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PRODUCTION OF AMMONIUM SULPHATE FROM UTILITY BOILER WASTE GAS

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RESUME

GE Environmental Systems a mis au point et breveté un procédé unique qui produit du sulfate d'ammonium de haute qualité à partir de gaz résidu de chaudière à utilités. La plupart des chaudières à utilités ont des niveaux significatifs de dioxyde de soufre (SO_2) qui réagit avec l'eau de l'atmosphère pour donner de l'acide sulfurique. Dans le monde entier, les agences de protection de l'environnement imposent que les utilités réduisent leurs émissions de SO_2. Le nouveau procédé GE combine notre leadership mondial dans la technologie du contrôle du SO_2 avec un procédé chimique breveté qui, simultanément, élimine SO_2 et produit du sulfate d'ammonium.

Le procédé fait réagir les oxydes de soufre indésirables avec l'ammoniac pour donner du sulfate d'ammonium. De plus, ce procédé efficace au point de vue énergie utilise l'énergie résiduaire des gaz d'échappement de la chaudière pour évaporer l'eau en excès et cristalliser le produit. Ainsi, deux des trois éléments exigés dans la production de sulfate d'ammonium sont gratuits dans le procédé GE. Le premier système commercial d'oxydation forcée du sulfate d'ammonium (AFO) est en cours d'installation à l'unité de carburants de synthèse de Great Plains, près de Beulah, ND, Etats-Unis, de la Société de Gazéification du Dakota (DGC). Cette unité est conçue pour produire 600 t/j de sulfate d'ammonium granulé.

Ce procédé produit le sulfate d'ammonium de meilleure qualité tout en purifiant l'air simultanément des oxydes de soufre indésirables. Cette communication présente le procédé, la première unité industrielle, la qualité et les contrôles de qualité pour le produit et la rentabilité de la production du sulfate d'ammonium.

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INTRODUCTION

The presence of sulphur oxides (SO_2, SO_3) in a boiler flue gas has been identified and recognized by most environmental protection agencies around the world as a source of « acid rain ». Acid rain results when sulphur oxides react with water to form sulphuric acid and then return to the earth with the rain. This has had detrimental effects in many areas world wide. As a result, specific technologies have been developed to capture the sulphur oxides and convert them to byproducts, typically gypsum or calcium sulphite. Gypsum has a relatively low value in the wall board and cement manufacturing industry, and calcium sulphite has little or no value. Both products are generally landfilled as a waste product.

In 1987, GEESI was awarded a patent for the removal of sulfur oxides from gases and the simultaneous production of ammonium sulfate. In 1991 GEESI and Dakota Gasification Company (DGC) installed a 3 MW equivalent process demonstration plant on a slip stream from the DGC boiler flue gas. The purpose of the pilot plant was to demonstrate the following:

- Greater than 95% SO_2 removal
- Less than 10 ppm ammonia slip
- No increase in opacity when compared with a limestone operation
- 95% pure ammonium sulfate production

The results of the process demonstration plant, detailed below, were outstanding:

- Greater than 99% SO_2 removal
- Less than 10 ppm ammonia slip
- No increase in opacity
- Greater than 99% pure ammonium sulfate

After more than a year of operation, testing in the process demonstration unit was discontinued and the unit was dismantled to install the commercial flue gas desulfurization system.

COMMERCIAL ORDER

As a result of the performance of the process demonstration plant and the quality of the ammonium sulfate byproduct produced, General Electric Environmental Services, Inc. (GEESI), Morrison Knudsen Corporation (MK) and the Dakota Gasification Company (DGC) entered into a contract to design, procure, install, start-up and test the first ammonium sulfate system at DGC's Great Plains Synfuels plant located near Beulah, ND. The project was awarded in March of 1994 and first flue gas is scheduled for June of 1996.

PROCESS CHEMISTRY

The chemistry for the production of ammonium sulfate from boiler flue gas is simple. The sulfur dioxide, SO_2 from the flue gas, is absorbed in an open spray tower by water according to the following equation:

$$SO_2 + H_2O \longleftrightarrow H_2SO_3 \qquad \text{EQ. (1)}$$

The H_2SO_3 is then reacted with ammonia to form ammonium sulfite according to the following equation:

$$H_2SO_3 + 2NH_3 \longleftrightarrow (NH_4)_2SO_3 \qquad \text{EQ. (2)}$$

The ammonium sulfite further reacts with H_2SO_3 to form ammonium bisulfite according to the following equation:

$$H_2SO_3 + (NH_4)_2SO_3 \longleftrightarrow 2(NH_4)HSO_3 \qquad \text{EQ (3)}$$

The ammonium sulfite is also oxidized in the absorber to form ammonium sulfate according to the following equation:

$$(NH_4)_2SO_3 + \tfrac{1}{2}O_2 \longleftrightarrow (NH_4)_2SO_4 \qquad \text{EQ. (4)}$$

Similarly, ammonium bisulfite is also oxidized in the absorber to form ammonium bisulfate according to the following equation:

$$(NH_4)HSO_3 + \tfrac{1}{2}O_2 \longleftrightarrow (NH_4)HSO_4 \qquad \text{EQ. (5)}$$

The ammonium bisulfate then can be further neutralized in the presence of ammonia and water to form ammonium sulfate according to the following equation:

$$(NH_4)HSO_3 + NH_3 + H_2O \longleftrightarrow (NH_4)_2SO_4 \qquad \text{EQ (6)}$$

All of these reactions take place in the absorber vessel. The ammonium sulfate is recovered through crystallization when the excess water is evaporated in the prescrubber at the absorber.

BASIC PROCESS REVIEW

The basic process design for an ammonium sulfate process is shown in Figures 1-2. The flue gas leaving an electrostatic precipitator is processed by a prescrubber and absorber. The flue gas enters the counter current prescrubber just above liquid level. The hot flue gas is contacted with a recirculating spray of ammonium sulfate slurry. In this vessel, the flue gas becomes saturated by evaporation of water from the recirculating slurry. The saturated flue gas leaves the prescrubber through a mist eliminator designed to remove slurry entrained in the flue gas.

After leaving the prescrubber, the flue gas enters a counter current absorber where it is contacted by a recirculating solution of subsaturated ammonium sulfate liquor. Ammonia is added with the oxidation air to maintain the recycle liquor at a pH of 5.2-5.8, thus ensuring the desired SO_2 removal is achieved. The cleaned flue gas then passes through two stages of high efficiency mist eliminators to remove any entrained droplets.

The process functions of SO_2 absorption and oxidation are separated from the function of ammonium sulfate crystallization. SO_2 absorption and oxidation take place in the absorber while ammonium sulfate crystallization takes place in the prescrubber. The process functions of SO_2 absorption, reaction with ammonia, oxidation to ammonium sulfate and crystallization can occur simultaneously in a single vessel. However, it is more cost effective to separate these two functions when the fuel sulfur content is greater than 3-4 wt% sulfur.

At the DGC plant, the design fuel sulfur content is over 5 wt% and the maximum fuel sulfur content exceeds 7 wt%. The nature of the DGC fuel made installation of the prescrubber the most cost effective alternative.

The thermal energy associated with the flue gas is used to evaporate water from the prescrubber slurry as the flue gas is saturated. The evaporation of water causes crystallization of ammonium sulfate product and liquid level reduction in the prescrubber vessel. The subsaturated ammonium sulfate solution in the absorber is used to wash the prescrubber mist eliminator and maintain the prescrubber vessel liquid level. As a result, subsaturated ammonium sulfate solution is introduced into the prescrubber where the excess water is evaporated and crystallization of product occurs.

In the absorber, the SO_2 is removed and reacted with ammonia. The ammonia is introduced into the absorber with the oxidation air. The process can use either anhydrous or aqueous ammonia. If anhydrous ammonia is used, the ammonia is stored in a pressurized or refrigerated vessel and pumped as a liquid to a vaporizer. The vaporizer typically uses steam to vaporize the ammonia prior to introducing it into the oxidation air. If aqueous ammonia is used, the ammonia is stored in a tank and pumped to the absorber directly. With either form of the reagent, the ammonia is added to the absorber to control pH.

Oxidation air is introduced into the absorber to oxidize the ammonium sulfite to ammonium sulfate. Ammonium sulfate solution (10-25 wt% dissolved solids) is bled from the absorber to the prescrubber to maintain level in the prescrubber tank. The fresh make up water required by the process is added to the absorber reaction tank to maintain tank level.

Slurry is bled from the prescrubber to a dewatering hydroclone which increases the slurry density from 10 wt% slurry to 50 wt% slurry. The underflow is fed directly to a centrifuge. A tank can be installed for surge capacity if there is a desire to separate the absorber and dewatering areas. The overflow of the hydroclone is returned to the prescrubber. The hydroclone underflow slurry is dewatered to 99% solids using a centrifuge.

To maximize the byproduct value in the U.S., the ammonium sulfate material in the storage silo is converted from sugar like crystals to the larger granular crystals. To accomplish this, the raw unprocessed ammonium sulfate material is fed from an intermediate storage system to the compaction system where it is mixed with recycle material and fed to a compactor. The compactor presses the material at a high force producing large flakes of ammonium sulfate. This flake is ground in sizing mills, screened and dried. The final on-size product is sent to a large storage dome. All of the compacted product that does not meet the required quality is recycled to the beginning of the compaction process and mixed with fresh feed material. This provides for a closed loop system.

PRODUCT QUALITY

The quality and thus the value of the ammonium sulfate byproduct is subject to four basic physical criteria; purity, size, moisture and hardness. The following represents the quality of the ammonium sulfate produced in this unique process.

Purity	99.0 %
Size	
- Granular Grade Particle Size	1.0 - 3.5 mm
- Standard Grade Particle Size	0.1 - 0.8 mm
Residual Moisture	< 1.0 wt%
Hardness	Less than 5% loss

Purity

The purity of the ammonium sulfate is a function of the purity of the various feed stocks. In the GEESI process, no additives or other compounds are added in the production of ammonium sulfate. The GEESI process can use ammonia in any form. The commercial unit in North Dakota will be using anhydrous ammonia because it is available at site. The process is equally effective when using aqueous ammonia containing various concentrations of ammonia in water. The process consumes water by saturation of the flue gas. The water in the aqueous ammonia simply displaces a portion of the required make-up water to the system. This flexibility in reagent use allows the producer of the ammonium sulfate the greatest economic benefits from the selection of the feed stock.

In the GEESI process, the sulfur required to produce ammonium sulfate is recovered as unwanted sulfur dioxide in the boiler flue gas. The SO_2 is removed with ammonium sulfate solution and reacted with excess ammonia and air to form ammonium sulfate. The presence of other impurities in the make-up water and/or the flue gas are the only sources of impuritifes in the final product. Typically flue gas will have trace amounts of hydrochloric acid (HCl) and fine particulate ash. The make-up water will also typically contain some low level chloride ions and other trace salt compounds.

The HCl in the flue gas is readily removed in the prescrubber and reacted with ammonia to form ammonium chloride (NH_4Cl). For most fuels the chloride concentration is considerably lower than the sulfur concentrations. In this process, the chloride species is allowed to increase in the process liquor until it co-precipitates with the ammonium sulfate. Typically this results in a residual ammonium chloride concentration of less than 0.5 wt% of the total product. In a rare occurrence where a relatively low sulfur coal has a high chloride content, the resulting ammonium sulfate product may be 97.5 wt% ammonium sulfate and 2.5 wt% ammonium chloride. This results in a product that is 21.3 wt% N, 23.7 wt% S and 1.5% CL. Thus, the presence of ammonium chloride actually increases the nitrogen content of the final product.

The particulate in the flue gas may vary based on boiler and ESP performance. Typically during normal operation of a modern precipitator system, not enough ash is present to significantly impact the purity of the ammonium sulfate byproduct. Table 1 shows the byproduct purity of various high quality ammonium sulfate. The presence of trace metals in the food and reagent grade are important in the manufacture of ammonium sulfate. During boiler and or ESP upsets, ash content in the flue gas may dramatically increase thus negatively impacting the purity of the ammonium sulfate.

Table 1 - Various Grades of Ammonium Sulfate

	Fertilizer Grade	Food Grade	Reagent Grade
Ammonium Sulfate	99.3%	99.3%	99.7%
Insoluble Matter	NM	0.3%	0.005%
Free Sulfuric Acid	0.05%	0.01%	0.005%
Moisture	1.0%	0.15%	0.15%
Arsenic	NM	0.5 ppm	0.5 ppm
Iron	27 ppm	15 ppm	5 ppm
Selenium	NM	5 ppm	5 ppm
Other Heavy Metals	10 ppm	8 ppm	3 ppm

NM = Not measured

The GEESI system uses a solids waste removal system to remove captured particulate from the ammonium sulfate slurry prior to dewatering, thus maintaining the product purity. Typically, removing particulate matter takes on a two step process. In the first step, the particulate impurity is separated from the ammonium sulfate slurry in a device called a hydrocyclone. The hydrocyclone functions as a particulate separation device based on particle size. Typically, the ammonium sulfate particles at this stage of the process are 100-900 microns. The ash particulate removed from the boiler typically range less than 10 microns. The hydrocyclone uses centrifugal action which causes the smaller lighter particles to move to the hydrocyclone overflow and the larger heavier particles to move to the hydrocyclone underflow. In this way, the smaller impurity particles are separated from the larger product particles.

The second step of this process is to take the hydrocyclone overflow, which is rich in impurity particles, and process it with a higher pressure filter press (see Figure 3). The dilute slurry (1-3 wt% suspended solids) is fed to a filter press directly from a filter press feed tank which takes its feed from the hydrocyclone overflow. From the filter press feed tank, slurry is pumped at higher pressure through a multi-stage filter press which allows the liquor to pass through while capturing the solids. When the filter feed pump discharge registers a high pressure, the filter cake which is formed is washed with clean water and pressed dry (~50-60 wt% solids). The cake is then discharged into a waste bin to be disposed of with the boiler ash.

In the event that undesirable metal species are soluble at the operating pH, the pH of the slurry in the filter press feed tank can be raised to precipitate out the metal ions as metal hydroxide prior to the filtering step. This pH adjustment precipitates the heavy metals which are then removed by the filter press (See Figure 4).

Table 2 shows the purity of the ammonium sulfate byproduct produced in the process demonstration unit in North Dakota. The actual plant flue gas and available reagent were used to produce this byproduct. In this small unit, all of the impurities in the system were allowed to co-precipitate with the final product. No steps were taken to improve the product purity with a filter press or similar device. The flue gas at the DGC plant is relatively free of chlorides and ash so the impurities in the feed stock were low. However, on two occasions the boiler system had a major upset resulting in larger amounts of ash being absorbed in the FGD system. With no way to remove the ash from the slurry, the concentration of fine particulate in the hydrocyclone overflow was high. As can be seen from Table 2, the product purity did not suffer significantly.

Table 2 - FGD Ammonium Sulfate vs. Various Grades of Ammonium Sulfate

	DGC Ammonium Sulfate	Fertilizer Grade	Food Grade	Reagent Grade
Ammonium Sulfate	99.6%	99.3%	99.3%	99.7%
Insoluble Matter	0.03%	NM	0.3%	0.005%
Free Sulfuric Acid	0.01%	0.05%	0.01%	0.005%
Moisture	< 1.0%	1.0%	0.15%	0.15%
Arsenic	< 1.0 ppm*	NM	0.5 ppm	0.5 ppm
Iron	33 ppm	27 ppm	15 ppm	5 ppm
Selenium	< 1.0 ppm*	NM	5 ppm	5 ppm
Other Heavy Metals	4 ppm	10 ppm	8 ppm	3 ppm

* Detectable limit of the instrument

Size

Size is also a major criterion of the ammonium sulfate byproduct value. There are essentially two grades of ammonium sulfate particles that can be generated by the GEESI process. The first grade is "standard" grade ammonium sulfate that ranges in particle size from 0.1 mm to 0.8 mm. Figure 5 shows the particle size distribution from this process. This is the distribution of the solids as they are recovered from a centrifuge and dried. This particle size distribution requires no additional cost to generate.

Typically, the U.S. markets blend ammonium sulfate with other nitrogen, phosphorous, and potassium compounds. Blending processes require that all of the particles from each of the sources be essentially the same size. This minimizes the segregation of the blends during storage, transportation and application. Most blended products require the individual compounds to have a particle size range such as 1.0 - 3.5 mm. This size ammonium sulfate is commonly referred to as a granular grade ammonium sulfate.

When a granular product is required, the GEESI process uses a compaction system that takes the dewatered and dried standard grade ammonium sulfate and processes it with a roll press compactor (see Figure 6). In this process, the fresh feed ammonium sulfate material is mixed with the fine particles from the compaction process which are recycled to the front of the process. The recycle and fresh feed ratio are controlled to produce the ammonium sulfate product with the hardest particle characteristics. The fresh feed and recycle ammonium sulfate are mixed in a pug mill mixer to insure the recycle and fresh feed material are fully mixed prior the compactor.

The material is fed to a compactor feed screw system that feeds the compactor rolls at high force. The material is forced between the rolls that press or compact the solids into a hard flake which is discharged into a flake breaker. The flake breaker granulates the large flakes into smaller pieces which can then be sized in a series of sizing mills. The sizing mills uses hammers and/or chains and specifically sized screens to generate a larger fraction of the material between one and three millimeters in diameter. After being discharged from the mill the particles are screened with all particles less than one millimeter being recycled to the beginning of the process. The particles greater than one millimeter are sent to a dryer where the residual moisture is dried to less than one weight percent.

After being dried, the material is cooled to minimize the amount of moisture adsorbed during storage and handling. The cooled product is screened in a two stage screening process with the material over three millimeters returned to the sizing mills and the material less than one millimeter recycled to the beginning of the process. The final on-size product is transported to the storage dome. In this way the size distribution of the granular product is controlled very closely.

Moisture

It is important to maintain the moisture of the final product as low as is possible. Ammonium sulfate is highly hydroscopic and will have a tendency to set up or bridge in storage. To minimize this potential, the GEESI process uses three specific processing steps to control moisture in the final product.

First, the product is discharged from the centrifuge at approximately 1 wt% moisture. This material is dried immediately to less than 1 wt% moisture using a rotary drum dryer. This makes the moisture of the fresh feed material less than 1 wt% moisture which is important in the control of the hardness of the compacted flake that is produced.

During the process of initial compacting, sizing and screening the material has a trace amount of moisture added to enhance the hardness of the compacted flake. This and any residual moisture is then removed in the final product dryer. The purpose of the second product dryer is to dry any residual moisture from the compacted material to ensure that the final moisture requirements are met.

Finally, as an added measure, the material is cooled to less than $40^{\circ}C$ before being sent to storage. Cooling the product prior to storage minimizes the potential for the ammonium sulfate to absorb water from the air. This helps prevent the bridging phenomenon.

Hardness

The hardness of ammonium sulfate is particularly critical for the granular grade material. The granular material can not be too soft or too brittle or it will not be able to stand up to the rigors of transportation, handling and ultimately blending. During a number of steps in the process, the material has a trace amount of moisture added to the particles to soften and then re-crystallize the surface of the particles. This re-crystallization of the particle surface adds great strength and hardness to the particle.

The hardness is measured by a specific test which involves combining a known weight of steel balls and a known amount of ammonium sulfate on a series of sieves. The entire apparatus is shaken for a set length of time. The amount of material that passes a one millimeter screen during this test is an accurate reflection of the hardness of the material. Typically, the material is deemed acceptable if less than five percent of the original sample passes a one millimeter screen as a result of this test. The material produced in the GEESI process typically averages 1-2% attrition.

PROCESS ECONOMICS

The economics of this process are very important. As with most other forms of manufacture of ammonium sulfate, the GEESI process produces ammonium sulfate as a byproduct. In this case, the production of ammonium sulfate is a byproduct of cleaner air and energy. Typically, the utility or industrial customer are under regulatory compliance to remove SO_2 from the gas exiting their stack.

For a typical 500 MW boiler burning 3 % sulfur fuel, the utility may be required to reduce the SO_2 emissions to 5% of the uncontrolled emission. Traditional technologies will cost the utility approximately $240/ton of SO_2 removed. To make standard grade ammonium sulfate using the GEESI process will cost approximately 20% more capital than traditional technologies. Assuming $180/ton for ammonia consumed by the process, the utility or industrial producer would need to sell the standard grade ammonium sulfate at $38/ton to equal the life cycle economics of the traditional control technologies.

To produce granular ammonium sulfate an additional 20% capital investment for the compaction granulation system is required. For this added investment, the sale price of the ammonium sulfate would need to be $48/ton to have equivalent life cycle economics with traditional technologies. Selling either the standard or the granular grade ammonium sulfate above these threshold values makes the utility or industrial producer more cost effective. For example, at $90/ton for ammonium sulfate in the same economic model, the utility or industrial producer will reduce his cost of environmental compliance by 55% of that using traditional technologies.

With these type of economics for production, the ammonium sulfate made in this process becomes competitive with other nitrogen fertilizers solely on a per ton of nitrogen basis.

Table 3 - Price Comparison of Ammonium Sulfate with Other Nitrogen Fertilizers

Fertilizer	$/Ton	$/Ton N
Urea	$ 200	$ 429
Ammonium Nitrate	$ 160	$ 457
Ammonium Sulfate	$ 90	$ 424

There are additional beneficial effects of the ammonium sulfate that other nitrogen fertilizers do not have and thus make the value of the ammonium sulfate far greater than simply for its nitrogen content alone.

Table 4 - Benefits of Ammonium Sulfate

- Non volatile nitrogen source
- Sulfur is an ideal micro-nutrient for many crops
- Non-explosive
- Compaction system ideal place for slow release polymer addition

As the world requires increasingly stringent controls of air quality, the sources of sulfur in soils are diminishing. Studies in the U.S., Europe and Asia show a steady decrease of sulfur in the soil on each of these continents. Since many crops greatly benefit from sulfur and nitrogen in non-volatile release form, the use of ammonium sulfate as a high valued fertilizer is steadily increasing.

The GEESI process provides an additional source of high quality, high purity ammonium sulfate at competitive prices while simultaneously reducing the emission of harmful acid gasses to the environment.

CONCLUSION

- The GEESI ammonia scrubbing system was successfully demonstrated at a 3 MW scale with the Dakota Gasification Company. The GEESI system was selected for installation on a 300 MW equivalent steam generating boiler at Dakota Gasification Company's Great Plains Synfuels plant.
- The GEESI process produces a very high quality, high purity ammonium sulfate byproduct in both standard and granular grades.
- The economics of this unique system allow for production of a low cost ammonium sulfate byproduct which is competitive with other nitrogen fertilizers on a per ton nitrogen basis.
- In addition to its nitrogen value, the ammonium sulfate byproduct also provides crops with the needed micro-nutrient sulfur.
- Decreasing sulfur levels in the soils throughout the world ensures the sustained long term growth of ammonium sulfate use.

Figure 1: GE Ammonium Sulfate Process Absorber Island

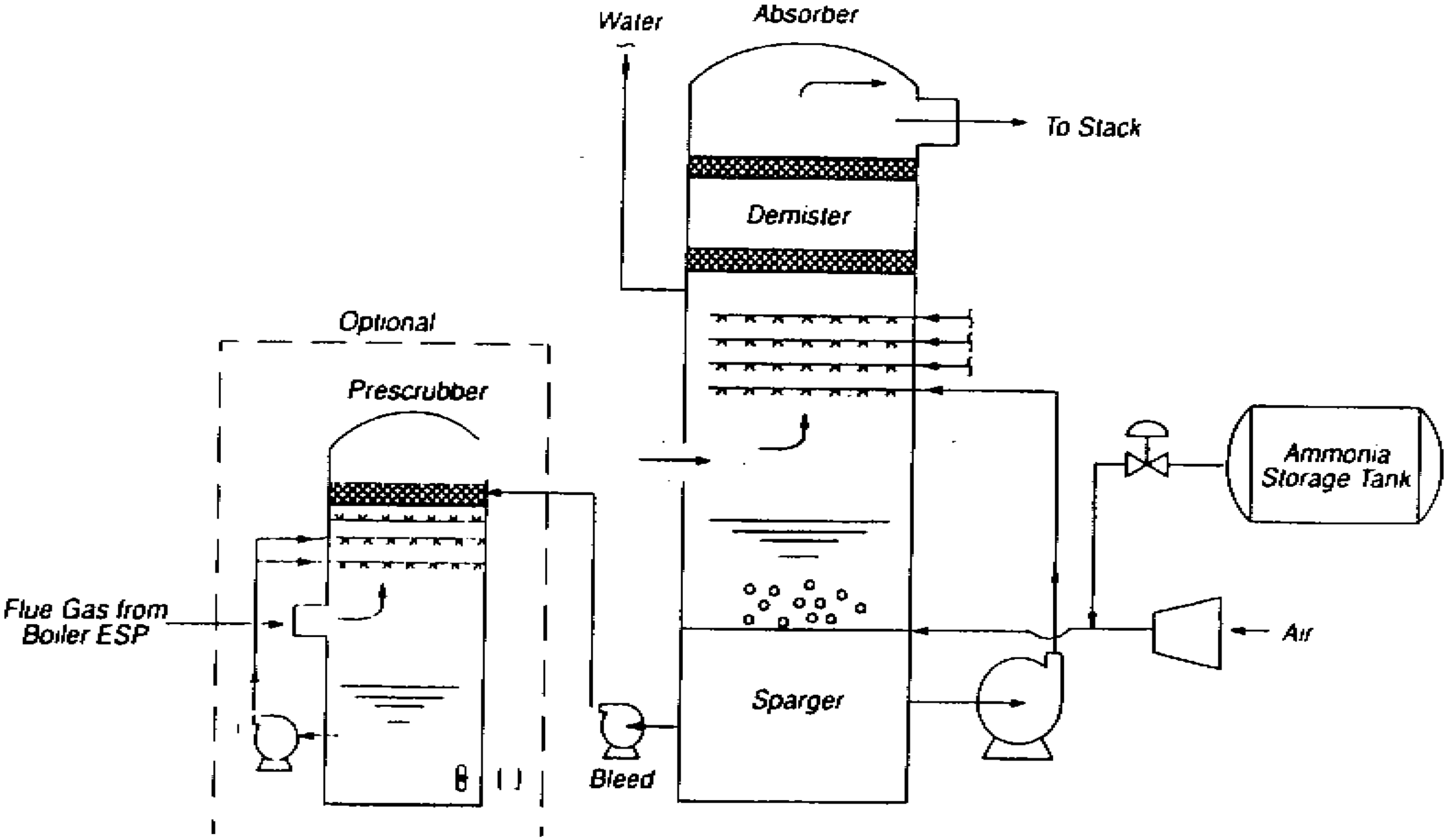


Figure 2: GE Ammonium Sulfate Process Dewatering Island

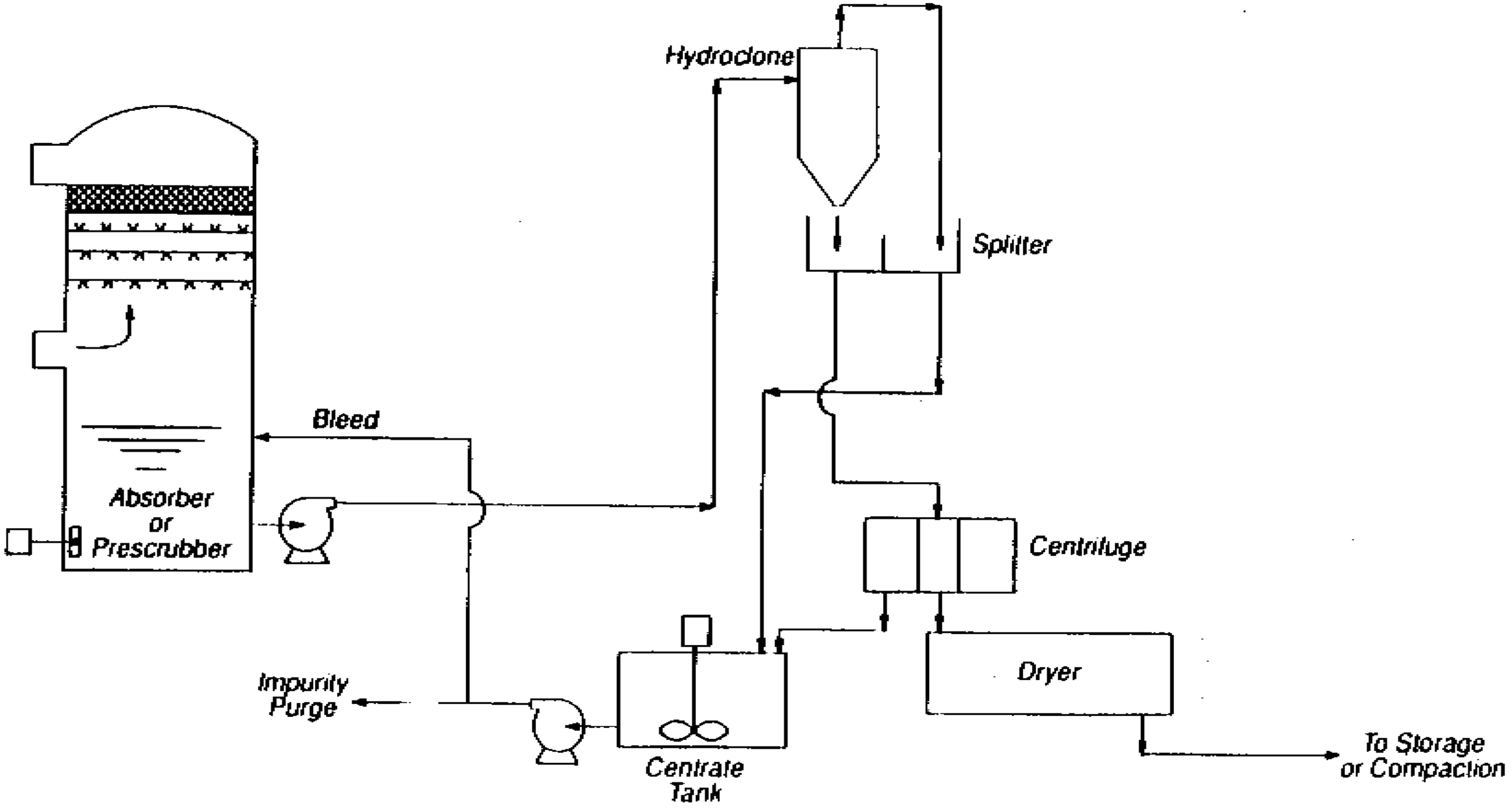


Figure 3: Impurities Purging Slipstream

Suspended Impurities Removal

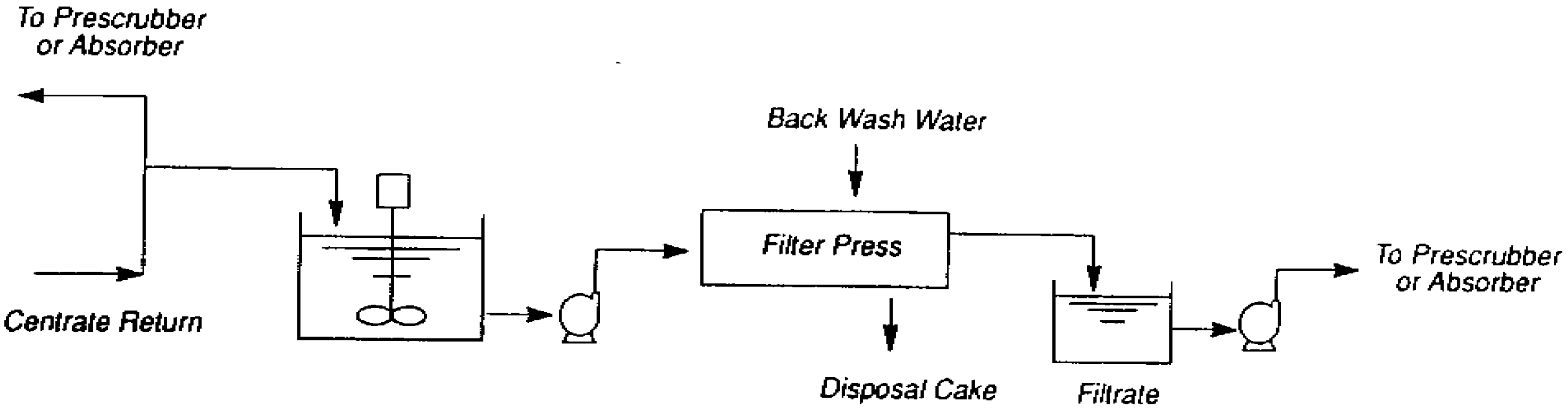
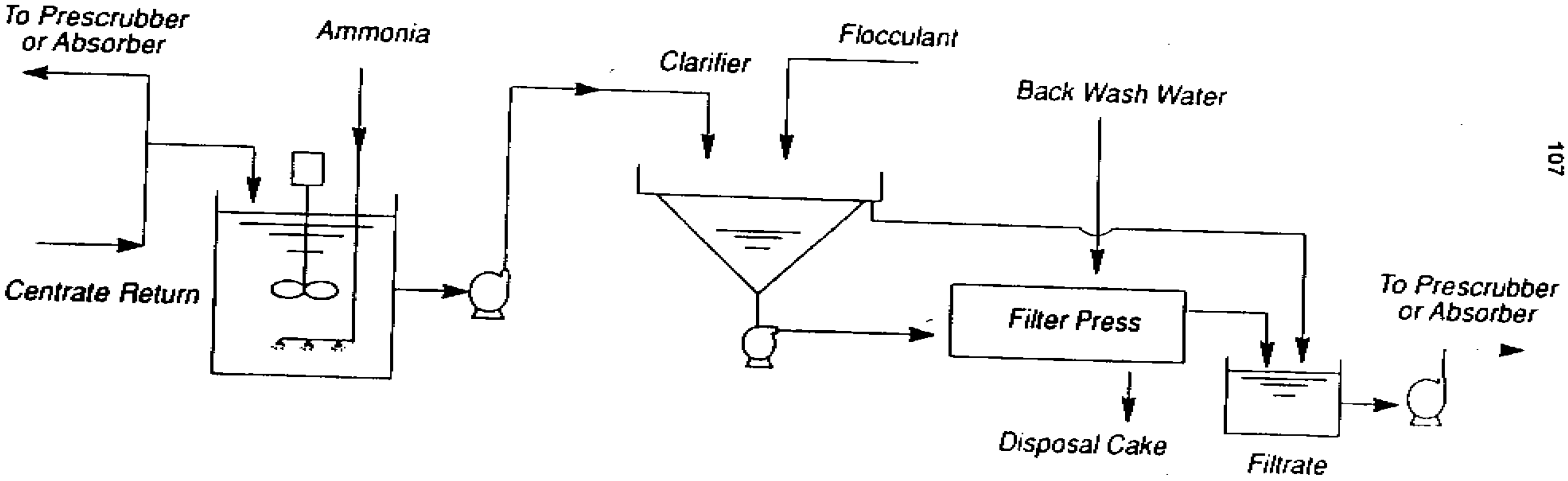


Figure 4: Impurities Purging Slipstream

Suspended & Dissolved Trace Metals Removal



$$\mathbf{M}\ SO_4 + 2NH_4OH \rightarrow (NH_4)_2SO_4 + \mathbf{M}\ (OH)_2$$

M = trace metals

Figure 5: Particle Size Distribution for FGD Ammonium Sulfate

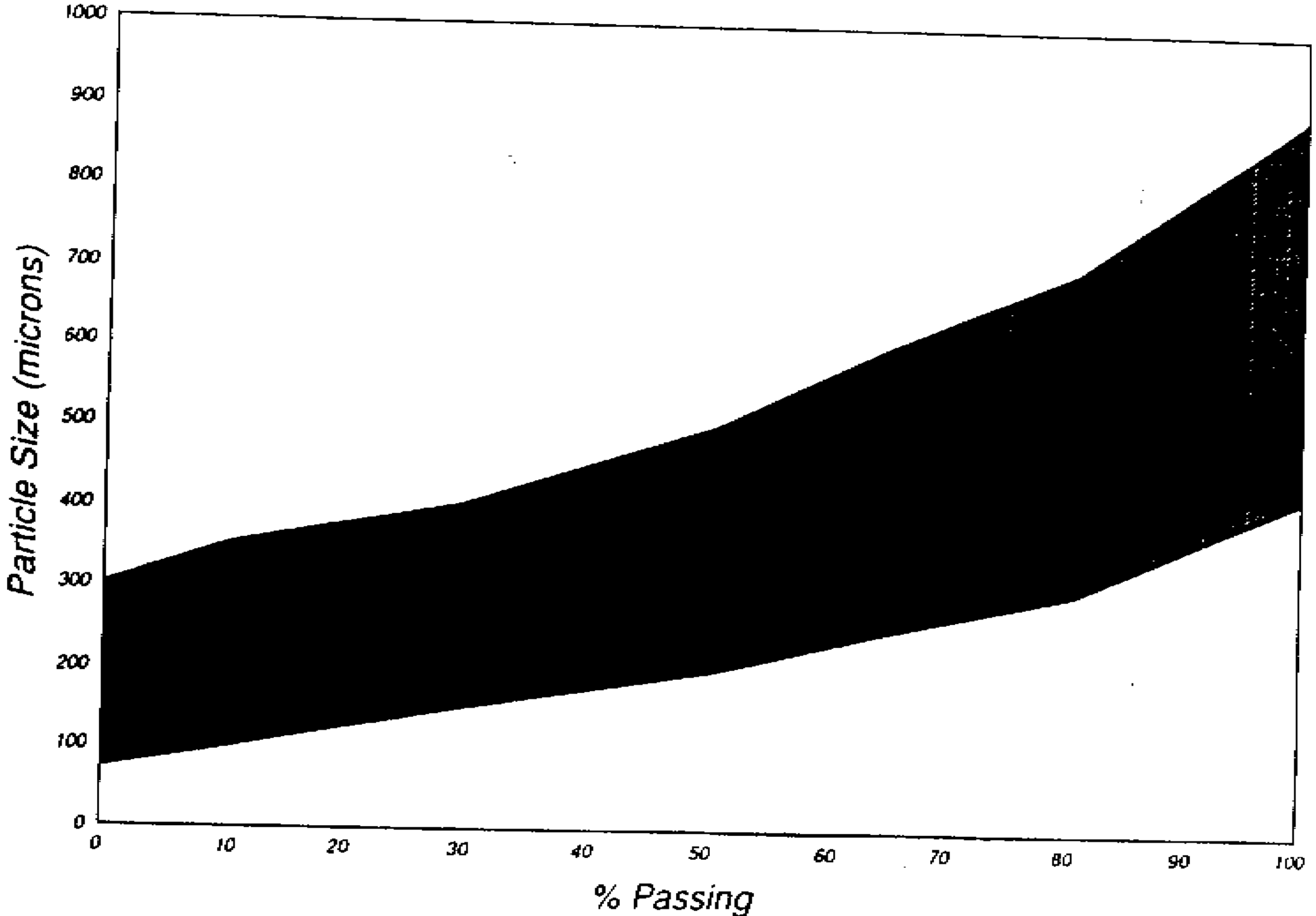


Figure 6: GE Ammonium Sulfate Compaction Granulation System Process Flow Diagram