250,000,000 liters (about 350,000 metric tons) of sulfuric acid were generated from recycling of 1990's batteries.

The SO_2 gas waste stream from lead smelting operations can be used in production of ammonium bisulfite solutions (ABS) and ammonium thiosulfate solutions (ATS) for fertilizer use; these topics are discussed in the following section on SO_2 recovery. Waste hard rubber from secondary lead smelting is used to supply carbon needed in the smelter, and the excess rubber (containing imbedded lead particles from crushing) is sent to hazardous landfills. The slag is stabilized and sent to a hazardous landfills.

LEAD-ACID BATTERY RECYCLING



PBRECYCL
JLB 7-7-93

FIGURE 33

Over the past several years, NFERC has conducted laboratory tests, researched literature, and provided technical and marketing information to assist lead-acid battery recyclers/secondary lead smelters in choosing alternatives for management of waste sulfuric acid from spent lead-acid batteries. In particular, work conducted for one industry consisted of literature research, laboratory solubility tests, and material balance calculations to determine the effects of the addition/reaction of varying quantities of ammonia, fresh sulfuric acid or by-product AS, and by-product ABS to the spent battery acid on the plant nutrient value and solubility characteristics of the resulting AS/ABS finished product, Figure 34. This information was developed to provide the lead recycler with alternatives for sale of the spent acid by incorporating it into one of their currently generated by-products, ABS from SO_2 recovery, which the lead recycler was already marketing to a fertilizer producer (Figure 34). The lead recycler's proposed method for removing metals from the spent battery acid consisted of precipitation of metal sulfates by addition of ammonia and pH control, separation of the metal sulfates from the resulting AS solution by filtration or other means, and feeding of the removed metal sulfates to their smelting operations.

At the time this study was being conducted, the lead recycler was paying a substantial price to have the spent sulfuric acid shipped to distant locations for utilization by other industries. Prior to this method of waste management, the spent sulfuric acid was simply neutralized and sent to sewers, which was even more expensive than paying other industries for removal. The study on neutralization, purification, and incorporation of the spent sulfuric acid into the lead recycler's currently-generated by-product provided alternatives for reducing net costs for management of the waste acid.

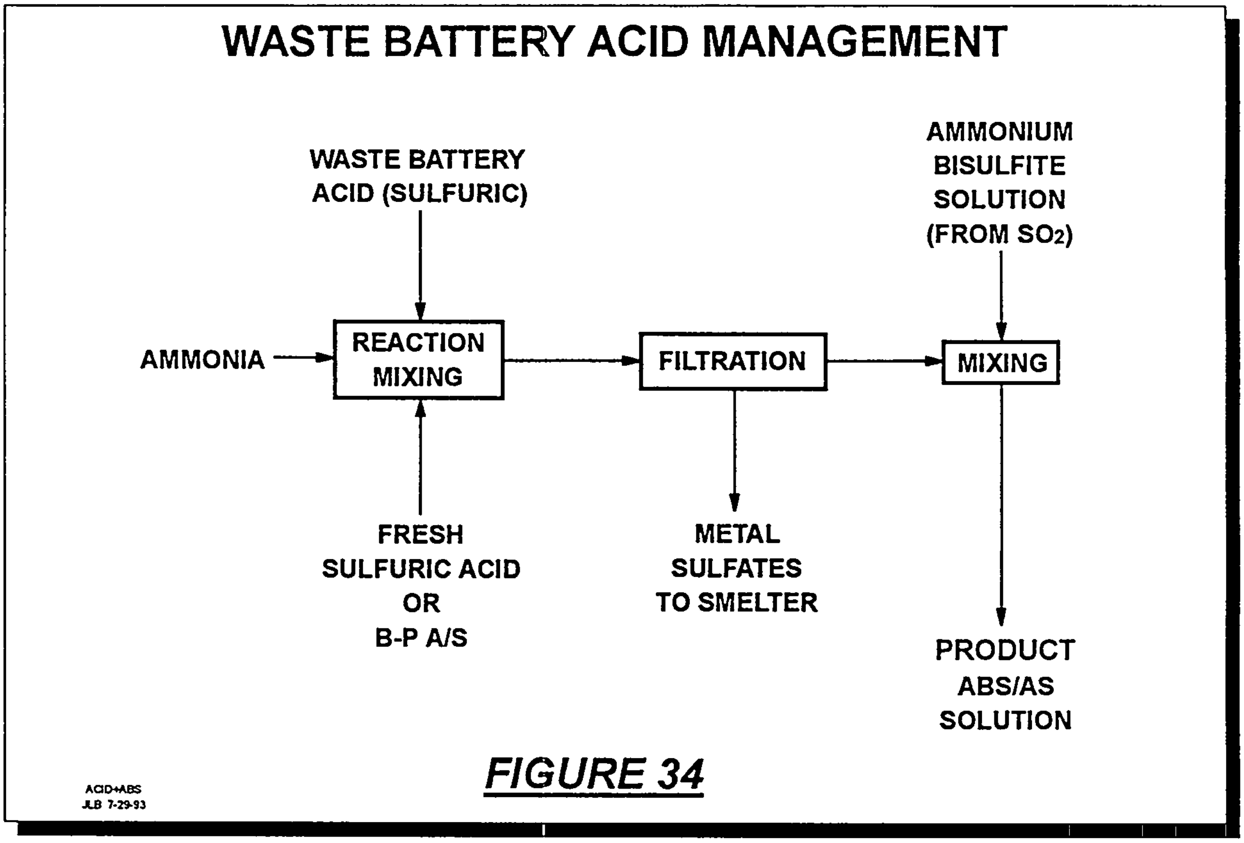


FIGURE 34

Further work consisted of literature research and calculations to provide information on the feasibility of utilizing the waste battery acid as part of the sulfuric acid feed stream to scrub ammonia from coke gases in generating by-product AS at a nearby coke plant, as depicted in Figure 35. Preliminary results indicated that both the lead recycler and the coke producer could save money with such an arrangement -- one industry's waste becomes another industry's raw material.

USING WASTE BATTERY ACID TO SCRUB COKE GAS

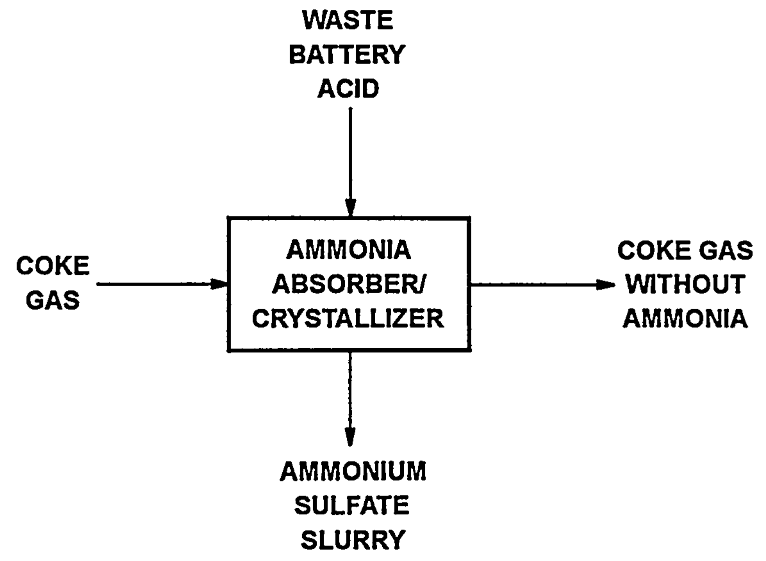


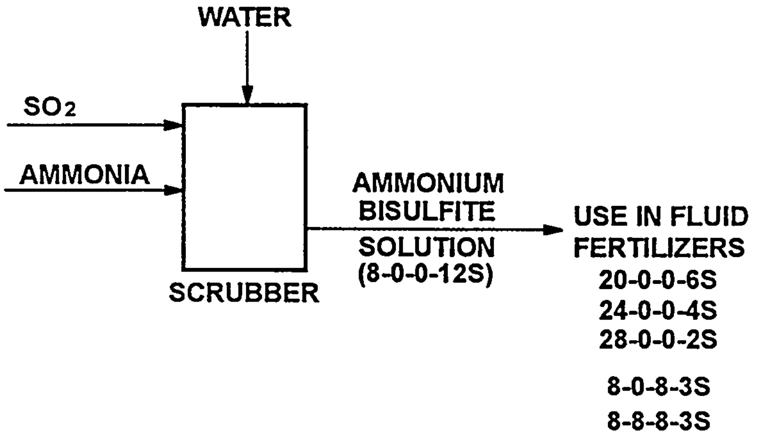
FIGURE 35

Recovery of SO_2 Emissions - Conversion to Ammonium Bisulfite and Ammonium Thiosulfate Solutions

SO_2 emissions can be recovered by scrubbing with ammonia, which results in formation of by-product ABS. The plant nutrient content of ABS typically ranges from 8-0-0-12S to 9-0-0-13S, making it a valuable source of both nitrogen and sulfur. Secondary lead smelters recover SO_2 by this process, shown in Figure 36, and sell the material for use in fluid fertilizers. This material is useful as a source of nitrogen and sulfur in blending with UAN solutions to produce a variety of grades, such as 20-0-0-6S, 24-0-0-4S, and 28-0-0-2S, as shown in Figure 36. These are much less expensive to produce than similar grades produced by blending UAN solutions with the higher priced 12-0-0-26S ATS solution, which is the conventional method. Also, the ABS solution is very versatile as a sulfur source in production of a wide variety of multicomponent solution or suspension blends, such as 8-8-8-3S and 8-0-8-3S solutions, as shown in Figure 36. Over the past few years, NFERC has conducted laboratory tests and provided technical and marketing information to assist the private sector in implementing SO_2 recovery systems via ABS production. Assuring a market for the ABS is of paramount importance in choosing this option for SO_2 recovery.

If a product with concentration higher than ABS is required due to long shipping distances, ATS solution can be easily produced from the ABS solution by the addition of elemental sulfur and additional ammonia in a second step, as shown in Figure 37. To assist the private sector in

PRODUCTION OF ABS/ATS SOLUTIONS FROM SO_2 EMISSIONS



WATER

SO_2

AMMONIA

SCRUBBER

AMMONIUM BISULFITE SOLUTION (8-0-0-12S)

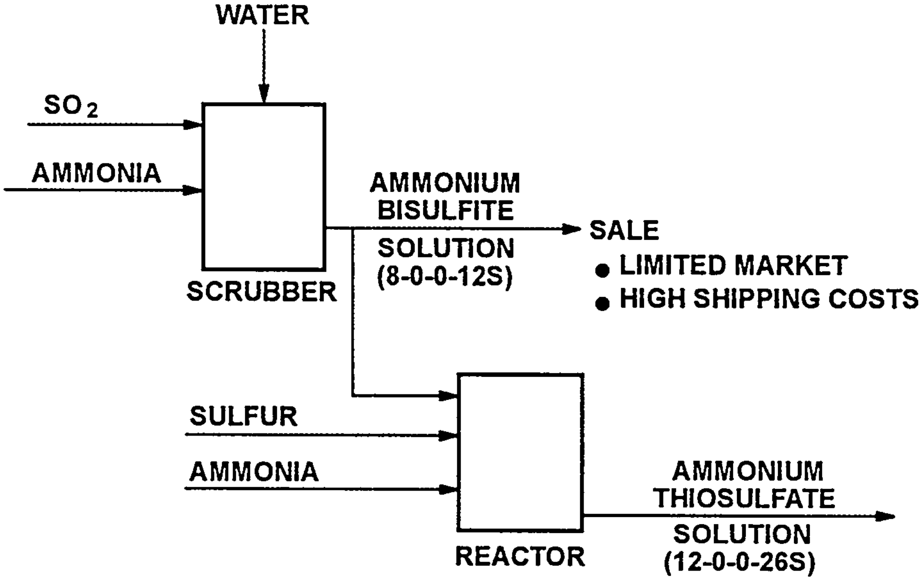
USE IN FLUID FERTILIZERS
20-0-0-6S
24-0-0-4S
28-0-0-2S

8-0-8-3S
8-8-8-3S

SO2-1
JLB 7-7-93

FIGURE 36

PRODUCTION OF ABS/ATS SOLUTIONS FROM SO_2 EMISSIONS



WATER

SO_2

AMMONIA

SCRUBBER

AMMONIUM BISULFITE SOLUTION (8-0-0-12S)

SALE
- LIMITED MARKET
- HIGH SHIPPING COSTS

SULFUR

AMMONIA

REACTOR

AMMONIUM THIOSULFATE SOLUTION (12-0-0-26S)

SO2-2
JLB 7-7-93

FIGURE 37

recovery of SO_2 by this procedure, laboratory tests were conducted at NFERC in which by-product sulfur (elemental, from natural gas production) was reacted with ABS solution and ammonia to successfully produce ATS with a grade of about 11-0-0-23S. Results show that altering process conditions somewhat would easily allow production of the conventional 12-0-0-26S grade ATS product.

Poultry Litter

About eight million metric tons of poultry litter is produced each year in the southeastern United States, much of it in the Tennessee Valley. Improper disposal of this waste results in surface and ground water contamination. NFERC is studying ways of dealing with this waste material. In one project, a poultry litter composting facility is being used to determine the effects of key variables in the composting process. In conjunction with the composting project, studies are underway on combining fresh or composted poultry litter with other materials to produce solid products suitable for a variety of applications, such as cattle feeds, multinutrient fertilizers, and soil amendments, as shown in Figure 38. Some work is being conducted in cooperation with Auburn University, the University of Arkansas, and Oregon State University. Also, combinations of poultry litter, zinc galvanizer waste, and waste polymers (Figure 38) have been produced in bench-scale equipment and field tested in Nebraska.

USEFUL PRODUCTS FROM POULTRY LITTER

CATTLE FEEDS
FRESH POULTRY LITTER
FOOD SUPPLEMENTS

SOIL AMENDMENTS
100% COMPOSTED POULTRY LITTER

ENAHANCED FERTILIZERS
MINIMUM 50% COMPOSTED POULTRY LITTER
OTHER PLANT NUTRIENTS

WASTE COMBINATIONS
COMPOSTED POULTRY LITTER
ZINC GALVANIZER WASTES
POLYMER WASTES

UTRUSE
JLB 7-22-93

FIGURE 38

In early 1992, a series of tests were conducted using a roll and die pellet mill to evaluate pelletizing composted broiler litter for use as enhanced fertilizers and soil amendments. Pellets produced for soil amendments consisted of 100% composted broiler litter, whereas the enhanced fertilizer pellets consisted of a minimum of 50% composted broiler litter in combination with various other fertilizer materials.

In March of 1992, seven enhanced fertilizers were produced for an ammonia volatilization study by the process illustrated in Figure 39. This process consists essentially of first pelletizing the composted litter, drying the pellets in a mechanical convection oven, crushing the dried pellets in a roll crusher, and then screening the crushed pellets to a size of 3-4 mm (-5 +10 Tyler mesh). Shown below are the grades of the seven enhanced fertilizers and the raw materials from which they were produced.

Nominal NPK Grade	Raw Materials
9 - 9 - 9	Composted broiler litter, urea, MAP, potassium chloride
12 - 4 - 6	Composted broiler litter, urea, MAP, potassium chloride
5 - 8 - 5	Composted broiler litter, ammonium sulfate (coke), MAP, potassium chloride
5 - 8 - 5	Composted broiler litter, ammonium sulfate (caprolactam), MAP, potassium chloride
8 - 8 - 8	Composted broiler litter, urea formaldehyde, MAP, potassium chloride
12 - 2 - 8	Composted broiler litter, methylene urea, potassium chloride
3 - 4 - 3	Composted broiler litter

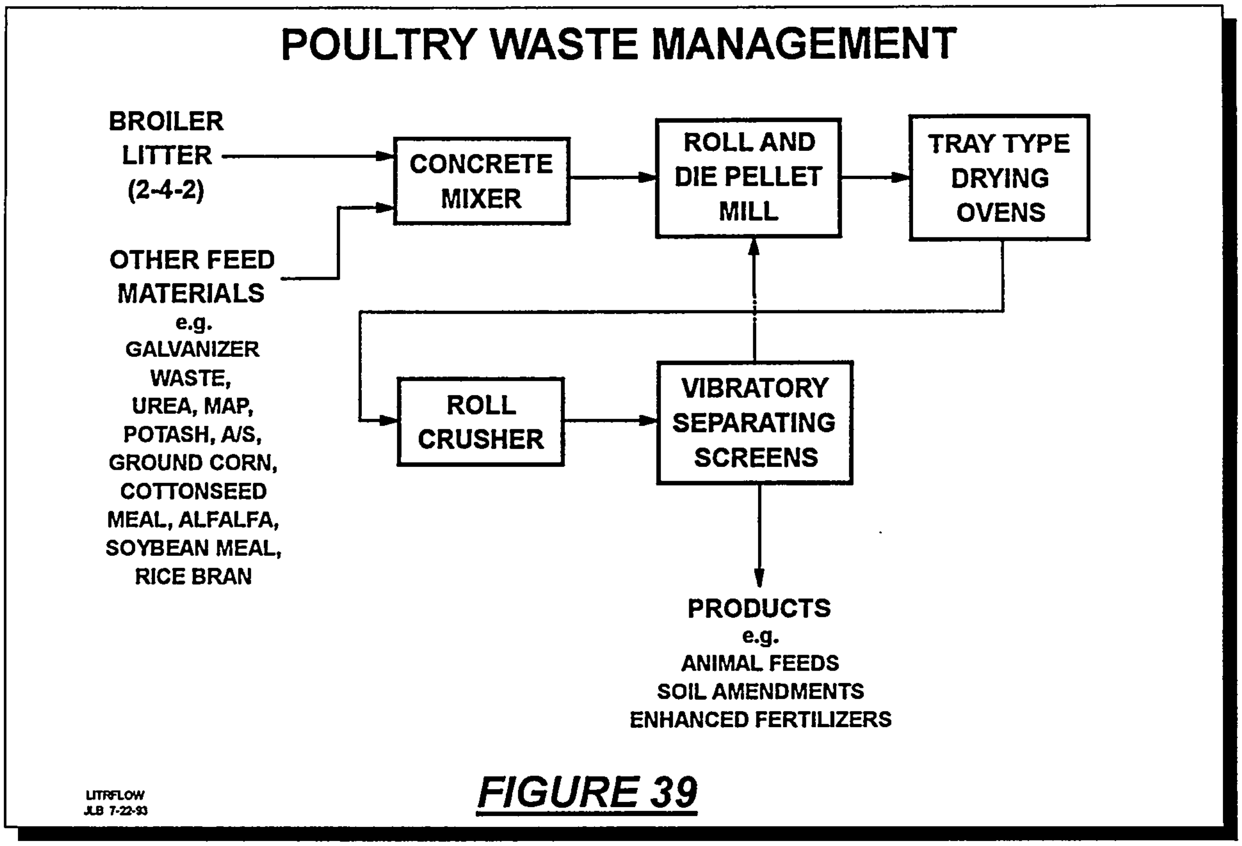


FIGURE 39

In July of 1992, four additional enhanced fertilizers were produced for greenhouse studies by the same process (Figure 39); grades and raw materials are shown below.

Nominal NPK Grade	Raw Materials
12 - 4 - 6	Composted broiler litter, ammonium sulfate (coke), MAP, potassium chloride
12 - 4 - 6	Composted broiler litter, ammonium sulfate (caprolactum), MAP, potassium chloride
12 - 4 - 6	Composted broiler litter, urea formaldehyde MAP, potassium chloride
12 - 4 - 6	Composted broiler litter, methylene urea, MAP, potassium chloride

Several enhanced fertilizers have been produced in the manner described above for various university greenhouse and plot studies, as shown below.

Date	Location	NPK Grade	Raw materials
4/92	Iowa State	6-2-1	Composted broiler litter, feathermill
4/92	University of Arkansas	12-4-8	Composted broiler litter, urea formaldehyde MAP, potassium chloride
		8-14-8	Composted broiler litter, urea, MAP, potassium chloride
		8-14-8	Fresh broiler litter, urea, MAP, potassium chloride
		8-8-8	Composted broiler litter, urea formaldehyde, MAP, potassium sulfate
7/92	Oregon State	12-4-8	Composted broiler litter, methylene urea, MAP, potassium sulfate
3/93	Colorado State and University of Nebraska	------	Composted broiler litter, galvanizer waste, cottonseed meal, wax, waste polymer
3/93	Florida A&M University	8.5-10.2-10.2	Composted broiler litter, urea, MAP, potassium chloride
		6.5-7.8-7.8	Composted broiler litter, ammonium sulfate (coke), MAP, potassium chloride
		3.2-3.8-3.8	Composted broiler litter, urea, MAP, potassium chloride

In August 1992, the roll and die pellet mill was used to pelletize five feed materials for cattle palatability studies at the University of Arkansas. The results of the study were used by a pelletizing company in Russellville, Arkansas, to determine the formulation used in production of 18 t (20 tons) of pelletized material for a large-scale feeding study. Raw materials consisted of fresh broiler litter combined with various supplements which included coarse ground corn, cottonseed meal, alfalfa, soybean meal, and rice bran. The raw materials and proportions of each formulation are shown below.

Raw Materials	**Proportion of Raw Materials, wt %**				
Broiler litter	50	50	50	30	50
Coarse ground corn	40	35	40	25	50
Cottonseed meal	10	10	--	15	--
Alfalfa	--	5	--	--	--
Soybean meal	--	--	10	--	--
Rice bran	--	--	--	30	--
Total	100	100	100	100	100

Five 23-kg (50-pound) batches were formulated and blended in a concrete mixer. The batches were pelletized using a die with a 51-mm (2-inch) length and a 13-mm (1/2-inch) pellet diameter. Holes of the die were packed with fresh litter to initiate pelleting. To ensure that no harmful bacteria remained and to prevent molding, the pellets from all five batches were dried in mechanical convection ovens at 71°C (160°F) for approximately 16 to 18 hours. The final moisture contents of the products ranged from 7-12%. These feed materials were shipped to the Cooperative Extension Service in Little Rock, Arkansas for the cattle palatability studies.

Wood Ash

NFERC has conducted research on sawmill wood ash fines which are currently landfilled for disposal. The material was pelletized, Figure 40, and tested in turfgrass plots at Alabama Agricultural & Mechanical (A&M) University to compare its effectiveness with other granular soil liming agents. The first research goal was to develop a method for processing the wood ash fines into a granular material to decrease dust levels sufficiently to allow satisfactory application to the soil. To accomplish this goal, the following product property criteria were established as requirements for the wood ash granules:

- Minimum crushing strength of 1.8 kg (4 pounds) to withstand handling.
- Short term water solubility to allow turfgrass to immediately obtain the liming effects.
- Granule size in the range of 2 to 4 mm (-5 +10 Tyler mesh).
- Binders harmless to grass and not to exceed 5% of the total formulation (to prevent being cost prohibitive).

USE OF WOOD ASH AS LIMING AGENT

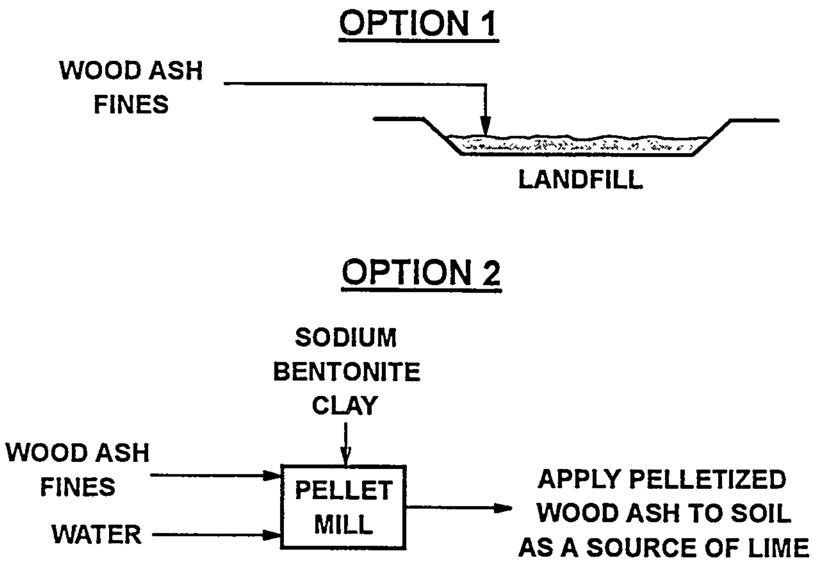


FIGURE 40

In February 1992, feasibility tests were conducted using three types of agglomeration equipment: a roll compactor, a pan granulator, and a roll and die pellet mill. The pellet mill showed the greatest feasibility for agglomerating the wood ash fines. Tests were conducted with the pellet mill using several dies with varying length-to-diameter ratios. To aid in pelletizing, water was added to the wood ash; the raw material mixture contained approximately 60-70% wood ash, 5% binder, and the remaining percentage as water. Results indicated that use of sodium bentonite clay as a binder yielded the most acceptable product.

After pelletizing, the wood ash was dried in mechanical convection ovens. The resultant dried pellets appeared to be in good condition and met the required criteria (above) with respect to solubility and crushing strength. Then, the pellets were crumbled with a roll crusher and screened to a size range of 2 to 4 mm by a process similar to that used for the broiler litter (Figure 39).

Alabama A&M University conducted turfgrass plot studies with pelletized wood ash material to compare its liming effect with conventional granular limestone. The Alabama A&M study (AUTRC-TVA Project No. 91-05 A&M titled "Wood Ash Utilization in Fine Turf Liming and Fertilization") reported that some of the pellets did not break down in the field. Alabama A&M has proposed additional studies to develop a pellet which will not harden when exposed to high humidity after application. The study also recommended searching for a wood ash with a higher calcium carbonate equivalency (CCE) than the material supplied, which had a CCE of 30-35%. A material with a CCE of 50% or greater would be expected to produce a better liming product.

Utilization of Cellulosic Wastes in Plant Nutrient Management

Large quantities of cellulosic wastes are being disposed of in landfills; it is estimated that cellulosic wastes currently comprise 60-70% of all municipal landfill disposals. To address this environmental problem, NFERC is studying methods to extract the cellulosic components from these wastes and convert them to useful compounds for coatings on fertilizers that will control the release rate of nutrients into the soil and thereby minimize or eliminate surface and ground water contamination. Much of the current ground water contamination is attributable to application of conventional solid fertilizers which have high dissolution rates and are therefore subject to rapid leaching and runoff by rainfall. NFERC's objective is to use various cellulosic wastes as feedstocks for conversion to cellulose derivatives to coat or mix with fertilizers for reducing nutrient release rates. Conventional cellulose derivatives pose no environmental concerns, and the cost of the cellulosic waste feedstocks would be very low.

NFERC has categorized cellulosic wastes into two large categories and several small categories based on the source of the waste. The large categories are municipal solid waste (MSW) and paper mill waste (PMW). MSW consists of newsprint, magazines, corrugated paper containers, etc. PMW consists of sludge from the paper mill industries. This sludge can be produced from kraft, sulfite, sulfate, soda, or lime pulping processes. For example, the sludge from the kraft pulping process consists of approximately 5% hemicellulose, 26% cellulose, and 20% lignin. The small categories of cellulosic wastes include cotton gin trash, bur trash, sawdust, etc. Cotton gin trash consists of 28% hemicellulose, 38% cellulose, and 26% lignin. Bur trash consists of 30% hemicellulose, 40% cellulose, and 25% lignin.

NFERC's cellulosic waste utilization study presently involves information gathering from a number of sources, including personal contacts, literature search, and conferences. The information, which includes lists of cellulosic wastes and by-products, yearly tonnage, contaminants, costs, specific company names, and contact persons is compiled in a database.

Cellulosic derivatives of interest for controlled nutrient release properties are ethylcellulose, methylcellulose, cellulose acetate, and cellulose nitrate. Studies are being conducted on potential conversion processes for production of the cellulosic derivatives, including chemical reactions, initial and final cleanups, and disposal of the wastes/by-products remaining from the conversion processes. Laboratory experiments will be conducted to verify technical feasibility of the proposed processes. After the feasible processes are selected, cost estimations will be made for modifications to existing manufacturing equipment, new equipment, and operating costs required for conversion of the wastes to useful cellulosic derivatives.