

## 8.2 Urea

### 8.2.1 General<sup>1-13</sup>

Urea [ $\text{CO}(\text{NH}_2)_2$ ], also known as carbamide or carbonyl diamide, is marketed as a solution or in solid form. Most urea solution produced is used in fertilizer mixtures, with a small amount going to animal feed supplements. Most solids are produced as prills or granules, for use as fertilizer or protein supplement in animal feed, and in plastics manufacturing. Five U. S. plants produce solid urea in crystalline form. About 7.3 million megagrams (Mg) (8 million tons) of urea were produced in the U. S. in 1991. About 85 percent was used in fertilizers (both solid and solution forms), 3 percent in animal feed supplements, and the remaining 12 percent in plastics and other uses.

### 8.2.2 Process Description<sup>1-2</sup>

The process for manufacturing urea involves a combination of up to 7 major unit operations. These operations, illustrated by the flow diagram in Figure 8.2-1, are solution synthesis, solution concentration, solids formation, solids cooling, solids screening, solids coating and bagging, and/or bulk shipping.

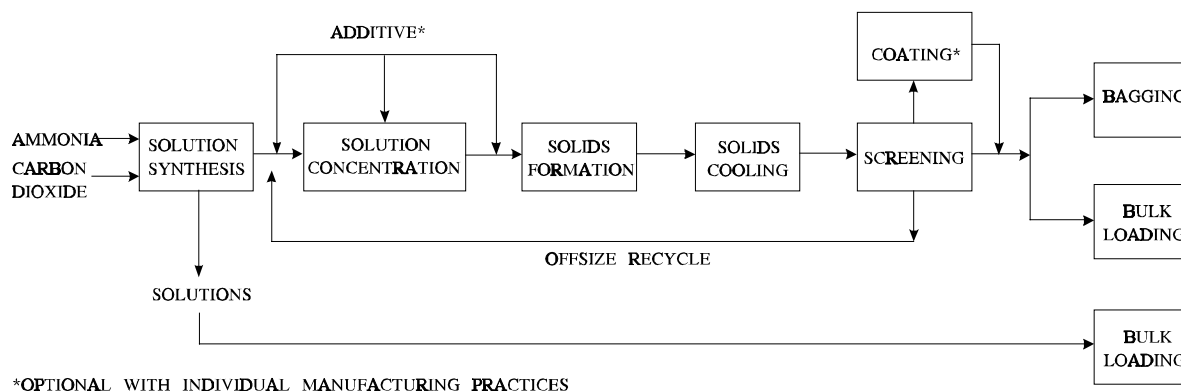
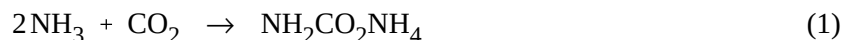
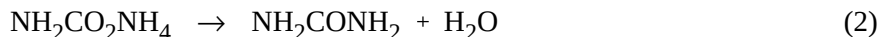


Figure 8.2-1. Major area manufacturing operations.

The combination of processing steps is determined by the desired end products. For example, plants producing urea solution use only the solution formulation and bulk shipping operations. Facilities producing solid urea employ these 2 operations and various combinations of the remaining 5 operations, depending upon the specific end product being produced.

In the solution synthesis operation, ammonia ( $\text{NH}_3$ ) and carbon dioxide ( $\text{CO}_2$ ) are reacted to form ammonium carbamate ( $\text{NH}_2\text{CO}_2\text{NH}_4$ ). Typical operating conditions include temperatures from 180 to 200°C (356 to 392°F), pressures from 140 to 250 atmospheres (14,185 to 25,331 kilopascals)  $\text{NH}_3$ : $\text{CO}_2$  molar ratios from 3:1 to 4:1, and a retention time of 20 to 30 minutes. The carbamate is then dehydrated to yield 70 to 77 percent aqueous urea solution. These reactions are as follows:





The urea solution can be used as an ingredient of nitrogen solution fertilizers, or it can be concentrated further to produce solid urea.

The 3 methods of concentrating the urea solution are vacuum concentration, crystallization, and atmospheric evaporation. The method chosen depends upon the level of biuret ( $\text{NH}_2\text{CONHCONH}_2$ ) impurity allowable in the end product. Aqueous urea solution begins to decompose at 60°C (140°F) to biuret and ammonia. The most common method of solution concentration is evaporation.

The concentration process furnishes urea "melt" for solids formation. Urea solids are produced from the urea melt by 2 basic methods: prilling and granulation. Prilling is a process by which solid particles are produced from molten urea. Molten urea is sprayed from the top of a prill tower. As the droplets fall through a countercurrent air flow, they cool and solidify into nearly spherical particles. There are 2 types of prill towers: fluidized bed and nonfluidized bed. The major difference is that a separate solids cooling operation may be required to produce agricultural grade prills in a nonfluidized bed prill tower.

Granulation is used more frequently than prilling in producing solid urea for fertilizer. Granular urea is generally stronger than prilled urea, both in crushing strength and abrasion resistance. There are 2 granulation methods: drum granulation and pan granulation. In drum granulation, solids are built up in layers on seed granules placed in a rotating drum granulator/cooler approximately 4.3 meters (14 feet) in diameter. Pan granulators also form the product in a layering process, but different equipment is used and pan granulators are not commonly used in the U. S.

The solids cooling operation is generally accomplished during solids formation, but for pan granulation processes and for some agricultural grade prills, some supplementary cooling is provided by auxiliary rotary drums.

The solids screening operation removes offsize product from solid urea. The offsize material may be returned to the process in the solid phase or be redissolved in water and returned to the solution concentration process.

Clay coatings are used in the urea industry to reduce product caking and urea dust formation. The coating also reduces the nitrogen content of the product. The use of clay coating has diminished considerably, being replaced by injection of formaldehyde additives into the liquid or molten urea before solids formation. Formaldehyde reacts with urea to form methylenediurea, which is the conditioning agent. Additives reduce solids caking during storage and urea dust formation during transport and handling.

The majority of solid urea product is bulk shipped in trucks, enclosed railroad cars, or barges, but approximately 10 percent is bagged.

### 8.2.3 Emissions And Controls<sup>1,3-7</sup>

Emissions from urea manufacture are mainly ammonia and particulate matter. Formaldehyde and methanol, hazardous air pollutants, may be emitted if additives are used. Formalin<sup>TM</sup>, used as a formaldehyde additive, may contain up to 15 percent methanol. Ammonia is emitted during the solution synthesis and solids production processes. Particulate matter is emitted during all urea processes. There have been no reliable measurements of free gaseous formaldehyde emissions. The chromatographic procedure that has been used to measure formaldehyde is not capable of distinguishing between gaseous

formaldehyde and methylenediurea, the principle compound formed when the formaldehyde additive reacts with hot urea.

Table 8.2-1 summarizes the uncontrolled and controlled emission factors, by processes, for urea manufacture. Factors are expressed in units of kilograms per megagram (kg/Mg) and pounds per ton (lb/ton). Table 8.2-2 summarizes particle sizes for these emissions. Units are expressed in terms of micrometers ( $\mu\text{m}$ ).

In the synthesis process, some emission control is inherent in the recycle process where carbamate gases and/or liquids are recovered and recycled. Typical emission sources from the solution synthesis process are noncondensable vent streams from ammonium carbamate decomposers and separators. Emissions from synthesis processes are generally combined with emissions from the solution concentration process and are vented through a common stack. Combined particulate emissions from urea synthesis and concentration operations are small compared to particulate emissions from a typical solids-producing urea plant. The synthesis and concentration operations are usually uncontrolled except for recycle provisions to recover ammonia. For these reasons, no factor for controlled emissions from synthesis and concentration processes is given in this section.

Uncontrolled emission rates from prill towers may be affected by the following factors: (1) product grade being produced, (2) air flow rate through the tower, (3) type of tower bed, and (4) ambient temperature and humidity.

The total of mass emissions per unit is usually lower for feed grade prill production than for agricultural grade prills, due to lower airflows. Uncontrolled particulate emission rates for fluidized bed prill towers are higher than those for nonfluidized bed prill towers making agricultural grade prills, and are approximately equal to those for nonfluidized bed feed grade prills. Ambient air conditions can affect prill tower emissions. Available data indicate that colder temperatures promote the formation of smaller particles in the prill tower exhaust. Since smaller particles are more difficult to remove, the efficiency of prill tower control devices tends to decrease with ambient temperatures. This can lead to higher emission levels for prill towers operated during cold weather. Ambient humidity can also affect prill tower emissions. Air flow rates must be increased with high humidity, and higher air flow rates usually cause higher emissions.

The design parameters of drum granulators and rotary drum coolers may affect emissions. Drum granulators have an advantage over prill towers in that they are capable of producing very large particles without difficulty. Granulators also require less air for operation than do prill towers. A disadvantage of granulators is their inability to produce the smaller feed grade granules economically. To produce smaller granules, the drum must be operated at a higher seed particle recycle rate. It has been reported that, although the increase in seed material results in a lower bed temperature, the corresponding increase in fines in the granulator causes a higher emission rate. Cooling air passing through the drum granulator entrains approximately 10 to 20 percent of the product. This air stream is controlled with a wet scrubber which is standard process equipment on drum granulators.

In the solids screening process, dust is generated by abrasion of urea particles and the vibration of the screening mechanisms. Therefore, almost all screening operations used in the urea manufacturing industry are enclosed or are covered over the uppermost screen. This operation is a small emission source; therefore particulate emission factors from solids screening are not presented.

Emissions attributable to coating include entrained clay dust from loading, inplant transfer, and leaks from the seals of the coater. No emissions data are available to quantify this fugitive dust source.

Table 8.2-1 (Metric And English Units). EMISSION FACTORS FOR UREA PRODUCTION

EMISSION FACTOR RATING: A (except as noted)

| Type Of Operation                                 | Particulate <sup>a</sup> |                    |                    |                    | Ammonia             |                    |                         |                   |
|---------------------------------------------------|--------------------------|--------------------|--------------------|--------------------|---------------------|--------------------|-------------------------|-------------------|
|                                                   | Uncontrolled             |                    | Controlled         |                    | Uncontrolled        |                    | Controlled <sup>b</sup> |                   |
|                                                   | kg/Mg Of Product         | lb/ton Of Product  | kg/Mg Of Product   | lb/ton Of Product  | kg/Mg Of Product    | lb/ton Of Product  | kg/Mg Of Product        | lb/ton Of Product |
| Solution formation and concentration <sup>c</sup> | 0.0105 <sup>d</sup>      | 0.021 <sup>d</sup> | ND                 | ND                 | 9.23 <sup>e</sup>   | 18.46 <sup>e</sup> | ND                      | ND                |
| Nonfluidized bed prilling                         |                          |                    |                    |                    |                     |                    |                         |                   |
| Agricultural grade <sup>f</sup>                   | 1.9                      | 3.8                | 0.032 <sup>g</sup> | 0.063 <sup>g</sup> | 0.43                | 0.87               | ND                      | ND                |
| Feed grade <sup>h</sup>                           | 1.8                      | 3.6                | ND                 | ND                 | ND                  | ND                 | ND                      | ND                |
| Fluidized bed prilling                            |                          |                    |                    |                    |                     |                    |                         |                   |
| Agricultural grade <sup>h</sup>                   | 3.1                      | 6.2                | 0.39               | 0.78               | 1.46                | 2.91               | ND                      | ND                |
| Feed grade <sup>h</sup>                           | 1.8                      | 3.6                | 0.24               | 0.48               | 2.07                | 4.14               | 1.04                    | 2.08              |
| Drum granulation <sup>j</sup>                     | 120                      | 241                | 0.115              | 0.234              | 1.07 <sup>k</sup>   | 2.15 <sup>k</sup>  | ND                      | ND                |
| Rotary drum cooler                                | 3.89 <sup>m</sup>        | 7.78 <sup>m</sup>  | 0.10 <sup>n</sup>  | 0.20 <sup>n</sup>  | 0.0256 <sup>m</sup> | 0.051 <sup>m</sup> | ND                      | ND                |
| Bagging                                           | 0.095 <sup>n</sup>       | 0.19 <sup>n</sup>  | ND                 | ND                 | NA                  | NA                 | NA                      | NA                |

<sup>a</sup> Particulate test data were collected using a modification of EPA Reference Method 3. Reference 1, Appendix B explains these modifications. ND = no data. NA = not applicable.

<sup>b</sup> No ammonia control demonstrated by scrubbers installed for particulate control. Some increase in ammonia emissions exiting the control device was noted.

<sup>c</sup> References 9,11. Emissions from the synthesis process are generally combined with emissions from the solution concentration process and vented through a common stack. In the synthesis process, some emission control is inherent in the recycle process where carbamate gases and/or liquids are recovered and recycled.

<sup>d</sup> EPA test data indicated a range of 0.005 to 0.016 kg/Mg (0.010 to 0.032 lb/ton).

<sup>e</sup> EPA test data indicated a range of 4.01 to 14.45 kg/Mg (8.02 to 28.90 lb/ton).

<sup>f</sup> Reference 12. These factors were determined at an ambient temperature of 14 to 21°C (57 to 69°F). The controlled emission factors are based on ducting exhaust through a downcomer and then a wetted fiber filter scrubber achieving a 98.3% efficiency. This represents a higher degree of control than is typical in this industry.

<sup>g</sup> Only runs 2 and 3 were used (test Series A).

<sup>h</sup> Reference 11. Feed grade factors were determined at an ambient temperature of 29°C (85°F) and agricultural grade factors at an ambient temperature of 27°C (80°F). For fluidized bed prilling, controlled emission factors are based on use of an entrainment scrubber.

<sup>j</sup> References 8-9. Controlled emission factors are based on use of a wet entrainment scrubber. Wet scrubbers are standard process equipment on drum granulators. Uncontrolled emissions were measured at the scrubber inlet.

<sup>k</sup> EPA test data indicated a range of 0.955 to 1.20 kg/Mg (1.90 to 2.45 lb/ton).

<sup>m</sup> Reference 10.

<sup>n</sup> Reference 1. EMISSION FACTOR RATING: E. Data were provided by industry.

Table 8.2-2 (Metric Units). UNCONTROLLED PARTICLE SIZE DATA FOR UREA PRODUCTION

| Type Of Operation         | Particle Size<br>(cumulative weight %) |                |                |
|---------------------------|----------------------------------------|----------------|----------------|
|                           | ≤ 10 μm                                | ≤ 5 μm         | ≤ 2.5 μm       |
| Solid Formation           |                                        |                |                |
| Nonfluidized bed prilling |                                        |                |                |
| Agricultural grade        | 90                                     | 84             | 79             |
| Feed grade                | 85                                     | 74             | 50             |
| Fluidized bed prilling    |                                        |                |                |
| Agricultural grade        | 60                                     | 52             | 43             |
| Feed grade                | 24                                     | 18             | 14             |
| Drum granulation          | — <sup>a</sup>                         | — <sup>a</sup> | — <sup>a</sup> |
| Rotary drum cooler        | 0.70                                   | 0.15           | 0.04           |

<sup>a</sup> All particulate matter ≥ 5.7 μm was collected in the cyclone precollector sampling equipment.

Bagging operations are sources of particulate emissions. Dust is emitted from each bagging method during the final stages of filling, when dust-laden air is displaced from the bag by urea. Bagging operations are conducted inside warehouses and are usually vented to keep dust out of the workroom area, as mandated by Occupational Safety and Health Administration (OSHA) regulations. Most vents are controlled with baghouses. Nationwide, approximately 90 percent of urea produced is bulk loaded. Few plants control their bulk loading operations. Generation of visible fugitive particles is negligible.

Urea manufacturers presently control particulate matter emissions from prill towers, coolers, granulators, and bagging operations. With the exception of bagging operations, urea emission sources are usually controlled with wet scrubbers. Scrubber systems are preferred over dry collection systems primarily for the easy recycling of dissolved urea collected in the device. Scrubber liquors are recycled to the solution concentration process to eliminate waste disposal problems and to recover the urea collected.

Fabric filters (baghouses) are used to control fugitive dust from bagging operations, where humidities are low and binding of the bags is not a problem. However, many bagging operations are uncontrolled.

#### References For Section 8.2

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