5 Agricultural Chemicals: Fertilizers

5.1 Overview of Fertilizers

Ammonia and Sulfuric Acid Are Key Chemicals In Fertilizer Production

Approximately 85 percent of the **ammonia** produced worldwide is used to make agricultural fertilizers. While ammonia can be applied directly to the soil, it is usually first converted to a solid by reacting it with carbon dioxide or certain acids. Ammonia is also used as a raw material in the manufacture of polymeric resins, explosives, nitric acid, and other products (see Figure 5-1).

Ammonia is ranked seventh among the top fifty chemicals, with an annual production of 28.4 billion pounds, and has ranked among the top ten chemicals for the last thirty years. Ammonia is derived from methane, an organic feedstock, but has traditionally been grouped with inorganic chemicals because its primary derivatives are inorganic. Many of its derivatives are also among the top fifty chemicals, including nitric acid, ammonium nitrate, ammonium sulfate, and urea (Chenier 1992, CMA 1998).

Nitric acid is a powerful oxidizing agent and is used primarily to manufacture ammonium nitrate. Its minor uses include the manufacture of adipic acid, nitroglycerin, trinitrotoluene (TNT), nitrobenzene, and other chemicals.

After World War II, the chief use of **ammonium nitrate** was as an explosive. Although it is still used in the manufacture of more than 75 percent of all explosives, its primary use today is as a fertilizer because of its high nitrogen content. Nitric acid and ammonium nitrate ranked

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Production of Major Agricultural Chemicals (1997)

Ammonia (28.4 billion lbs)
Nitric Acid (13.5 billion lbs)
Ammonium Nitrate (12.3 billion lbs)
Urea (11.8 billion lbs)
Ammonium Sulfate (4.1 billion lbs)
Sulfuric Acid (71.4 billion lbs)
Phosphoric Acid (9.9 billion lbs)
Ammonium Phosphates (18.9 billion lbs)
Super Phosphates (3.4 billion lbs)
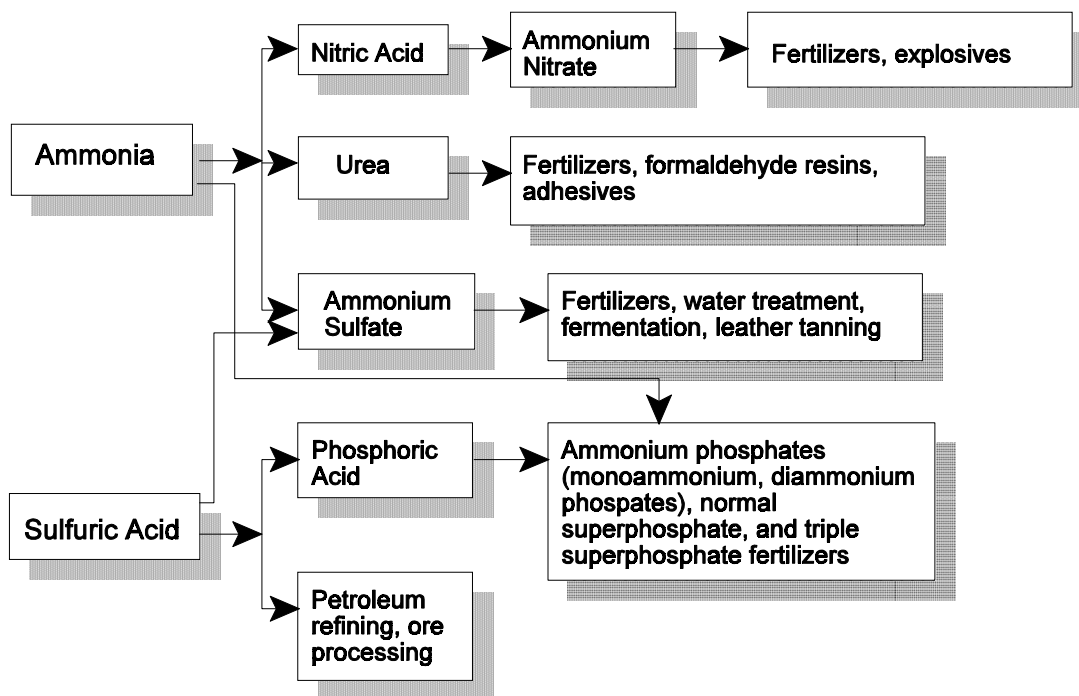
Source: CMA 1998, TFI 1999.

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                                            ┌──────────────────┐       ┌─────────────────────────┐
                              ┌──►│ Nitric Acid │──►│ Ammonium        │──►│ Fertilizers, explosives │
                              │   └─────────────┘   │ Nitrate         │   └─────────────────────────┘
                              │                     └──────────────────┘
┌──────────────┐             │   ┌─────────────┐   ┌─────────────────────────────┐
│   Ammonia    │──┬──────────┼──►│    Urea     │──►│ Fertilizers, formaldehyde    │
└──────────────┘  │          │   └─────────────┘   │ resins, adhesives            │
                  │          │                     └─────────────────────────────┘
                  │          │   ┌─────────────┐   ┌─────────────────────────────┐
                  │          └──►│ Ammonium    │──►│ Fertilizers, water treatment,│
                  │              │ Sulfate     │   │ fermentation, leather tanning│
                  │              └─────────────┘   └─────────────────────────────┘
                  └──────────────────────────────┐
                                                  ▼
                              ┌─────────────┐   ┌─────────────────────────────┐
                         ┌───►│ Phosphoric  │──►│ Ammonium phosphates          │
                         │    │ Acid        │   │ (monoammonium, diammonium    │
┌──────────────┐        │    └─────────────┘   │ phospates), normal           │
│ Sulfuric Acid│──┬─────┤                       │ superphosphate, and triple   │
└──────────────┘  │     │    ┌─────────────┐   │ superphosphate fertilizers   │
                  │     └───►│ Petroleum   │   └─────────────────────────────┘
                  │          │ refining, ore│
                  │          │ processing  │
                  │          └─────────────┘
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Figure 5-1. Agricultural Chemicals: The Fertilizer Chain

seventeenth and eighteenth, respectively, among the top fifty chemicals in 1997 (Chenier 1992, CMA 1998).

Although **urea** is considered an organic compound, it is usually grouped with other ammonia-derived synthetic nitrogen compounds because of its importance to the fertilizer industry. About 53 percent of the urea produced is used in solid fertilizers, 31 percent is used in liquid fertilizers, and the rest is found in other products, including animal feed, formaldehyde resins, and adhesives. Urea is often combined with other fertilizers, such as the commonly used urea-ammonium nitrate mixture. Formaldehyde resins made from urea are found in dinnerware and other consumer products (e.g., Formica®).

Ammonium sulfate, which ranked thirty-two on the top-fifty list in 1997, is used almost entirely as a fertilizer. Minor uses include water treatment, fermentation, and leather tanning (Chenier 1992).

Sulfuric acid is an essential input to the manufacture of agricultural chemicals. In 1997, it was the chemical produced in the second largest amount in the United States, at over 71 billion pounds annually. About 65 to 70 percent of the sulfuric acid produced is used to manufacture phosphoric acid. The remainder is used in chemical processing, petroleum refining (alkylation), pulp and paper production, plastics manufacture, and in non-chemical applications. Since its primary use is for fertilizer production, it is often grouped with agricultural chemicals (Chenier 1992, CMA 1998).

Phosphoric acid is the primary feedstock for producing phosphate fertilizers. Of the nearly 10 billion pounds of phosphoric acid produced in 1997, about 9 billion pounds were used to produce **ammonium phosphates**, **normal superphosphates**, and **triple superphosphates**. Ammonium phosphates contain both nitrogen and phosphorus, important fertilizer ingredients. The two most frequently used compounds are

monoammonium phosphate and diammonium phosphate (EPA 1997f, CMA 1998).

Superphosphates are fertilizers containing relatively large amounts of phosphorus. **Normal superphosphates** contain up to 22 percent phosphorus; **triple superphosphates** contain over 40 percent phosphorus (EPA 1997f).

Demand for Fertilizers Is Closely Linked to Export Markets

The production of fertilizers and their precursor chemicals has declined significantly in recent years, showing, for example, a drop of 20 to 30 percent from 1996 to 1997. This is due in part to the growing capacity for manufacturing fertilizers in Third World countries such as Asia and Mexico, which have previously been major importers of U.S. products. Trends in U.S. exports of major products are shown below in Table 5-1.

China has affected the demand for **urea** by banning its importation beginning in mid-1997, although it is the world's largest consumer of this fertilizer. China is striving to become self-sufficient in fertilizer production and continues to bring new capacity on-line. India has also reduced its urea imports following government controls on selected fertilizers. The result

has been weak prices in urea markets, which may not improve unless China resumes importing this product (CHEMWK 1999).The use of fertilizers in the United States has grown steadily over the last ten years and is now relatively stable. Rates of application range from about 140 to 270 pounds of fertilizer per acre (see Table 5-2).

The United States is currently the largest exporter of **ammonium phosphates**, providing over 70 percent of the world's supply. New capacity additions in Morocco, Australia, and India will create an oversupply of this fertilizer, however, and may force reductions in U.S. production in the future (CHEMWK 1999). A number of firms have shut down high-cost capacity for **phosphoric acid** over the past few years, which should help improve margins for phosphorus and a number of its derivatives (CHEMX 1997).

Ammonia production is closely tied to agriculture and the demand for fertilizers. In the past, ammonia plants have sometimes operated at close to 100 percent capacity to meet demand. Today, oversupply and depressed margins are affecting this trend, and forcing producers to look for cheap ways to increase capacity. Some analysts predict there will be a 1.4 million ton/year surplus in ammonia supplies this year (CE 1996). Production decreased by a substantial 20 percent between 1996 and 1997, reflecting primarily decreased margins and changes in export demand for fertilizers.

Table 5-1. Export Trends of U.S. Fertilizers (1000 tons)				
	1994	**1995**	**1996**	**1997**
Ammonia	288	426	584	561
Ammonium Sulfate	840	1011	909	957
Urea	1005	971	1621	1028
Phosphoric Acid	308	342	339	323
Super-phosphates	882	787	752	766
Di-ammonium Phosphate	10135	11088	8727	10405

Source: TFI 1999.

Table 5-2. Percentage of U.S. Acres Receiving Fertilizer				
Crop	**Total lb/acre**	**Nitro-gen**	**Phos-pho-ic Acid**	**Potash**
Corn	268	99	84	72
Cotton	202	90	67	58
Soybeans	163	20	28	33
Wheat	139	87	63	18

Source: TFI 1999.

Similar decreases of over 25 percent were noted for **sulfuric acid**, the primary input to phosphoric acid and phosphate fertilizer production. Future production trends will be quite dependent on export markets, particularly those in the Asia-Pacific region.
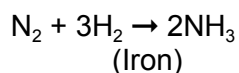
5.1.1 Ammonia Manufacture

Ammonia Is Still Produced by the Haber Process

Commercial synthesis and use of **ammonia** originated in Germany's need for nitrogen-rich compounds for explosives manufacture during World War I. In the early 1900s, German chemist Fritz Haber developed an ammonia synthesis process based on an iron catalyst that enabled large-scale production of ammonia. By1913, the German chemical company BASF[1] was making ammonia using this process at the rate of 30 metric tons per day. The new technology enabled greater, more rapid production of explosives and extended the war for many years. Haber, however, received the Nobel prize for his work in 1918, amidst objections from those who denounced his contributions to the war effort (Bristol 1999).

The **Haber process** is still the primary method for ammonia synthesis used today, and requires hydrogen, which can be produced from a variety of hydrocarbon sources, and nitrogen, which is supplied from air. The production of ammonia from coal-derived synthesis gas is considered one of the chemical engineering achievements of this

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Ammonia Formation

$$N_2 + 3H_2 \rightarrow 2NH_3$$
(Iron)

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century. Since the 1930s, however, the primary source of hydrogen for ammonia production in

this country has been steam reforming of natural gas. About 2 percent of the hydrogen required for the Haber process is obtained from electrolysis of brine at chlorine plants.

A typical process configuration for production of ammonia is shown in Figure 5-2. Natural gas is mixed with steam and charged to a primary reformer, where it is passed over a nickel catalyst. In the primary reformer, which operates at around 1300ºF–1500ºF (700ºC–815ºC), most of the gas is converted to hydrogen, carbon monoxide, and carbon dioxide. The exiting gas is mixed with air and charged to a secondary reformer operating at higher temperatures, 1650ºF-1700ºF (900ºC–925ºC), where the remaining natural gas is converted. The gas leaving the secondary reformer contains nitrogen, hydrogen, carbon monoxide, and carbon dioxide.

The reformed gas is cooled in a waste heat boiler where high-pressure, super-heated steam is generated. The cooled gas is then charged to high- and low-temperature shift converters containing different catalysts to convert the carbon monoxide into carbon dioxide to obtain additional hydrogen.

Shift Converter Reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

The mixture of gases is then charged to a carbon dioxide removal plant. Methods most commonly used for this purpose include absorption or wet scrubbing (e.g., with hot potassium carbonated or methyl diethanolamine). Outlet gas from the recovery plant is further purified through methanation and drying. The resulting pure synthesis gas is compressed and fed through heat exchangers to ammonia converters containing iron oxide catalysts (the Haber process). The gas stream is refrigerated to condense ammonia, and unreacted gases are recycled. The resulting product is anhydrous ammonia.

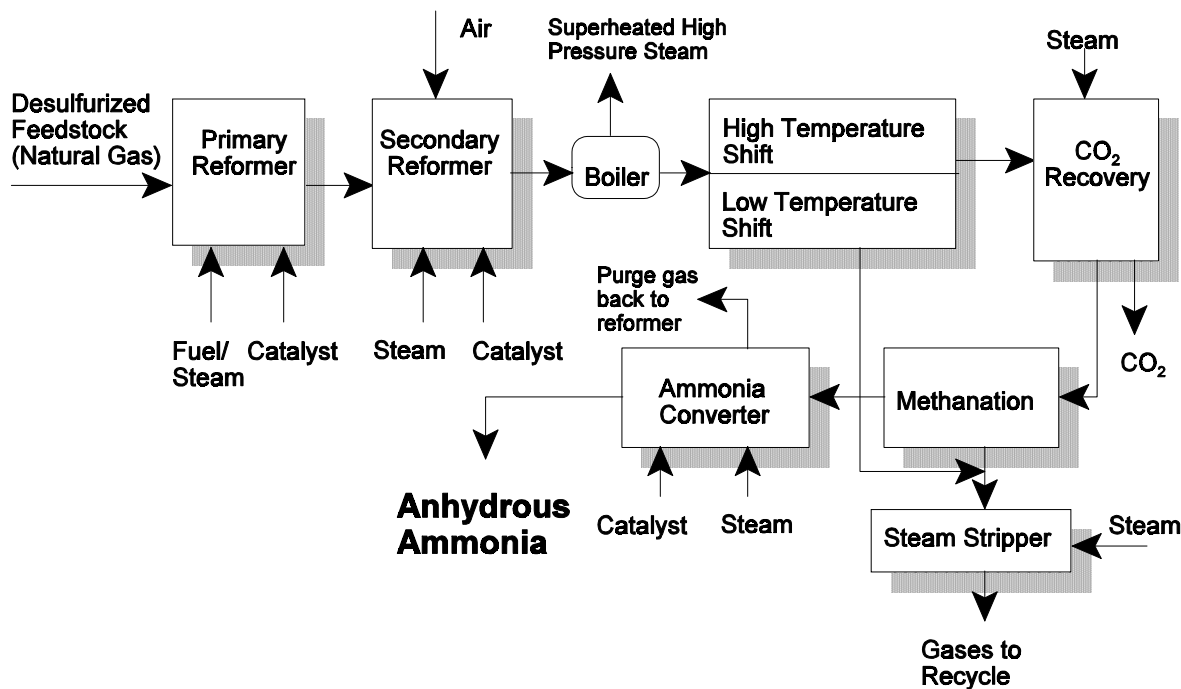
[1] BASF, or Badashe Analine und Soda Fabrik

Figure 5-2. Manufacture of Ammonia (EPA 1997a, Orica 1999, HP 1999)

Key Energy and Environmental Facts - Ammonia Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 12,150 Btu/lb (includes fuel and feedstock)*	*Largest source - fugitive emissions of ammonia*	*Largest source - process water*	*Carbon dioxide*

While all plants use a process similar to that described above, configurations will vary with respect to feedstocks (natural gas, hydrocarbon gases, naphtha), operating temperatures, pressures, and other parameters. In most cases, the natural gas feedstock will need to be desulfurized to prevent poisoning of the nickel catalyst used in steam reforming. Most ammonia plants use activated carbon fortified with metallic oxide additives for this purpose.

Carbon dioxide is produced as a byproduct of the ammonia manufacturing process, and is utilized in various ways–as a feedstock for urea production, or liquified and sold to food and beverage markets. Excess carbon dioxide may also be vented to the atmosphere (Process Description: EPA 1997a, Orica 1999, HP 1999).

5.1.2 Urea Manufacture

Urea Is Produced by Solution Synthesis of Ammonia and Carbon Dioxide

About 50 percent of the ammonia manufactured is used to produce **urea** (also known as carbamide or carbonyl diamide) in both solid and liquid forms. Most solids are produced as prills or granules, and are used as

fertilizers, protein supplements in animal feed, and in plastics.

A typical flow diagram for production of urea is shown in Figure 5-3. The actual configuration will depend on whether urea is to be produced in solid (crystalline) or liquid form. In the solution synthesis process, ammonia and carbon dioxide are first reacted under high pressure, 140–250 atmospheres, and moderate temperatures, 350ºF–400ºF (175ºC–200ºC). The resulting mixture is about 35 percent urea, 8 percent ammonium carbamate, 10 percent water, and 47 percent ammonia.

The ammonia is distilled, and the solution is dehydrated to form a 70–77 percent aqueous urea solution. The urea solution can be used in this form, or it can be further concentrated using vacuum concentration, crystallization, or atmospheric evaporation.

If a solid product is being manufactured, additives are often used to reduce the caking of solids and formation of urea dust during its storage and handling.

Concentration produces a urea "melt" that can then be used to produce solid urea through prilling or granulation methods. Prilling produces solid particles directly from molten urea; granulation, the process used more frequently, builds solids by creating layers of seed granules that are started by cooling (Process Description: EPA 1993d, Orica 1999, Enviro-Chem 1999c, HP 1999).

5.1.3 Nitric Acid Manufacture

Nitric Acid Is Made by Direct Oxidation of Ammonia

Nitric acid was made years ago by the reaction of sulfuric acid and salt peter (a common name for potassium nitrate or sodium nitrate).
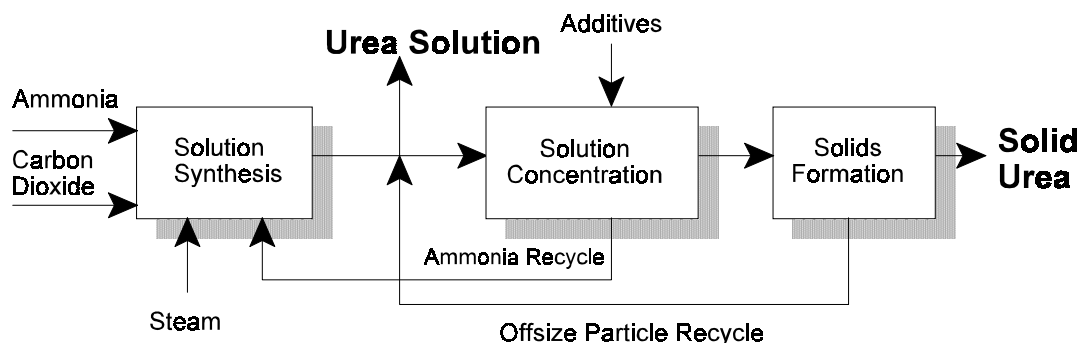

Figure 5-3. Manufacture of Urea
(EPA 1993d, Orica 1999, HP 1999, Enviro-Chem 1999c)

Key Energy and Environmental Facts -Urea Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 732 Btu/lb*	*Largest source - fugitive emissions (ammonia, formaldehyde, methanol) and particulates*	*Largest source - process water*	*Inert gases*

Today, most nitric acid is produced by high-pressure and -temperature catalytic oxidation of ammonia. A typical process flow for nitric acid production is shown in Figure 5-4.

While configurations may differ somewhat between plants, three essential steps are commonly employed. In the first step, ammonia is oxidized to nitric oxide (NO) in a catalytic convertor over a platinum catalyst (90 percent platinum, 10 percent rhodium gauze). The reaction is exothermic (heat-releasing) and produces nitric oxide in yields of 93–98 percent. The reaction proceeds at high temperatures ranging from 1380°F–1650°F (750°C–900°C).

The resulting mixture from this reaction is then sent to a waste heat boiler where steam is produced. In the second step, nitric oxide is oxidized by passage through a cooler/condenser, where it is cooled to temperatures of 100°F (38°C) or less, at pressures of up to 116 psia. During this stage, the nitric oxide reacts with residual oxygen to form nitrogen dioxide and nitrogen tetroxide.

The final step introduces this mixture of nitrogen oxides into an absorption process where the mixture flows countercurrent to deionized water and additional liquid dinitrogen tetroxide. The tower is packed with sieve or bubble cap distillation type trays. Oxidation
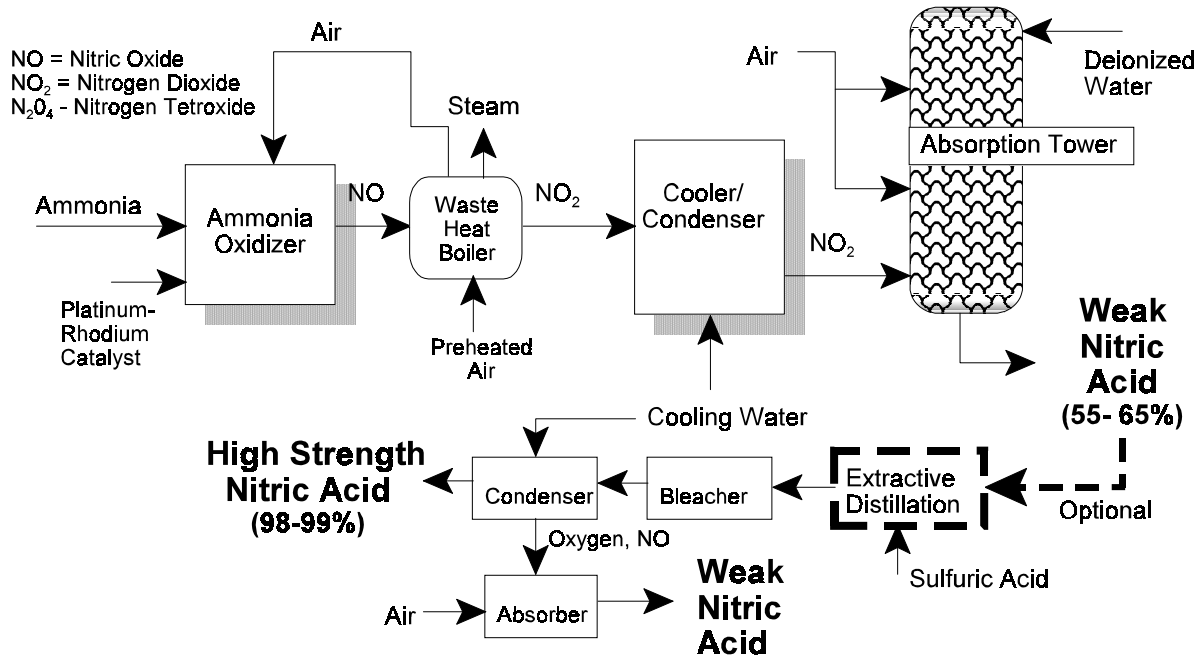

Figure 5-4. Manufacture of Nitric Acid
(EPA 1997b, Orica 1999, EFMA 1999, Enviro-Chem 1999a)

Key Energy and Environmental Facts -Nitric Acid Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy Exporter: *Net Steam: 311 Btu/lb*	*Largest source - fugitive emissions (oxides of nitrogen, nitric acid mist, ammonia)*	*Largest source - process water*	*Nitrogen oxides, spent catalysts, inert gases*

takes places in between the trays in the tower; absorption occurs on the trays. An exothermic reaction between NO_2 and water occurs in the tower to produce nitric acid and NO. Air is introduced into the tower to re-oxidize the NO that is being formed and to remove NO_2 from the nitric acid. A weak acid solution (of 55–65 percent, although this varies) is withdrawn from the bottom of the absorption tower.

To produce high strength nitric acid, the weak nitric acid solution is concentrated using extractive distillation with a dehydrating agent. Concentrated sulfuric acid is often used as the agent. During this process, the sulfuric acid and weak nitric solution are fed to the top of a packed dehydrating column at atmospheric pressure. Concentrated nitric acid leaves the top of the column as 99 percent vapor, with small amounts of NO_2 and oxygen. The concentrated vapor is sent to a bleacher and condenser system to condense the strong acid and separate oxygen and any nitrogen oxide byproducts, which are recycled. Inert gases are vented to the

atmosphere (Process Description: EPA 1997b, Orica 1999, EFMA 1999).

5.1.4 Ammonium Nitrate

Neutralizing Nitric Acid with Ammonia Produces Ammonium Nitrate

Ammonium nitrate is produced by neutralizing nitric acid with ammonia. The final product can be liquid, or a solid in the form of prills, grains, granules, or crystals, depending upon whether the end-use is for fertilizers or explosives. High-density solids are generally used as fertilizers, while low-density grains are typically used in explosives manufacturing.

Figure 5-5 illustrates the processing of both liquid and solid ammonia nitrate. Ammonia and nitric acid are first introduced into a stainless steel reactor, where the heat of neutralization boils the mixture and concentrates it to about 85 percent nitrate. If a liquid product is desired, it is drawn off at this time.
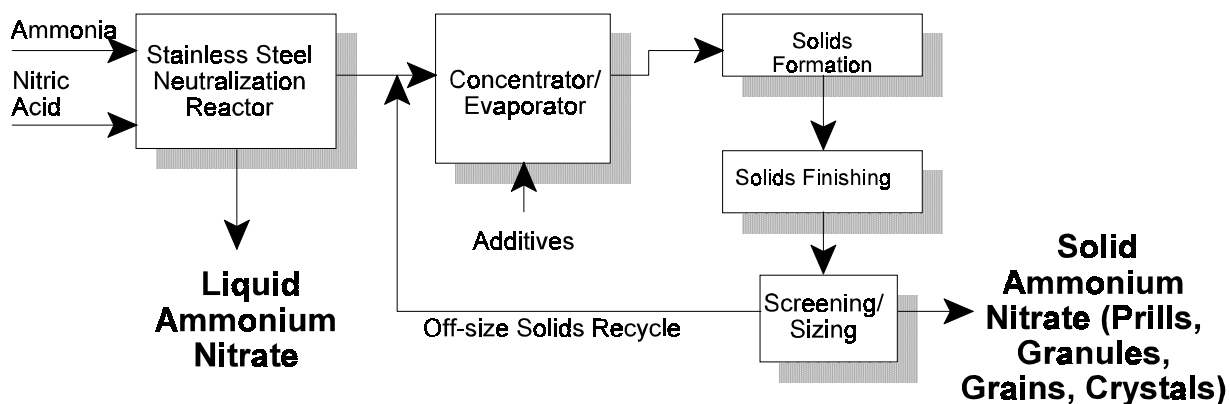

Figure 5-5. Manufacture of Ammonium Nitrate (EPA 1993c, Chenier 1992)

Key Energy and Environmental Facts - Ammonium Nitrate Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 341 Btu/lb*	*Largest source - particulates (ammonium nitrate and coating materials), ammonia and nitric acid*	*Largest source - process water*	*negligible*

About 60 percent of ammonium nitrate is currently produced in solid form. To create the solid, the 85 percent nitrate solution is further concentrated through vacuum evaporation or in a concentrator. The resulting "melt" contains from 95 to 99.8 percent ammonium nitrate. The melt can then be used to produce a solid product in prill towers or rotary drum granulators.

Additives such as magnesium nitrate or magnesium oxide may be introduced into the melt prior to solidification to raise the crystalline transition temperature, act as a desiccant (removing water), or lower the temperature of solidification. Products are sometimes coated with clays or diatomaceous earth to prevent agglomeration during storage and shipment, although additives may eliminate the need for coatings. The final solid products are screened and sized, and off-size particles are dissolved and recycled through the process (Process Description: Chenier 1992, EPA 1993c).

5.1.5 Ammonium Sulfate Production

Ammonium Sulfate Can Be Synthesized Directly or Produced as a Byproduct

Ammonium sulfate was one of the first popular fertilizers, primarily because it was produced as a byproduct of coke ovens as early as 1893. While it is still widely used, it has been supplanted somewhat by urea and other fertilizers that promote green growth in plants. It is still often used as a component in many fertilizer blends.

Ammonium sulfate can be produced as a byproduct of caprolactam (see Section 4, The BTX Chain), as a coke oven byproduct, or by direct synthesis. A typical flow diagram for the synthetic process is shown in Figure 5-6. In this process, anhydrous ammonia and sulfuric acid are combined in a pipe reactor. A highly exothermic reaction occurs, producing ammonium sulfate and a bisulfate solution.
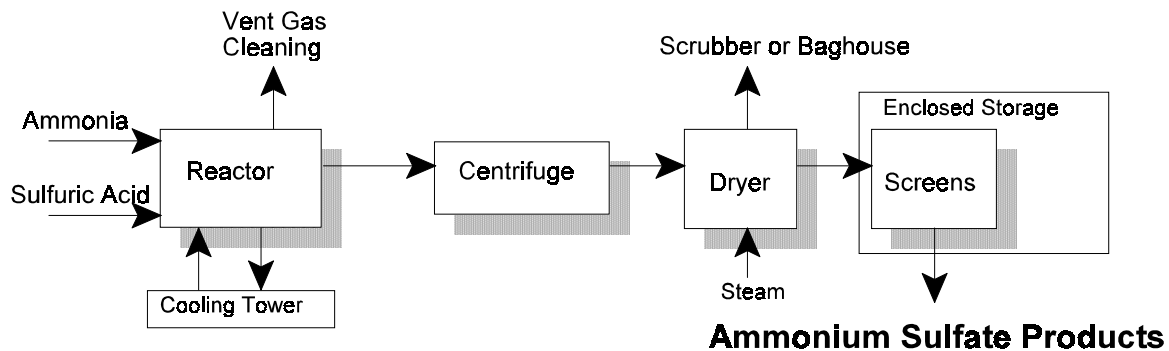

Figure 5-6. Manufacture of Ammonium Sulfate (EPA 1997d, Orica 1999)

Key Energy and Environmental Facts -Ammonium Sulfate Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 4,000 Btu/lb*	*Largest source - particulates (ammonium sulfate)*	*Largest source - process water*	*negligible*

Ammonium sulfate crystals are formed by circulating the solution through an evaporator where it thickens. A centrifuge separates the crystals from the mother liquor. The crystals contain 1 percent to 2.5 percent moisture, and are dried in a fluidized bed or rotary drum dryer. Dryer exhaust gases are sent to a particulate collection system (e.g., wet scrubber) to control emissions and recover residual product. Coarse and fine granules are separated by screening before they are stored or shipped (Process Description: EPA 1997d, Orica 1999).

5.1.6 Sulfuric Acid Manufacture

Most Sulfuric Acid Is Made by Oxidation of Sulfur

Historically, **sulfuric acid**[2] has been an important chemical, at least as far back as the tenth century. Processes for making sulfuric acid were first described in the fifteenth century, when chemists told of burning sulfur with potassium nitrate (sometimes called salt peter). The lead chamber process was introduced in the eighteenth century, which involved the oxidation of sulfur to sulfur dioxide by oxygen, further oxidation to sulfur trioxide with nitrogen oxide, and hydrolysis of sulfur trioxide to achieve the final product. Nineteenth century modifications made the early process economical until the 1940s, when it was displaced by the contact process.

Today, 99 percent of sulfuric acid is made using the contact method, an oxidation process based on the burning of elemental sulfur (brimstone) with dry air (see Figure 5-7) or the roasting of pyrite ore. Sources of elemental sulfur include mining or oxidation of hydrogen sulfide (via the Claus process) from "sour" natural gas wells or petroleum refineries.

The contact process utilizes the techniques of interpass absorption or double absorption. The typical flow diagram for this process is shown in Figure 5-7. Molten sulfur is burned at high temperatures (>1800ºF, or >980ºC) in excess dry air to produce sulfur dioxide. The sulfur dioxide is cooled in a waste heat boiler (that produces high-pressure steam and usually powers a turbine for electricity generation).

After cooling, the sulfur dioxide is sent along with oxygen to a staged converter with a set of chambers containing a vanadium catalyst. After passing through the third chamber, about 95 percent of the sulfur dioxide has been converted to sulfur trioxide. The mixture is then charged to a two-stage absorption process where it combines with water to form sulfuric acid. The exiting sulfuric acid can be passed over the vanadium catalyst again to attain a 99.7 percent conversion if desired. After the second absorption stage, the final concentration of sulfuric acid is 98 percent or greater.

If **oleum** is produced (a mixture of excess sulfur trioxide and sulfuric acid), sulfur trioxide from the converter is passed to an oleum tower that is fed with 98 percent acid from the absorbers. The gases from this tower are then pumped to the absorption column where sulfur trioxide is removed. Various concentrations of oleum can be produced. Common ones include 20 percent oleum (20 percent sulfur trioxide in 80 percent sulfuric acid, with no water), 40 percent oleum, and 60 percent oleum.

The sulfuric acid conversion process is highly exothermic, providing opportunities for energy recovery in many areas (e.g., after the sulfur burner, after the converter pass, and in the absorption towers). Energy recovered is used for process heating and/or electricity generation (Process Description: Chenier 1992, EPA 1992a, Enviro-Chem 1999b, Orica 1999).

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[2] A colorless, odorless, heavy, oily liquid that was once referred to as "oil of vitriol"
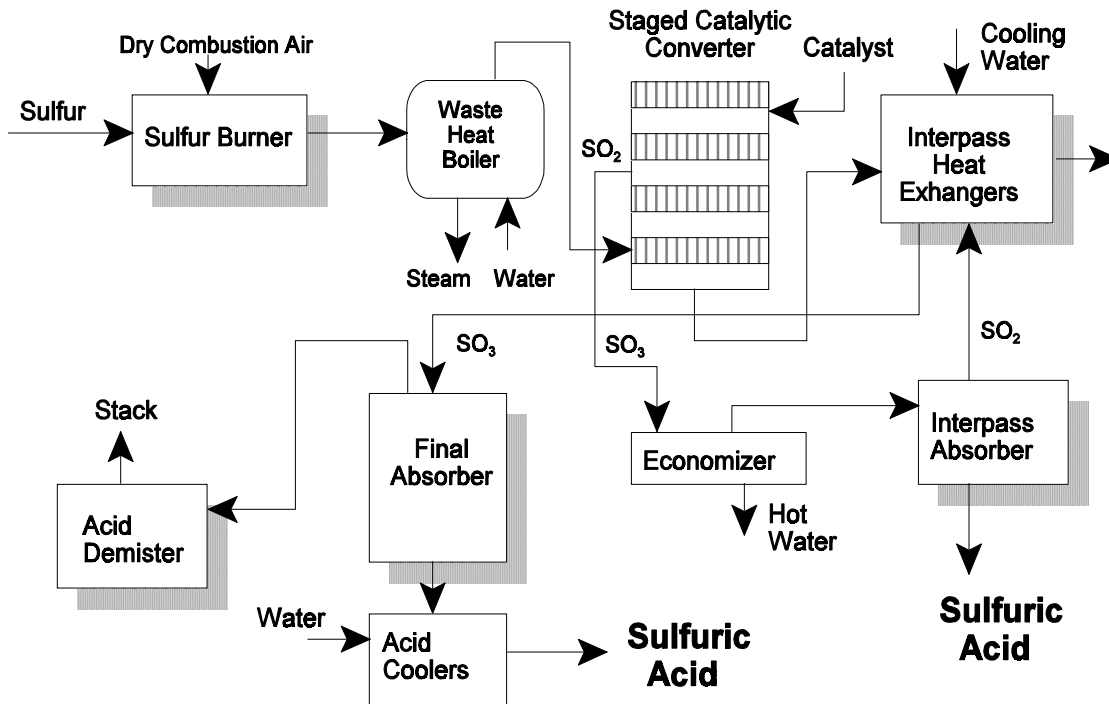
Figure 5-7. Manufacture of Sulfuric Acid
(EPA 1992a, Enviro-Chem 1999b, Orica 1999)

Key Energy and Environmental Facts - Sulfuric Acid Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy Exporter : (1,047 Btu/lb product)	Largest source - sulfur dioxide, acid mist	Largest source - process water	Spent catalysts

5.1.7 Phosphoric Acid Manufacture

Wet and Thermal Processing Methods Produce Different Grades of Phosphoric Acid

Phosphoric acid is the most important derivative of sulfuric acid. It has been used as fertilizer for hundreds of years, and is a key ingredient in today's phosphate fertilizers. The **wet process** is used to produce fertilizer-grade phosphoric acid, and accounts for more than 90 percent of phosphoric acid production (in the form of phosphorus pentoxide, or P_2O_5). The **thermal process** (sometimes called the furnace process) accounts for about 10 percent of production, and is used to make high purity phosphoric acid for use in manufacturing specialty chemicals, pharmaceuticals, detergents, food products, and beverages.

In the wet process (see Figure 5-8), sulfuric acid is reacted with naturally occurring phosphate rock. The rock usually contains a high percentage of fluorine, and if this is the case, the mineral is called fluorapetite. It is mined in
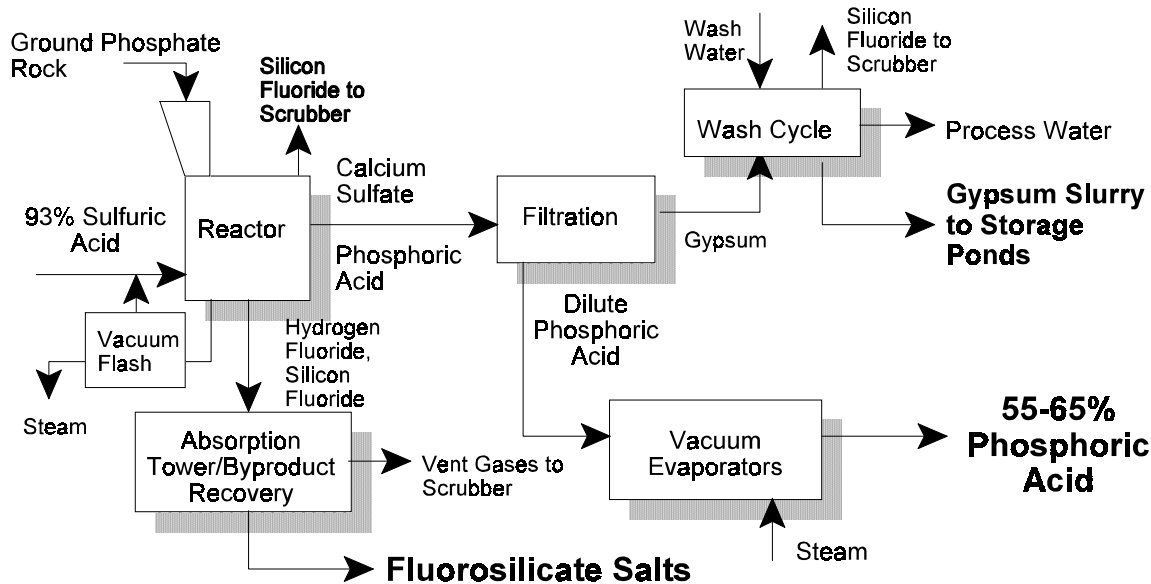
Figure 5-8. Manufacture of Phosphoric Acid - Wet Process (Chenier 1992, EPA 1997e)

Key Energy and Environmental Facts - Phosphoric Acid Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 1,810 Btu/lb*	*Largest source - gaseous fluorides (SiF$_4$ and HF) and particulates*	*Largest source - acidic cooling water with high concentrations of phosphorus and fluoride*	*Fluorosilicate salts, uranium oxides, gypsum slurry, silicon fluoride*

Florida, Texas, North Carolina, Idaho, and Montana; 30 percent of world reserves are in the United States.

The phosphate rock is dried, crushed, and fed continuously into a reactor along with sulfuric acid. During the reaction, calcium from the phosphate rock is combined with sulfate, forming calcium sulfate (gypsum) and phosphoric acid. Sulfuric acid with a concentration of 93 percent is used to decrease evaporation costs and ensure production of the strongest possible phosphoric acid.   The four to eight reactors are heated to about 175°F (80°C) for four to eight hours. Considerable heat is generated in the reactors. A portion of the reactor slurry is cooled by vacuum flashing and

subsequently recycled back to the reactor for heat control and recovery.

U.S. plants typically use dihydration to produce gypsum in the form of calcium sulfate with two water molecules attached (calcium sulfate dihydrate). Hemihydration processes are popular in Japan and produce calcium sulfate with a half molecule of water, which yields phosphoric acid with a higher phosphorus pentoxide concentration and fewer impurities. In recent years, some U.S. firms have switched to the hemihydration process.

After the gypsum crystals are formed, filtration is used to separate them from the solution. The separated crystals are washed to yield 99 percent or better recovery of filtered phosphoric

acid. The final wet phosphoric acid product contains about 26 to 30 percent P_2O_5, and is further concentrated to 40 to 55 percent by vacuum evaporation to make it suitable for fertilizer production.

After washing, the gypsum slurry is sent to a pond for storage. Water from this pond is recycled back to the phosphoric acid process. Water storage requirements are substantial: approximately 0.7 acres of cooling and settling pond area are required for every ton of P_2O_5 produced per day.

Side products from the reaction include fluorosilicate salt (H_2SiF_6) and uranium oxides ($U_3O_{8)}$. Both silicon oxide and uranium occur in many phosphate rocks in small percentages. Fluorosilicate salts are used in ceramics, pesticides, wood preservatives, and concrete hardeners. Processes for extraction of uranium are available (MEAB 1999), but it is often not economical to recover the uranium.

During the **thermal process**, liquid elemental phosphorus is burned in ambient air to form P_2O_5. The P_2O_5 is then hydrated to produce strong phosphoric acid. Demisting is used to remove the phosphoric acid mist from the combustion gas stream before it is released to the atmosphere (Process Description: Chenier 1992, EPA 1997e).

High-purity phosphoric acid (in a concentration of up to 50 percent and greater) can also be recovered from the wet process by using selective solvent extraction. A new membrane process was developed recently that does not require the use of solvents (KEMWorks 2000).

5.1.8 Phosphate Fertilizers

Ammonium Phosphate and Superphosphates Are Processed Differently

Ammonium phosphate is the most widely used phosphate fertilizer, and is found in both solid and liquid forms. Granular ammonium phosphate fertilizer is produced by the reaction

of phosphoric acid with anhydrous ammonia in ammoniation-granulation plants. In the United States, 95 percent of ammoniation-granulation plants use a slightly inclined open-end rotary drum mixer for this process.[3]

The ammoniation-granulation process is shown in Figure 5-9. Phosphoric acid is first mixed in a surge tank with 93 percent sulfuric acid and recycled acid. The acids are neutralized with liquid or gaseous anhydrous ammonia in an acid reactor with a brick lining. The reactor produces a slurry of about 22 percent ammonium phosphate and water, which is sent through steam-trace lines to the rotary drum ammoniator-granulator.

The reactor slurry is distributed on a bed in the granulator, while the remaining ammonia is sparged underneath. Granulation occurs through agglomeration and by coating particles with slurry. Part of this process occurs in the rotary drum, and is completed in a rotary concurrent dryer.

Ammonia-rich off-gases are produced, and these are passed through a wet scrubbing system before venting to the atmosphere. Cooled granules pass to a screening unit, where oversized and undersized granules are separated out and recycled back to the granulator (Process Description: EPA 1993e, EPA 1997f).

Normal superphosphates are made by reacting ground phosphate rock with a 65 to 75 percent concentration of sulfuric acid. Both virgin and spent (recycled) sulfuric acid from other industrial processes may be used, although spent acid may impart unusual colors, odors, or toxicity to the product. The amount of iron and aluminum present in the rock is also a consideration, as they can impart a condition of extreme stickiness to the superphosphate and make it difficult to handle.

In this process, ground phosphate rock and acid are mixed in a reaction vessel, stored until the

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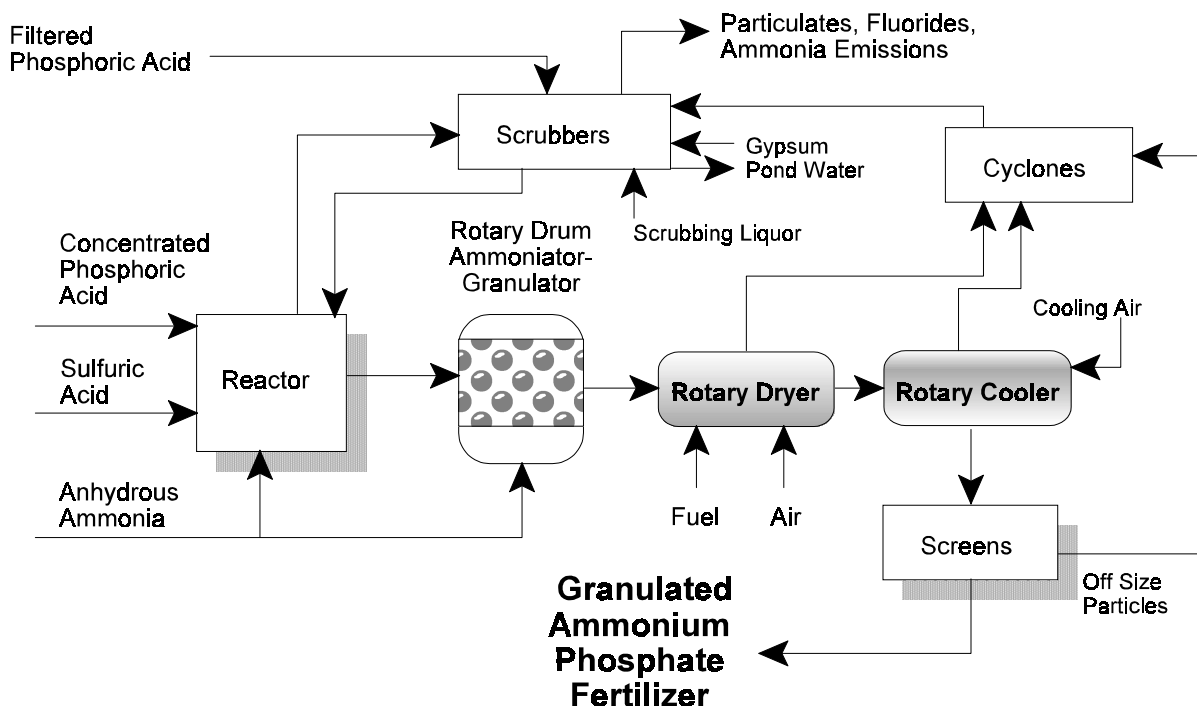[3] Developed and patented by the Tennessee Valley Authority (TVA)

Figure 5-9. Manufacture of Ammonium Phosphate (EPA 1993e, Brown 1996)

Key Energy and Environmental Facts - Ammonium Phosphate Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 206 Btu/lb*	*Largest source - gaseous ammonia, fluorides (SiF_4 and HF) and particulate ammonium phosphate*	*Largest source - acidic wastewater*	*Gypsum slurry, fertilizer dust*

reaction is completed (about 30 minutes), and transferred to a storage pile for curing. These processes are all conducted in enclosed areas to prevent venting of toxic emissions. After curing, the superphosphate is typically used as an additive to granular fertilizers, or it can be granulated in a rotary drum granulator/dryer/ cooing system.

Triple superphosphates are usually produced using the Dorr-Oliver granular process (see Figure 5-10). In this process, ground phosphate rock or limestone is reacted with low-concentration phosphoric acid in a reactor(s). A sidestream of the resulting slurry is continuously

removed and distributed onto dried, recycled fines, where the granular surfaces become coated and increase in size.

Rotating drum granulators are often used for granulation. They are open-ended, slightly inclined rotary cylinders with a cutter mounted inside. A bed of dry material is maintained in the unit, while slurry is introduced through pipes under the bed. The granules are wetted by the slurry and discharged to a rotary dryer to evaporate water and accelerate the chemical reaction to completion. Screening is used to remove off-size particles, which are recycled Process Description: Brown 1996, EPA 1997a).
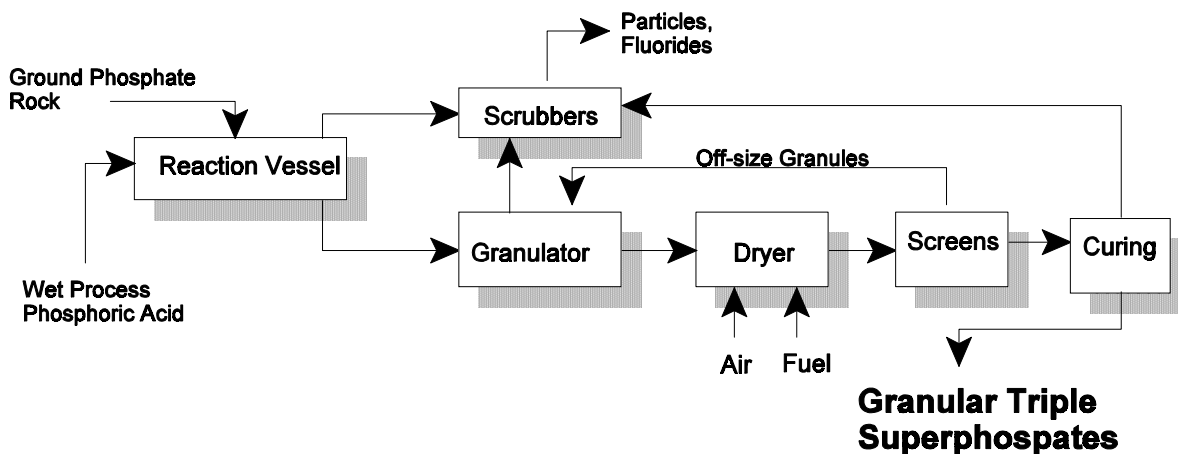
Figure 5-10. Manufacture of Triple Superphosphates
(EPA 1993e, Brown 1996)

Key Energy and Environmental Facts - Triple Superphosphates Manufacture			
Energy	*Emissions*	*Effluents*	*Wastes/Byproducts*
Net Energy use: *Process Energy: 690 Btu/lb*	*Largest source - gaseous fluorides (SiF$_4$ and HF), rock dust, particulates*	*Largest source - acidic wastewater*	*Rock dust, fertilizer dust*

4.2 Summary of Inputs/Outputs

The following summarizes the essential inputs and products, wastes and byproducts of the chemicals and chemical products included in the Agricultural Chemicals chain.

Ammonia

Inputs:

Natural Gas
Air
Catalyst
Steam/Fuel
Electricity

Outputs:

Anhydrous Ammonia
Carbon Dioxide
Export Steam
Recycle Gases
Process Water

Urea

Inputs:

Ammonia
Carbon Dioxide
Additives
Process Water
Steam/Fuel
Electricity

Outputs:

Solid Urea
Urea Solution
Process Water

Nitric Acid

Inputs:

Ammonia
Deionized Water
Sulfuric Acid
Catalyst
Air/Oxygen
Bleaching Agent
Process Water
Steam/Fuel
Electricity

Outputs:

Weak Nitric Acid
High Strength Nitric Acid
Process Water
Steam
Spent Catalyst
Nitrogen Oxides
Inert Gases

Ammonium Nitrate

Inputs:

Ammonia
Nitric Acid
Additives
Electricity

Outputs:

Solid Ammonium
Nitrate

Ammonium Sulfate

Inputs:

Ammonia
Sulfuric Acid
Cooling Water
Steam/Fuel
Electricity

Outputs:

Ammonium Sulfate
Scrubber Products
Vent Gas
Process Water

Sulfuric Acid

Inputs:

Elemental Sulfur
Dry Combustion Air
Catalyst
Cooling Water
Steam/Fuel
Electricity

Outputs:

Sulfuric Acid
Sulfur Dioxide
Process Water
Export Steam
Export Electricity
Spent Catalyst

Phosphoric Acid

Inputs:

Phosphate Rock
93% Sulfuric Acid
Process Water
Steam/Fuel
Electricity

Outputs:

Phosphoric Acid
Fluorosilicate Salts
Uranium Oxide
Silicon Fluoride
Export Steam
Gypsum Slurry
Process Water

Ammonium Phosphate

Inputs:

Phosphoric Acid
Sulfuric Acid
Anhydrous
  Ammonia
Air
Process Water
Gypsum Pond Water
Scrubbing Liquor
Steam/Fuel
Electricity

Outputs:

Ammonium Phosphate
  Fertilizer
Process Water
Gypsum Slurry
Gypsum Pond Water

Normal Superphosphates

Inputs:

Ground Phosphate
  Rock
Sulfuric Acid
Air
Electricity

Outputs:

N-Superphosphates
Rock Dust

Triple Superphosphates

Inputs:

Ground Phosphate
  Rock
Air
Process Water
Steam/Fuel
Electricity

Outputs:

Triple Superphosphates
Process Water
Rock/Fertilizer Dust

5.3 Energy Requirements

Process Energy for Some Agricultural Chemicals Is Relatively High

The **process and feedstock energy** used for the production of agricultural chemicals are shown in Tables 5-3 through 5-12 (PNNL 1994, Brown 1996, HP 1997d, Enviro-Chem 1999a, HP 1999). Each table provides net processing energy, which is the energy used to provide heat and power for the process, in the form of fuels, electricity, or steam. Each table also shows Total Process Energy, which includes processing energy for the final product, minus any steam or fuel generated by the process, plus electricity losses. Electricity losses are those incurred during the generation and transmission of electricity (regardless of whether it is purchased or produced on-site). Thus, Total Process Energy is the total primary energy consumption associated with production of the individual chemical.

For every category, energy use for process heat is distributed according to the various fuel types used throughout the industry. Fuel distribution for 1997 was as follows: fuel oil and LPG - 3 percent; natural gas - 77 percent; coal and coke - 10 percent; other - 10 percent (CMA 1998). The "other" category includes any other fuel source (e.g., byproduct fuel gases).

Processing energy consumption for heat and power associated with the production of **ammonia** is relatively high, on the order of 12,000 Btu/lb. Most of this energy is in the form of steam used for the reforming of methane, ammonia conversion, and vent gas stripping. The large energy input results primarily from the need for multiple passes over the catalyst to achieve acceptable product yields.

Feedstock energy in the form of natural gas or mixed hydrocarbon gases is required for ammonia production, and is included in the processing energy since it is normally reported this way in

Table 5-3. Estimated Energy Use in Ammonia Manufacture- 1997			
Energy	**Specific Energy[d] (Btu/lb)**	**Average Specific Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	885 - 953	919	26.1
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	121 - 130	126	3.6
Natural Gas	9,888 - 10,649	10,269	291.6
Coal and Coke	403 - 434	418	11.9
Other[c]	403 - 434	418	11.9
NET PROCESS ENERGY	**11,700 - 12,600**	**12,150**	345.1
Electricity Losses	1,838 - 1,979	1,908	54.2
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**13,538 - 14,579**	**14,058**	**399.3**

a   Does not include losses incurred during the generation and transmission of electricity.
b   Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies, including those licensed by ICI Katalco/Synetix, Linde AG, and Kellogg, Brown & Root, Inc. (EEA 1983, HP 1999, EFMA 1999).
e   Calculated by multiplying average energy use (Btu/lb) by1997 production values for ammonia (28.4 billion lbs) (CMA 1998).

Table 5-4. Estimated Energy Use in Urea Manufacture- 1997			
Energy	Specific Energy (Btu/lb)	Average Specific[d] Energy (Btu/lb)	Total Industry Use[e] (10^12 Btu)
Electricity[a]	23 - 188	106	1.2
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	19 - 25	22	0.3
Natural Gas	483 - 652	567	6.7
Coal and Coke	63 - 85	74	0.9
Other[c]	63 - 85	74	0.9
NET PROCESS ENERGY	650 - 1,035	843	9.9
Electricity Losses	48 - 390	219	2.6
Energy Export	(94) - (127)	(111)	(1.3)
TOTAL PROCESS ENERGY	604 - 1,298	951	11.2

a   Does not include losses incurred during the generation and transmission of electricity.
b   Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies, including CO_2 and NH_3 stripping, isobaric double recycle, and advanced processes (EFMA 1999, HP 1999).
e   Calculated by multiplying average energy use (Btu/lb) by1997 production values for urea (11.8 billion lbs) (CMA 1998).

Table 5-5. Estimated Energy Use in Manufacture of Nitric Acid - 1997			
Energy	Specific Energy[d] (Btu/lb)	Average Specific Energy (Btu/lb)	Total Industry Use[e] (10^12 Btu)
Electricity[a]	2 - 3	3	0.0
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	7 - 9	8	0.1
Natural Gas	178 - 229	203	2.7
Coal and Coke	23 - 30	26	0.4
Other[c]	23 - 30	26	0.4
NET PROCESS ENERGY	233 - 300	267	3.6
Electricity Losses	4 - 6	5	0.1
Energy Export	(594) - (561)	(578)	(7.8)
TOTAL PROCESS ENERGY	(255) - (357)	(306)	(4.1)

a   Does not include losses incurred during the generation and transmission of electricity.
b   Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values based on published fuel and electricity requirements for licensed technologies (Enviro-Chem, Inc.,1999a).
e   Calculated by multiplying average energy use (Btu/lb) by1997 production values (13.5 billion lbs) (CMA 1998).

Table 5-6. Estimated Energy Use in Ammonium Nitrate Manufacture- 1997			
Energy	Specific Energy (Btu/lb)	Average Specific[d] Energy (Btu/lb)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	55 - 187	121	1.5
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	5 - 8	7	0.1
Natural Gas	127 - 212	169	2.1
Coal and Coke	17 – 28	22	0.3
Other[c]	17 - 28	22	0.3
NET PROCESS ENERGY	220 - 462	341	4.2
Electricity Losses	114 - 388	251	3.1
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	334 - 850	592	7.3

a   Does not include losses incurred during the generation and transmission of electricity.
b   Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies (EFMA 1999).
e   Calculated by multiplying average energy use (Btu/lb) by1997 production values (12.3 billion lbs) (CMA 1998).

Table 5-7. Estimated Energy Use in Manufacture of Ammonium Sulfate - 1997		
Energy	Average Specific[d] Energy (Btu/lb)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	720	3.0
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	98	0.4
Natural Gas	2,526	10.4
Coal and Coke	328	1.3
Other[c]	328	1.3
NET PROCESS ENERGY	4,000	16.4
Electricity Losses	1,495	6.1
Energy Export	0	0.0
TOTAL PROCESS ENERGY	5,495	22.5

a   Does not include losses incurred during the generation and transmission of electricity.
b   Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for licensed technologies (PNNL 1994).
e   Calculated by multiplying average energy use (Btu/lb) by1997 production values (4.1 billion lbs) (CMA 1998).

Table 5-8. Estimated Energy Use in Manufacture of Sulfuric Acid - 1997		
Energy	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	28	2.0
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	1	0.1
Natural Gas	23	1.7
Coal and Coke	3	0.2
Other[c]	3	0.2
NET PROCESS ENERGY	**58**	**4.1**
Electricity Losses	58	4.2
Energy Export	(1,047)	(74.8)
TOTAL PROCESS ENERGY	**(931)**	**(66.5)**

a   Does not include losses incurred during the generation and transmission of electricity.
b   Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel and electricity requirements for licensed technologies (Enviro-Chem, Inc.,1999b).
e   Calculated by multiplying average energy use (Btu/lb) by1997 production values (71.4 billion lbs) (CMA 1998).

Table 5-9. Estimated Energy Use in Manufacture of Phosphoric Acid (Wet Process) - 1997			
Energy	**Specific Energy (Btu/lb)**	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	186 - 464	325	3.1
Energy for Steam/Process Heat[d]			
Fuel Oil and LPG[b]	17 - 73	45	0.4
Natural Gas	424 - 1,863	1,143	10.9
Coal and Coke	55 - 242	149	1.4
Other[c]	55 - 242	149	1.4
NET PROCESS ENERGY	**736 - 2,884**	**1,810**	**17.2**
Electricity Losses	386 - 963	675	6.4
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**1,122 - 3,847**	**2,485**	**23.6**

a   Does not include losses incurred during the generation and transmission of electricity. Does not include electricity for grinding phosphate rock, which requires about 4,180 Btu/lb (Brown 1996).
b   Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel and electricity requirements for wet process technologies (EFMA 1999, Brown 1996).
e   Calculated by multiplying average energy use (Btu/lb) by1997 production values (9.5 billion lbs) (CMA 1998). The wet process is used for about 96 percent of phosphoric acid manufacture.

Table 5-10. Estimated Energy Use in Manufacture of Phosphoric Acid (Furnace Process) - 1997		
Energy	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	14,581	58.0
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	3	0.0
Natural Gas	82	0.0
Coal and Coke	24,003	9.6
Other[c]	21	0.0
NET PROCESS ENERGY	**38,690**	**15.5**
Electricity Losses	30,277	12.1
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**68,967**	**27.6**

a Does not include losses incurred during the generation and transmission of electricity. Includes electricity for grinding phosphate rock..
b Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel and electricity requirements for furnace process technologies (Source: Brown 1996).
e Calculated by multiplying average energy use (Btu/lb) by1997 production values (0.4 billion lbs) (CMA 1998). The furnace process is used for about 4 percent of phosphoric acid manufacture.

the literature (see Table 5-3). Feedstock requirements usually comprise about 50–60 percent of combined processing energy. Despite their origin in hydrocarbon feedstocks, ammonia-derived compounds are generally considered inorganic. Thus, any organic feedstock energy embodied in the ammonia input is not considered in the remainder of the energy tables.

Process energy requirements for manufacture of **urea, ammonium nitrate, and ammonium sulfate** are relatively low. The bulk of energy is in the form of steam used for process heating. Electricity is used mostly for the centrifuging and screening of solid products.

Processes used for manufacturing **nitric acid** are generally net steam exporters, requiring very small amounts of electricity for driving air compressors and pumps. Steam consumption is somewhat higher in plants utilizing dual-pressure (rather than single-pressure) operations.

The **sulfuric acid** plants are large net steam exporters. Large amounts of high-pressure steam are used to power a turbo-alternator for electricity generation. The waste heat boiler used for cooling sulfur dioxide is the largest source of export steam, although energy may be recovered in many places throughout the process. Steam export values range from about 1,000 Btu/lb to over 2,600 Btu/lb of sulfuric acid in well-optimized, state-of-the art plants. Optimizing energy recovery from plants lowers production costs, and improvements are continually being made in this area. With advanced technology, net steam export values can reportedly double in amount (Enviro-Chem 1999d, EFMA 1999).

Table 5-11. Estimated Energy Use in Manufacture of Ammonium Phosphate - 1997		
Energy	**Average Specific[d] Energy (Btu/lb)**	**Total Industry Use[e] (10^{12} Btu)**
Electricity[a]	82	1.6
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	7	0.1
Natural Gas	186	3.5
Coal and Coke	24	0.5
Other[c]	24	0.5
NET PROCESS ENERGY	**323**	**6.1**
Electricity Losses	170	3.2
Energy Export	(117)	(2.2)
TOTAL PROCESS ENERGY	**376**	**7.1**

a   Does not include losses incurred during the generation and transmission of electricity.
b   Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on
    published fuel and electricity requirements for licensed technologies (Brown 1996).
e   Calculated by multiplying average energy use (Btu/lb) by1997 production values (18.9 billion lbs) (TFI 1999).

The wet process is used for 96 percent of the **phosphoric acid** manufactured. This process is moderately energy-intensive, requiring about 6,130 Btu/lb. An alternative method, the furnace process, is used for the remaining 4 percent of production and it is highly energy-intensive, consuming nearly 40,000 Btu/lb. This process is used solely for producing high-quality, chemical-grade phosphoric acid, not fertilizer-grade product.

Production of phosphate fertilizers requires very modest energy consumption, primarily in the form of steam used for drying. Ammonium phosphate processes also generate export steam. Electricity is used for granulating, milling, crushing, and screening solid products.

Table 5-12. Estimated Energy Use in Manufacture of Superphosphates - 1997		
Energy	Average Specific[d] Energy (Btu/lb)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	340	1.2
Energy for Steam/Process Heat[d]		
Fuel Oil and LPG[b]	11	0.1
Natural Gas	270	0.9
Coal and Coke	35	0.1
Other[c]	35	0.1
NET PROCESS ENERGY	690	2.4
Electricity Losses	706	2.4
Energy Export	0	0.0
TOTAL PROCESS ENERGY	1,396	4.8

a   Does not include losses incurred during the generation and transmission of electricity.
b   Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.
c   Includes net purchased steam, and any other energy source not listed (e.g., renewables).
d   Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel and electricity requirements for granulated triple superphosphate processes (Brown 1996).
e   Calculated by multiplying average energy use (Btu/lb) by1997 production values for normal and triple superphosphates (3.4 billion lbs) (TFI 1999).

5.4 Air Emissions

Ammonia and Sulfur Compounds Are the Primary Source of Air Contaminants from Production of Agricultural Chemicals

The primary sources of emissions in the agricultural chemicals chain are fugitive and point air source emissions of particulates and volatile compounds emitted from equipment and process operations. Fugitive emissions of volatile compounds arise from leaks in valves, pumps, tanks, flanges, and other similar sources. Particulates arise from granulation processes used for production of solid fertilizers, and from rock dust during ore processing.

Ammonia is one of the top five toxic chemicals released every year, primarily from point air and fugitive emissions sources. Ammonia is released during its manufacture as well as during its use in other chemical processes. Releases of ammonia are reported annually in the Toxic Release Inventory (TRI). In 1996, nearly 110 million pounds of ammonia were released by the chemical industry to the air, land, and water. Over 10 million pounds were also released from petroleum refineries (EPA 1998, EPA 1997c).

Pollutants from **ammonia manufacture** are emitted from regeneration of the desulfurization bed, heating of the catalytic steam, regeneration of carbon dioxide scrubbing solution, and steam stripping of the process condensate. Emission factors for each of these emission points are given in Table 5-13. Nearly all U.S. ammonia plants use activated carbon fortified with metallic oxide additives to desulfurize feedstocks. These

beds are regenerated about once a month. The vented regeneration steam contains sulfur oxides and hydrogen sulfide, some hydrocarbons, and carbon monoxide.

Carbon dioxide is a byproduct of the reaction and is removed from the synthesis gas by scrubbing with hot potassium carbonate or similar compounds. Regeneration of this scrubbing solution liberates water, ammonia, carbon monoxide, and volatile scrubbing solution compounds. Stripping of process condensate yields steam, which is vented to the atmosphere and contains ammonia, carbon dioxide, and methanol.

The primary emissions from **urea manufacture** are ammonia and particulates. Small amounts of volatile additive components (e.g., methanol, formaldehyde) may also be emitted. Additives like Formalin^{TM}, for example, may contain up to 15 percent methanol. Ammonia may be emitted during solution synthesis and production of solid products. Particulates are emitted throughout the process. Table 5-14 provides emission factors for urea production.

The recycling of carbamate gases or liquids allows some emission control. Emissions from the synthesis process are usually combined with those from concentrating the solution and vented through stacks. Particulate control is usually only carried out in the solids-producing areas; other emissions of particulates are small by comparison. In the solids-screening process, dust is generated as urea particles collide and the screen vibrates. In urea manufacture, almost all the screening operations are enclosed or covered to reduce emissions. Coating of the product may emit entrained clay dust during loading and product transfer, but no emission factors are available to quantify this source (EPA 1993d).

Emissions from the **manufacture of nitric acid** include mostly nitrogen oxides (NO and NO_2), and trace amounts of ammonia and nitric acid mist. The tail gas from the acid absorption tower is the largest source of nitrogen oxide emissions. These emissions can increase when insufficient air is supplied to the oxidizer and absorber, under low absorber pressure conditions, and during high temperature conditions in the cooler/condenser and absorber. Other factors may contribute, such as high throughputs, very high-strength products, or faulty compressors or pumps. Emission factors for nitric acid plants are shown in Table 5-15.

Table 5-13. Air Emissions from Ammonia Manufacture					
Emission Point	**CO (lb/ton)**	**SO$_2$ (lb/ton)**	**TOC[a] (lb/ton)**	**NH$_3$ (lb/ton)**	**CO$_2$ (lb/ton)**
Desulfurization unit regeneration[b]	13.8	0.0576	7.2		ND
Carbon dioxide regenerator	2.0		1.04[c]	2.0	2440
Condensate steam stripper			1.2[d]	2.2	6.8 (±60%)

a   Total organic compounds.
b   Intermittent source; regeneration is done every 30 days. SO$_2$ is a worst case factor (all sulfur entering tank is emitted).
c   0.1 lb/ton is monoethanolamine.
d   Primarily methanol.

Source: EPA 1997a.

Control of emissions from nitric acid plants is usually accomplished through either extended absorption or catalytic reduction. Extended absorption works by increasing the efficiency of the absorption process. Catalytic reduction oxidizes nitrogen oxides in the tail gas and reduces them to nitrogen. While catalytic reduction is more energy-intensive, it achieves greater emission reductions than the extended absorption method. Less-used control options include wet scrubbers or molecular sieves, both of which have higher capital and operating costs than the other options (EPA 1997b).

The **manufacture of ammonium nitrate** produces particulate matter, ammonia, and nitric acid emissions. Emission factors are shown in Table 5-16. Emissions from ammonia and nitric acid occur primarily when they form solutions (neutralizers and concentrators), and when they are used in granulators.

Particulate matter is the largest source and is emitted throughout the process during the formation of solids. Prill towers and granulators are the largest sources of particulates. Microprills can form and clog orifices, increasing fine dust loading and emissions.

Emissions occur from screening operations by the banging of ammonium nitrate solids against each other and the screens. Most of these screening operations are enclosed or have partial covers to reduce emissions. The coating of products may also create some particulate emissions during mixing in the rotary drums. This dust is usually captured and recycled to coating storage. Another source of dust is bagging and bulk loading, mostly during final filling when dust-laden air is displaced from bags (EPA 1993c).

Table 5-14. Air Emissions from Urea Manufacture				
Type of Operation	**Particulates (lb/ton)**		**Ammonia (lb/ton)**	
	Uncontrolled	**Controlled**	**Uncontrolled**	**Controlled**
Solution formation and concentration[a]	0.021		18.46	
Nonfluidized bed prilling[b]	3.7	0.063	0.87	
Fluidized bed prilling[c]	4.9	0.63	3.53	2.08
Drum Granulation[c]	241	0.234	2.15	
Rotary Drum Cooler	7.78	0.20	0.051	
Bagging	0.19			

a   Emissions from synthesis are usually combined with those from solution concentration and vented through a common stack. In synthesis, some emission control is inherent in the recycle process where carbamate gases and/or liquids are recovered and recycled.
b   Controlled factors are based on ducting exhaust through a downcomer, then a wetted fiber filter scrubber (98.3% efficient), a higher degree of control than is typical in the industry.
c   Controlled factors are based on use of an entrainment scrubber.

Source: EPA 1993d.

Table 5-15. Air Emissions from Nitric Acid Plants		
Source	**Control Efficiency %**	**Nitrogen Oxides (lbs/ton[a])**
Weak Acid Plant Tail Gas		
Uncontrolled[b]	0	57
Catalytic Reduction **Natural Gas** **Hydrogen** **Natural Gas/Hydrogen**	99.1 97-98.5 98-98.5	0.4 0.8 0.9
Extended Absorption **Single-Stage** **Dual-Stage**	95.8	1.9 2.1
Chilled Absorption & Caustic Scrubber	n/a	2.2
High Strength Acid Plant	n/a	10

a   Based on 100% nitric acid.
b   Single-stage pressure process.

Source: EPA 1993b.

Table 5-16. Air Emissions from Ammonium Nitrate Manufacture				
Process	**Particulate Matter (lb/ton)**		**Ammonia (uncontrolled) lb/ton**	**Nitric Acid lb/ton**
	Uncontrolled	**Controlled[a]**		
Neutralizer	0.090-8.6	0.004-0.44	0.86-36.0	0.084-2.0
Evaporation/concentration operations	0.52		0.54-33.4	
Solids Formation operations	298.8	2.2	58.5	
Coolers and Dryers[b]	220.4	2.2	1.93	
Coating Operations	<4.0	<0.04		

a   Based on the following efficiencies for wet scrubbers: neutralizer, 95%; high density prill towers, 62%; low density prill towers, 43%; rotary drum granulators,99.9%; pan granulators,98.5%; coolers, dryers, and coaters,99%.
b   Combined cooler and precooler emissions, and combined dryer and predryer emissions.

Source: EPA 1993c.

Table 5-17. Air Emissions from Ammonium Sulfate Manufacture		
Dryer Type	**Particulate (lb/ton)**	**VOC[a] (lb/ton)**
Rotary Dryers **(Uncontrolled)** **(Wet Scrubber)**	46 0.04	1.48 0.22
Fluidized-bed Dryers **(Uncontrolled)** **(Wet Scrubber)**	218 0.28	1.48 0.22

a VOC emissions occur only at caprolactam plants where ammonium sulfate is produced as a byproduct. The emissions are caprolactam vapor.

Source: EPA 1997d.

Particulate ammonium sulfate is the air emission occurring in the largest amount from manufacture of this fertilizer. Dryer exhaust is the primary source of the particulates, and emission rates are dependent on gas velocity and particle size distribution. Particulate rates are higher for fluidized bed dryers than for the rotary drum type of dryer. Most plants use baghouses to control particulates of ammonium sulfate, although venturi and centrifugal wet scrubbers are better suited for this purpose.

Some volatile carbon emissions may be present in caprolactam plants where ammonium sulfate is produced as a byproduct. Emission factors for controlled and uncontrolled emissions of ammonium sulfate are shown in Table 5-17 (EPA 1997d).

Sulfur dioxide is the primary emission from **sulfuric acid manufacture**, and is found primarily in the exit stack gases. Conversion of sulfur dioxide to sulfur trioxide is also incomplete during the process, which gives rise to emissions. Dual absorption is considered the Best Available Control Technology (BACT) for meeting new source performance standards (NSPS) for sulfur dioxide. In addition to stack gases, small amounts of sulfur dioxide are emitted from storage and tank-truck vents during loading, from sulfuric acid concentrators, and from leaking process equipment. Emission factors for sulfur dioxide from sulfuric acid plants are shown in Table 5-18.

Acid mists may also be emitted from absorber stack gases during sulfuric acid manufacture. The very stable acid mist is formed when sulfur trioxide reacts with water vapor below the dew point of sulfur trioxide. Acid mist emission factors for controlled and uncontrolled plants are shown in Table 5-19 and Table 5-20. Typical control devices include vertical tube, vertical panel, and horizontal dual pad mist eliminators (EPA 1992a).

Major emissions from **wet process phosphoric acid manufacture** are comprised of gaseous fluorides in the form of silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF). The source of fluorides is phosphate rock, which contains from 3.5 to 4.0 percent fluorine. The fluorine is generally precipitated out with gypsum, leached out with phosphoric acid product, or vaporized in the reactor or evaporator.

The reactor where phosphate rock is contacted with sulfuric acid is the primary source of emissions. Vacuum flash cooling of the reactor slurry will minimize these emissions as the system is closed. During acid concentration, 20 to 40 percent of the fluorine in the rock may vaporize. Emission factors for fluorides from wet processing are shown in Table 5-21.

Table 5-18. Air Emissions from Sulfuric Acid Manufacture	
SO$_2$ to SO$_3$ Conversion Efficiency	SO$_2$ Emissions (lb/ton of product)
93	96
94	82
95	70
96	55
97	40
98	26
99	14
99.5	7
99.7	4
100	0.0

Source: EPA 1992a.

Table 5-19. Acid Mist Emissions from Uncontrolled Sulfuric Acid Plants		
Raw Material	Oleum Produced (% total output)	Uncontrolled (lb/ton)
Recovered Sulfur	0-43	0.348-0.8
Bright Virgin Sulfur	0	1.7
Dark Virgin Sulfur	0-100	0.32-6.28
Spent Acid	0-77	2.2-2.4

Source: EPA 1992a.

Table 5-20. Acid Mist Emissions from Controlled Sulfuric Acid Plants		
Raw Material	Oleum Produced (% total output)	Controlled (lb/ton)
Elemental Sulfur	-	0.64
Dark Virgin Sulfur	0-13	0.26-1.8
Spent Acid	0-56	0.014-0.20

Source: EPA 1992a.

Table 5-21. Air Emissions from Wet Process Phosphoric Acid Manufacture		
Source	**Controlled Fluorine (lb/ton P_2O_5 produced)**	**Controlled Fluorine (lb/ton P_2O_5 produced)**
Reactor	3.8×10^{-3}	0.38
Evaporator	0.044×10^{-3}	0.0044
Belt filter	0.64×10^{-3}	0.064
Belt filter vacuum pump	0.15×10^{-3}	0.015
Gypsum settling and cooling ponds[a]	Site-specific	Site-specific

a   Acres of cooling pond required range from 0.1 acre per daily ton phosphoric acid produced in the summer in the southeast U.S., to 0 (zero) in colder locations in winter months when cooling ponds are frozen. There are still considerable uncertainties in measurement of fluoride from gypsum ponds.

Source: EPA 1997e.

Table 5-22. Emission Factors for Thermal Process Phosphoric Acid Manufacture	
Source	**Particulate Acid Mist (lb/ton P_2O_5 produced)**
Packed Tower	2.14
Venturi Scrubber	2.53
Glass fiber mist eliminator	0.69
Wire mesh mist eliminator	5.46
High pressure drop mist	0.11
Electrostatic Precipitator	1.66

Source: EPA 1997e.

Scrubbers (venturi, wet cyclonic, and semi-cross flow) are used to control emissions of fluorine. Leachate fluorine may settle in settling ponds, and if the water becomes saturated, it will be emitted to the air as fluorine gas.

Thermal or furnace processing of phosphoric acid results in phosphoric acid mist, which is contained in the gas stream exiting the hydrator. A large amount of phosphorus pentoxide product may be present as liquid phosphoric acid particles suspended in the gas stream, so most plants attempt to control this loss. Control equipment includes venturi scrubbers, cyclonic separators with wire mesh mist eliminators, fiber mist eliminators, high energy wire mesh contactors, and electrostatic precipitators. Emission factors for thermal processing are given in Table 5-22.

Normal superphosphate manufacture produces emissions of gaseous fluorides in the form of

silicon tetrafluoride (SiF$_4$) and hydrogen fluoride (HF). Particulates composed of fluoride and phosphate material are also emitted. Sources include rock unloading and feeding, mixing operations, storage, and fertilizer handling (see Table 5-23 for emission factors).

Sources of emissions for **triple super-phosphates manufacture** include the reactor, granulator, dryer, screens, cooler, mills, and transfer conveyors (see Table 5-24). Particulates may be emitted during unloading, grinding, storage, and transfer of ground phosphate rock. Baghouses, scrubbers, or cyclonic separators are used to control emissions.

Emissions from **production of ammonium phosphate fertilizers** come from the reactor, the

ammoniator-granulator, dryers, coolers, product sizing, material transfer, and the gypsum pond (see Table 5-25). Silicon tetrafluoride (SiF$_4$), hydrogen fluoride (HF), gaseous ammonia, and ammonium phosphate particulates are produced by the reactor and ammoniator-granulator. These emissions are controlled by primary and secondary scrubbers. Exhaust gases from the dryer and cooler contain similar emissions and are passed through cyclones and scrubbers, as are emissions from product sizing and material transfer (EPA 1997f).

Combustion of fuels in boilers to produce steam and in process heaters or furnaces also produce criteria air pollutants that are regulated under the Clean Air Act. Current emission factors for process heaters and boilers are discussed in Section 7, Supporting Processes.

Table 5-23. Air Emissions from Normal Superphosphate Manufacture			
Emission Point	**Particulates (lb/ton)**	**PM 10[c] (lb/ton)**	**Fluoride (lb/ton)**
Rock unloading[a]	0.56	0.29	-
Rock feeding[a]	0.11	0.06	-
Mixer and den[b]	0.52	0.44	0.20
Curing building	7.2	6.1	3.80

a   Factors are for baghouses with estimated collection efficiency of 99 percent.
b   Factors are for wet scrubbers with an estimated 97 percent control efficiency.
c   Particulate matter 10 microns and above. Based on AIRS listing for criteria air pollutants.

Source: EPA 1997f.

Table 5-24. Air Emissions from Triple Superphosphate Manufacture			
Emission Point	**Particulates (lb/ton)**	**PM 10[c] (lb/ton)**	**Fluoride (lb/ton)**
Rock unloading[a]	0.18	0.08	-
Rock feeding[a]	0.04	0.02	-
Reactor, granulator, dryer, cooler, and screens[b]	0.1	0.08	0.24
Curing building	0.20	0.17	0.04

a   Factors are for baghouses with estimated collection efficiency of 99 percent.
b   Factors are for wet scrubbers with an estimated 97 percent control efficiency.
c   Particulate matter of 10 microns and larger. Based on AIRS listing for criteria air pollutants.

Source: EPA 1997f.

Table 5-25. Air Emissions from Ammonium Phosphate Manufacture				
Emission Point	Fluoride as F (lb/ton)	Particulate (lb/ton)	Ammonia (lb/ton)	SO_2 (lb/ton)
Reactor / ammoniator-granulator	0.05	1.52	ND	
Dryer/Cooler	0.04	1.50		
Product sizing and material transfer	0.002	0.06		
Total Plant Emissions	0.04	0.68	0.14	0.08

Source: EPA 1997f.

5.5 Effluents

Wastewaters May Contain Phosphorus, Fluorides, Nitrogen Compounds, Carbon Dioxide, or Acids

Wastewaters from manufacture of agricultural chemicals consist mostly of wash water, scrubber water, boiler and vaporizer blow down, or stripper water. These may contain phosphorus, fluorides, ammonia, carbon dioxide, or weak acids. Many of these waters are treated and recycled to the process. Valuable components (e.g., ammonia) may also be recovered. Water scrubbing of the purge gases in **ammonia** production, for example, creates an ammonia water solution that can be used in another process (e.g., urea production). In **urea** production, ammonia, carbon dioxide, and urea are removed from process waters by water treatment, and the gases are recycled to the synthesis process (EFMA 1999).

Plants producing **nitric acid and ammonium nitrate** produce waste waters containing these compounds as well as ammonia. Wastewater containing ammonia and nitric acid must be neutralized to produce ammonium nitrate.

In **phosphoric acid** production, the fluorine released from reactors and evaporators is usually recovered as a by-product that can be sold. The remainder is passed to the condenser that produces a liquid effluent with mostly fluoride and small amounts of phosphoric acid. Closed systems recycle this effluent; in other cases, it is discharged to open waters (EFMA 1999).

Limitations for toxic or hazardous compounds contained in these wastewaters are given by the U.S. Environmental Protection Agency in 40 CFR, Chapter 1, Part 418, which was originally promulgated in 1974 and has undergone several revisions. The chemicals in the agriculturalchain are covered under Subparts A-G.

Specific limitations for restricted compounds and total suspended solids (TSS) are shown in Tables 5-26 through 5-30. BPT indicates the use of best practicable control technology currently available; BAT refers to the best available technology economically achievable.

Table 5-26. Effluent Pretreatment Standards: Phosphate Fertilizers		
Effluent	Maximum for any 1 day (micrograms/liter)	Maximum for Monthly Average (micrograms/liter)
Total Phosphorus (as P)	105	35
Fluoride	75	35
Total Suspended Solids	150	50

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart A.

Table 5-27. Effluent Pretreatment Standards: Ammonia		
Effluent	BPT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lb product)	BAT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lb product)
Ammonia (as N)	0.0625	0.025
pH	6.0-9.0	-

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart B.

Table 5-28. Effluent Pretreatment Standards: Urea				
Effluent	BPT Standards: Average Daily Value for 30 Consecutive Days (Micrograms/liter)		BAT Standards: Average Daily Value for 30 Consecutive Days (micrograms/liter)	
	Solution Urea	Prills or Granules	Solution Urea	Prills or Granules
Ammonia (as N)	0.48	0.59	0.27	0.27
Organic Nitrogen	0.33	0.8	0.24	0.46

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart C.

Table 5-29. Effluent Pretreatment Standards: Ammonium Nitrate		
Effluent	BPT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lb/product)	BAT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lb product)
Ammonia (as N)	0.39	0.04
Nitrate (as N)	0.37	0.07

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart D.

Table 5-30. Effluent Pretreatment Standards: Nitric Acid				
Effluent	**BPT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lbs product)**		**BAT Standards: Average Daily Value for 30 Consecutive Days (lb/1000 lbs product)**	
	Gaseous Form	**Liquid Form**	**Gaseous Form**	**Liquid Form**
Ammonia (as N)	0.0007	0.008	0.00045	0.008
Nitrate as N	0.044	0.044	0.023	0.023

Source: 40 CFR Chapter 1, Part 418, Fertilizer Manufacturing Point Source Category, Subpart E.

5.6 Wastes, Residuals, and Byproducts

Spent Catalysts, Sludges, and Baghouse Dust Are Residuals of Agricultural Chemical Manufacture

The manufacture of agricultural chemicals produces some solid wastes and byproducts, the majority from spent catalysts and particulates that have been trapped in various capture systems. Solid wastes from **ammonia production**, for example, include spent catalysts and molecular sieves that are removed and sent off-site for removal of valuable precious metals. Sulfur may be recovered in plants that use partial oxidation (EFMA 1999).

Solid wastes from **nitric acid** manufacture include spent catalysts that are either returned to the manufacturer or disposed of. Dust from the catalyst may settle out in the equipment, but if it contains precious metals, it is recovered and sent for reprocessing to an outside vendor. Precious metals (e.g., platinum) lost from the ammonia oxidation catalyst are captured by a recovery gauze (getter), which must be replaced periodically and is reprocessed by a gauze manufacturer. Filters used for ammonia/air filtration must also be replaced. They are often disposed of, but can be recycled (EFMA 1999).

During the production of **sulfuric acid,** a sludge is produced in the carbon dioxide removal unit used to absorb solvent gas. A hydrocarbon solvent is used in the unit, which breaks down into a hydrocarbon sludge during the process. This sludge is usually combusted in another part of the process. Sulfuric acid manufacture also produces a solid waste containing the heavy metal vanadium, when the convertor catalyst is regenerated or screened. This waste is sent to an off-site vendor for reprocessing. Additional solid wastes from sulfuric acid production may contain both vanadium and arsenic, depending on the raw materials used, and care must be taken to dispose of them properly in landfills (EFMA 1999).

The production of **solid fertilizers** produces dust, some of which is collected in baghouses. It must be disposed of or is recycled to the process when possible. Some processes (e.g., thermal processing of phosphoric acid) produce an acid mist consisting of entrained acid particles in gas. This particulate acid is usually controlled and recovered as a valuable product.

The manufacture of **phosphoric acid** produces a gypsum slurry that is sent to settling ponds to allow the solids to settle out. About 5 pounds of phosphogypsum are generated per pound of phosphoric acid. This phosphogypsum contains trace elements from phosphate rock, such as cadmium and uranium. Pond systems are usually fitted with lining systems and collection ditches to maintain control of trace elements and avoid contamination of ground water (EFMA 1999).