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# UREA TECHNOLOGY:

## A Critical Review

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The history of the fertilizer industry has been one of shifting from one product to another in a continuing effort to increase the nutrient content. In phosphate the shift has been from ordinary superphosphate to triple superphosphate to ammonium phosphate, and in the future perhaps to ammonium polyphosphate; in nitrogen the sequence has been ammonium sulfate to ammonium nitrate to urea. Today the planning of major new fertilizer complexes almost always involves ammonium phosphate and urea as the main products.

In each of these shifts a more complex and difficult technology has been encountered and a major research and development effort has been necessary to overcome the new problems. This has been especially true of urea, so much so that only since 1950 has the technology been developed far enough to give urea a significant place in world nitrogen supply. In the past 20 years important improvements have been made in production technology. However, the development is not complete and there is considerable question as to the relative merits of the techniques proposed by the various process developers. The purpose of this paper is to review critically the various phases of current urea production methods.

The main complicating factor in making urea is that carbonic acid ( $H_2CO_3$ ) does not form a stable ammonium salt as do nitric acid, sulfuric acid, and phosphoric acid. As a result, the simple neutralization of this acid with ammonia cannot be utilized to produce a satisfactory nitrogen fertilizer. However, anhydrous ammonia and carbon dioxide can be combined directly to make

ammonium carbamate ( $NH_2CO_2NH_4$ ), which, although also unstable, can be dehydrated by heating under pressure to form urea ( $NH_2CONH_2$ ), a stable compound. Unfortunately, the overall reaction is completely reversible and even at the high pressures (up to 300 atm.) and temperatures (about  $200^\circ C.$ ) used in urea synthesis, the average maximum degree of conversion is less than 70% in a single pass through the reactor. Hence two complications arise as compared with making ammonium sulfate and ammonium nitrate: the reaction must be carried out under pressure to maximize conversion and the unconverted reactants must be recovered and recycled for economic reasons. Most of the problems inherent in urea synthesis stem from these two factors, plus the very corrosive nature of the chemical system at the high reaction temperature and the tendency of the urea to decompose in the finishing steps.

Various urea producers and engineering firms have developed ways of minimizing or avoiding the problems in urea manufacture. The usual practice in reviewing urea technology is to discuss each company process as a unit. In the present discussion, however, each principal design or operating problem will be treated as a unit and the contribution of each company given; the main companies involved are Chemical Construction Corporation (Chemico; U. S.), CPI-Allied (Chemical Processes of Ohio, Inc.-Allied Chemical Corporation; U. S.), Lonza AG (Switzerland), Mitsui Toatsu Chemicals, Inc. (Japan), Montecatini Edison SpA (Italy), Norsk Hydro-Elektrisk Kvaelstof A/S (Norway), SNAM Progetti SpA (Italy), Stamicarbon NV (The Netherlands), and D. M. Weatherly Company (U. S.).

2 Proc. Admin. Sect. Prod. Technol. New Delhi, India  
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## Reactor Design

Because of the combined high temperature and pressure (180°-220°C. and 125-300 atm.), corrosion of the reactor has been a major difficulty throughout urea history. The problem goes beyond the usual drawbacks of corrosion, because susceptibility of metals to attack by the reactants limits the reactor temperature and therefore governs the degree of conversion and the amount of recycle necessary. In the early work, use of silver and lead as reactor linings was not fully satisfactory for several reasons, including cost and product contamination. Passivation of stainless steel by oxygen, an established method for inhibiting corrosion, was then successfully applied to urea production; this was a major step forward and is the method generally used today. The technique is covered by a 1955 patent issued to Stamicarbon (1), in which a range of 0.1 to 3% O<sub>2</sub> is specified.

Even with air injection, however, use of stainless steel still limits the reactor temperature to about 195° C. In an effort to increase conversion, by increasing temperature, CPI-Allied has worked with zirconium linings. This has allowed temperatures as high as 220° C. and a resulting conversion (carbon dioxide basis) of 85 to 90%. Difficulties in welding zirconium caused initial lining failures; the present preferred method, which has been successfully applied, is a loose liner with a pressure-equalizing purge of water between liner and shell. The cost of zirconium is on the order of four to five times that of stainless steel but a thinner lining is normally used (2).

Titanium alloy liners have also been used, particularly by Mitsui Toatsu (3). Higher operating temperature apparently is questionable (2); however, the amount of air required to protect the metal is considerably less than for stainless steel.

Use of these new materials has been limited, mainly because stainless steel costs less. However, the use of air to passivate stainless steel presents some problems. It is important to use enough air, as too little leads to rapid and serious corrosion of the liner. There is a considerable difference of opinion among producers as to the minimum critical amount; a range of 500 to 5000 ppm (oxygen in carbon dioxide) is reported. The minimum depends to a considerable extent on the temperature in the reactor and the NH<sub>3</sub>:CO<sub>2</sub> ratio,

as more oxygen is required at higher temperature and lower ammonia content in the gas. There is also an upper limit, because of ammonia loss in the inert gas purge, adverse effect on conversion, danger of explosion, and nitrogen oxide formation in the product (4).

Because of these drawbacks, there may be a trend in the industry to use of titanium. Recent decreases in price of the material have made it more competitive.

The interior mechanical features of the reactor have also gone through a sequence of development stages. In the early days cooling coils were often placed in the reactor to remove excess heat. Later, when higher NH<sub>3</sub>:CO<sub>2</sub> ratios and solution recycle processes came into use, reactors were generally free of internal parts because the additional liquid flow removed the heat. In recent practice internal parts have been introduced again, this time for the purpose of improving contact between reactants. In the Stamicarbon design, for example, the reactor is actually a gas bubble contactor designed as a cascade of bubble washers, with the reactor divided into several compartments by means of horizontal screen plates (5). This multiple-stage effect from bottom to top of the reactor has been an important factor in increasing conversion and reactor volumetric efficiency.

Some designers, however, hold that internal parts in the reactor give more trouble than they are worth, and that although there is some theoretical advantage, in practice it is better to have the reactor interior free of equipment. Others claim a small but important increase in conversion. The first version of the Dutch State Mines stripper process, in which a relatively large amount of gas passes through the reactor, appears to be a special case, requiring the screen plates mentioned above. For more conventional processes there is much less need for such devices but they have been used in some plants.

Developments have also taken place in the feeding of reactants to the reactor. As in ammonia plant practice, centrifugal compressors are gradually replacing the reciprocating type because of lower investment and operating cost. The main use has been for the first stages of compression, up to 20 atmospheres or so, followed by a reciprocating compressor on the higher stages. It

has been generally considered that full use of the centrifugal type would not be feasible except in very large plants, 1200 tons or more per day per train. This situation has been changed somewhat by introduction of the stripper processes, which operate at lower pressure and therefore are more amenable to use of centrifugals. Moreover, Nuovo Pignone (Italy) has recently announced (6) development of a centrifugal compressor capable of operating at much lower gas throughput than previous types. A 900-ton-per-day, single-train plant with all-centrifugal compression is being built in Italy and a 750-ton-per-day unit is planned in South America. The 900-ton unit is a stripper type operating at about 150 atmospheres. However, Nuovo Pignone has designed a compressor capable of operating at 350 atmospheres.

Feed pumps, both for ammonia and for carbamate solution (see later discussion), have been major problems. A horizontal type with guided plunger rods has given good service in some plants. Packing wear is especially troublesome and even with advanced practice the packing must be replaced frequently. Preferred design features include relatively low piston speed, case-hardened plungers, and dual packing with a water purge between. A centrifugal pump, now being tested, is showing promise.

#### Recycle of Unconverted Reactants

Since the effluent from the urea reactor is a solution containing urea and unconverted carbamate, the solution must be heated to decompose and remove the carbamate. The decomposition products are evolved as a hot, gaseous mixture of ammonia, carbon dioxide, and water vapor. Recycling of this corrosive gas probably can qualify as the most difficult problem that has been encountered in the development of urea synthesis.

Early attempts by I. G. Farben to recycle the gas by compression failed because the reciprocating compressors of that day were not capable of such service. The practice then swung to once-through operation with the unconverted ammonia used, without separation from the carbon dioxide, in production of ammonium sulfate, ammonium nitrate, or nitric acid. This is still a fairly major practice in the United States, especially for making urea - ammonium nitrate fertilizer solution, and

could well be applicable to the modern fertilizer, urea - ammonium phosphate. The major practice, however, is total recycle; the growing demand for urea as such and the difficulty in integrating manufacture of two products has greatly reduced the applicability of once-through and partial-recycle operation.

*Gas Separation*— During the 1930-1950 period several recycle processes were developed in various parts of the world. One was separation of the ammonia and carbon dioxide by scrubbing with a selective solvent, developed first by Holzverzuckerungs AG (Inventa; Ems, Switzerland) and adapted in the United States by Chemico and Vulcan-Inventa (now CPI-Allied). Chemico no longer offers the process but CPI-Allied has built plants in recent years incorporating both the zirconium reactor liner and an MEA (monoethanolamine) scrubbing system to scrub carbon dioxide from the gas and leave ammonia for recycling. (In the original Inventa method, urea nitrate or ammonium nitrate solution was used to scrub out ammonia.)

The process has the advantage that conversion is not reduced by recycling water to the reactor and that the problem of recycling corrosive solution to the reactor is avoided. Offsetting this is difficulty in recovering heat and cost of MEA makeup. The number of plants using the method is relatively small and none of the current giant plants (800 to 1500 tons per day) are of this type.

*Carbamate Solution*— Du Pont (U. S.), in the 1930-1950 period, worked with a recycle method that involved merely cooling the  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$  gas mixture to condense it (with some addition of water) and pumping the resulting solution back into the reactor. Although there are some obvious drawbacks, this system has stood the test of time and is now the standard for new plants. Of the nine licensors mentioned earlier, eight offer some version of the solution recycle process.

Some years ago there was considerable variation in the design features of the various solution recycle processes; these differences have gradually disappeared, until today the "conventional" methods are much the same. All use similar reactor conditions (temperature about  $185^\circ\text{C}$ . and pressure about 200 atm.), maintain an  $\text{NH}_3\text{:CO}_2$  mole ratio of about 4:1 in the synthesis loop, and

get about the same conversion (65-67%). All reduce the reactor effluent pressure to an intermediate level and then pass the solution through two or three stages of decomposition (by heating) at successively lower pressure levels. In each stage the evolved gas mixture is condensed (or absorbed in weak solution condensed in a later stage) and the resulting solutions are worked back through the system to the reactor. The excess ammonia (from the excess used in the initial reactor feed) passes through the absorbers, is condensed, and is fed back to the reactor.

Although these major steps are common to the various conventional methods, there is considerable difference in the carbamate solution recycle systems—in pressure and temperature levels, equipment arrangement, and process flow. This phase of the development is still in a state of flux; even for a given company, the flowsheet for a current plant will likely be somewhat different from the immediately preceding one. The general design objectives are to:

1. Maximize heat recovery.
2. Minimize amount of carbamate solution recycled (smaller pumps and less power), and amount of water returned to the reactor (better conversion).
3. Minimize power requirement.
4. Maximize ammonia recovery (lower operating cost and less pollution).

Another major objective, of course, is to minimize investment, so that the problem becomes the usual one of finding the best balance between utility consumption and maintenance on the one hand and investment on the other.

Several parameters are involved in design of the carbamate solution recycle system, and they are so interrelated and interdependent that it is difficult to analyze them separately. Changing one parameter in the direction of improvement almost always changes one or more of the others in an adverse direction, and the extent of the adverse effect can only be determined by somewhat complicated calculations. Hence it is difficult to evaluate quantitatively the various schemes that have been developed.

One important consideration is the *number of decomposition stages*. Reducing the number lowers plant investment but increases the amount of water returned to the reactor, makes heat recovery less attractive (decomposer pressures generally lower),

and results in higher ammonia loss in gaseous or liquid effluents. The current trend is to three stages as the optimum number. The third stage generally involves both decomposition of carbamate and evaporation of water, with vacuum applied to remove the ammonia down to a very low level as a means of minimizing atmospheric pollution. The flashed gas is passed through a water-cooled condenser, the condensate stripped of ammonia, and the stripped condensate preferably discarded rather than returned to the reactor. Such a procedure gives only traces of ammonia in the gaseous and aqueous effluents.

The *point of heat recovery* also varies. The main source of heat in the system is carbamate formation in the reactor. In some past designs, recovery or removal of heat directly from the reactor was practiced—by water coils in the reactor or a cooling jacket outside. Today, however, the ammonia and carbamate solution recycled take up the reaction heat and carry it out of the reaction zone.

In the decomposition section, heat must be added in order to get an adequate rate of carbamate decomposition, thus adding to the heat available for recovery. Much of this is released when the evolved gases are recondensed and it is at this point that heat is usually recovered. The recovery is limited to the first decomposition stage, however, because the gases are at so low a pressure in the later stages that condensation temperature is uneconomically low for heat recovery.

Thus the usual heat source for recovery is hot condensed liquor from the first-stage absorber. Practice varies as to the stream used to absorb this heat. In some cases, water is heated and steam is produced; in other published flowsheets a process stream is involved:

Company	Heat-absorbing stream
Chemico	Solution to second decomposer (7)
Montecatini <sup>a</sup>	Solution to first decomposer (8)
Mitsui Toatsu <sup>a</sup>	Solution to crystallizer (7)
Weatherly	Solution to evaporator (7)

<sup>a</sup>Not the latest process offered.

*Gas release process* can have an important effect on the amount of water recycled to the reactor. The simplest arrangement—merely releasing pressure, flowing the solution into a vessel, heating it, and allowing the evolved gases to escape—is

relatively inefficient because it gives maximum evaporation of water. Two systems have evolved, both of which minimize water evaporation. The first involves a sequence, in each stage, of (1) pressure reduction, (2) gas release, (3) heating, and (4) further gas release. The advantage is that gas which can be evolved by release of pressure alone comes off at lower temperature than in the heated decomposer. The partial-pressure relationships involved are such that this procedure gives less evaporation of water.

In the second system a rectifying column is used as the decomposer; relatively cold incoming solution flows downward in countercurrent flow to the hotter gas evolved in a heated section (or reboiler) at the bottom. Thus, the composition of gas leaving the column approaches equilibrium with the incoming solution, which has a relatively low partial pressure of water because of the reduced temperature.

Both systems are used but there seems to be a trend to the rectifying column type. Heaters on the main flow line are preferred by some, however, because of the rapid heat transfer at the high flow rate.

Both heat recovery and amount of water recycled are affected by the *pressure level in the first decomposition stage*. Higher pressure gives less water in the off-gas and a higher heat level when the gases are condensed but makes it more difficult to evolve the gases. As pressure is increased, the temperature level required to decompose carbamate at an adequate rate becomes higher until corrosion and urea decomposition become the limiting factors. Until recently, designers seemed to have settled on 15 to 20 atmospheres as the optimum; however, Mitsui Toatsu has recently (7) a new process ("Process D") in which the first decomposer is operated at 58 to 77 atmospheres. The evolved gases are scrubbed in a high-pressure absorber with carbamate solution from later stages and the ammonia gas escaping from this absorber is condensed by contact with the incoming feed ammonia rather than by cooling water, thus conserving heat which is recovered by producing steam in a mixer into which the three feed streams are introduced before the reactor. Montecatini also has a new process (7), in which the first decomposition takes place at about 80 atmospheres. The evolved gases pass into a high-pressure condenser where about one-third of

the feed carbon dioxide is also introduced. This reacts with excess ammonia in the decomposer off-gas, thus producing additional heat and avoiding the usual step of condensing the excess ammonia. The steam raised in the condenser is at 3-atmosphere pressure; part of it is used in the solution evaporation section and the remainder is compressed to 5-7 atmospheres and used in the second and third decomposition steps.

The Mitsui method presumably has been tested in the company's own plants. A 600-ton-per-day plant incorporating the Montecatini process has been operating since June 1968 and larger units are under construction.

Process developers have also looked for some additional driving force, beyond the usual addition of heat and reduction of pressure, to help volatilize the ammonia and carbon dioxide. In an obvious analogy to water evaporation technology, an inert stripping gas has been employed, making the decomposer similar in principle to an air-swept evaporator. Instead of air, which might overload the reactor with inerts, ammonia or carbon dioxide is used. These gases act as inerts when one or the other is present in excess over the carbamate ratio; the addition of one reduces the partial pressure of the other over the solution.

Such gas sweeping could be used in the decomposers at conventional pressures to reduce the steam requirement, but designers have preferred to use the method as a means of going to much higher decomposition pressure, approaching and including reactor pressure level. The resulting processes have generally been called the "*stripping*" types as opposed to "conventional."

The pressure level in the first decomposition stage varies considerably:

<u>Process</u>	<u>Stripping gas</u>	<u>Pressure in first decomposition stage, atm.</u>
Norsk Hydro	Carbon dioxide	70-100
SNAM	Ammonia	135
Stamicarbon	Carbon dioxide	135-150
Weatherly	Ammonia plus inert gas	230

*Norsk Hydro* (9) considers the intermediate pressure to be best because most of the carbamate can be removed at this level by the combination of heating with steam generated in the process and

stripping with the feed carbon dioxide. The stripped solution contains only about 8% of its nitrogen content as carbamate, which is removed in a subsequent standard decomposer. The gases evolved in the first stage are boosted to reactor pressure (190-230 atm.) by centrifugal compression, after which carbamate condensation takes place at full pressure in a "condenser-prereactor-boiler." At this high pressure level, the pressure of the steam generated is 5 to 8 atmospheres absolute; this is further increased, by a turbocompressor, to give steam hot enough (10-15 atm. abs.) for use in the stripper-decomposer. That part of the steam not needed in the stripper is used in the evaporator at the 5- to 8-atmosphere level.

The Norsk Hydro method has not yet been optimized and a full-scale demonstration has not been made; it is claimed, however, that capital cost should be 10 to 20% lower than for established processes and that energy cost should be about \$1 less per ton of urea.

In the *SNAM* process, the stripper operates at near reactor pressure but the pressure is much lower (about 147 atm.) than in conventional processes; some sacrifice in conversion is made but the lower pressure permits efficient stripping and makes use of centrifugal carbon dioxide compression feasible. A carbamate pump of the usual type is not required for the high-pressure loop. The small head required to move the solution from condenser to reactor is supplied by a simple ejector actuated by the incoming stream of liquid ammonia (only part of the ammonia is used in the stripper-decomposer) (10). Steam at 5.5 and 3.5 atmospheres is recovered in the condenser.

Only one *SNAM* plant has been built (in Italy); however, five more are being erected, in Europe, Mexico, and Venezuela.

In the *Stamicarbon* process, stripping is carried out at full reactor pressure but again the pressure (135-150 atm.) is much lower than normal. Since the stripper-decomposer, condenser-boiler, and reactor are all at the same pressure, no carbamate pump is needed for the high-pressure loop. In the first version of the process, a stacked condenser-reactor-stripper arrangement was used to give the head required for flow from condenser to reactor. The overall height, as much as 150 feet, was undesirable so a new arrangement has been developed and is being incorporated into a large

plant. In this the gas from the stripper is introduced into the top of the condenser (along with part of the ammonia) rather than into the reactor as in the earlier version. As a result, the condenser does not have to be above the reactor.

The method is the best proven of any of the stripping processes. Some 16 plants are in operation in Europe and Asia and the process has been licensed by about 20 engineering contractors.

The *Weatherly* method, the newest of the stripping type, and as yet unproven on a plant scale, has several unique departures. The main feature is circulation of an ammonia-inert gas mixture through the stripper and condenser at full reactor pressure, which is at the conventional level of about 230 atmospheres. Small amounts of the inert gas are added to the feed gases. Heat recovery is accomplished by exchange of sensible heat in the stripper off-gas to evaporator section feed solution. There is no heat recovery in the carbamate condenser; the condenser is cooled by introducing the feed ammonia into the unit where it vaporizes. Part of the vaporized ammonia is recondensed in a water-cooled condenser and fed to the reactor. The remainder, containing the inert gas, is superheated for use as stripping gas. The process combines the reactor and stripper in a single shell-and-tube unit; the feed reactants flow up the shell side and then down through the tubes, where stripping by the rising ammonia-inert gas mix takes place.

A steam-driven centrifugal compressor is employed, with the exhaust steam used for solution heating. No steam is required for the high-pressure decomposition stage, of course, because the initial heat of carbamate formation provides heat in the reactor-stripper for carbamate decomposition on the tube side. Although the heat of carbamate condensation is not recovered, the process has a good energy balance because of the direct use of reaction heat to decompose carbamate.

For stripping processes in general, it is not yet clear which is the best stripping agent, carbon dioxide or ammonia; there are several factors involved.

1. Carbon dioxide is theoretically the most effective for decomposing carbamate. The mole fraction of carbamate in solution can be expressed by the equation (9):

$$x = Ky_2 \cdot z$$

where K is a constant

x = mole fraction of carbamate  
in the solution

y = mole fraction of ammonia  
in the gas phase

z = mole fraction of carbon  
dioxide in the gas phase

Hence reducing the partial pressure of ammonia by increasing the partial pressure of carbon dioxide is more effective than the reverse because the ammonia partial pressure is squared in the equation.

2. Ammonia has the advantage of higher  $\text{NH}_3:\text{CO}_2$  ratio in the reactor; therefore, conversion is promoted and less trouble with corrosion and biuret formation is to be expected. (However, with due attention to temperature and retention time, carbon dioxide appears to be satisfactory in these respects.)
3. Since ammonia gives a decomposer effluent solution relatively high in ammonia content, additional heat is required to strip it out; however, this heat can be recovered.
4. Ammonia normally is supplied as a liquid and therefore heat must be expended in vaporizing it before it can be used as stripping gas. (However, ammonia flashed from the reactor effluent can be used.)

Because of these complications, determining the relative merits of the two stripping gases is quite difficult. Plant experience with the five new SNAM plants due to come on-stream in 1970-1971 should provide useful information for comparison.

High-pressure decomposition, with or without stripping, appears to be a significant step forward in urea technology. A summary of published claims for the various methods, some stated as guaranteed and others unspecified, is as follows:

Process	Utility requirement, per short ton of urea		
	Steam, lb.	Electricity, kw.-hr.	Cooling water, gal.
Conventional	2400-3200	132-170	16,000-29,000
Stamcarbon	2200	100	12,000
SNAM	2200	110	18,500
Montecatini	1980 <sup>a</sup> 2750 <sup>b</sup>	140 <sup>a</sup> 10 <sup>b</sup>	—
Weatherly	1600 <sup>a</sup> 2800 <sup>b</sup>	130 <sup>a</sup> 15 <sup>b</sup>	16,000 23,000
Mitsui Toatsu (Process D)	1700	155	14,500

<sup>a</sup>Electric-driven compressor.

<sup>b</sup>Steam-driven compressor.

On this basis, and assuming utility costs typical in the United States, a saving on the order of \$0.50 to \$0.80 per ton of urea is indicated for the newer processes. As noted earlier, Norsk Hydro estimates \$1.00 saving for their new process.

As to investment, the developers of the new methods claim some reduction; Norsk Hydro, for example, gives 10 to 20%. However, no clear trend seems to have been established in the bidding situations thus far. Competition is keen and differences in investment, if any, between the conventional and newer types appear to have been obscured by transient factors, peculiar to any bidding situation, that have no relation to intrinsic cost factors in the processes. Such factors also seem to have nullified, in many cases, the indicated operating cost saving of the new methods.

The stripping processes so far have not been applied in single plant trains larger than 600 to 700 tons per day. Design and construction problems for the high-pressure, tube-and-shell decomposer and condenser appear to have been limiting factors. However, progress in solving these problems seems to be under way. Single-train units of 1000- and 1400-ton-per-day capacity are under construction.

Among the new "high-pressure decomposition" processes, the relative merits of stripping and nonstripping are difficult to evaluate. There is no significant difference between utility requirements claimed, and no investment advantage for either has yet been evident. Elimination of the high-pressure carbamate pump seems to be the main advantage of the stripper methods.

*Carbamate Slurry*—In a further effort to reduce the amount of water recycled to the reactor, process developers have tried recycling a slurry of carbamate in a nonaqueous carrier liquid. The most noted example is the oil slurry recycle (originally called the Pechiney process) used in several plants built some years ago. The method has not been refined to the extent that solution recycle has in the past decade, and no new plants have been reported in some time.

A more recent development is carbamate-liquid ammonia slurry, developed by Montecatini and tested on a pilot-plant scale (7). The method is quite like the conventional one, except that the feed ammonia enters the system at the first-stage condenser. Formation of a carbamate-liquid ammonia slurry at this point makes it unnecessary to bring in condensate from later stages to dissolve

the carbamate, as is done in conventional processes. Gases evolved from the second decomposition stage (the final one) enter an ammonia recovery system that separates the ammonia as a gas and returns it to the first-stage decomposer. Reduced power requirement and investment are claimed as advantages.

*Hot Gas Recycle*--The concept of recycling unreacted ammonia and carbon dioxide as gases rather than in solution, the approach in the early work, has been revived recently by Chemico. Gases from each stage of decomposition are compressed in a centrifugal compressor to reactor pressure and condensed to recover heat as high-pressure steam. The original concept of full adiabatic compression has been altered somewhat in later patents to include cooling between stages by using the hot compressed gas from a given stage to decompose carbamate solution (by direct contact) in the next higher stage.

The process has the advantages that no carbamate pumps are needed, only one condenser is involved, and practically all the heat of carbamate decomposition is recovered. However, there are some obvious problems that require testing and tests can only be made on a large scale. The process thus remains unproven.

The approach to hot gas recycle taken by Norsk Hydro has been discussed in an earlier section.

*Integration with Ammonia Plant*--There have been various proposals, dating back several decades, for combining production of ammonia and urea. The main effort has been aimed at using energy from the ammonia plant to reduce pumping and heating costs in the urea unit. Mitsui Toatsu has taken the lead in this, having operated a pilot plant for a number of years. The process involves (1) heat exchange from shift converter exit gas to carbamate solution in decomposer reboilers, (2) compression of converter gas ( $H_2-N_2-CO_2$ ) to full ammonia and urea reactor pressure (300 atm.), (3) absorption of carbon dioxide at reactor pressure by liquid ammonia from the ammonia synthesis loop, and (4) feeding the resulting carbamate solution to the urea reactor (along with recycled carbamate solution from the condensers). The energy saving comes from three sources: (1) elevated pressure of carbon dioxide at the shift converter exit (about 24 atm.), (2) heat normally required in the ammonia plant to remove carbon dioxide from the

absorbent, and (3) pressure of liquid ammonia from the synthesis loop. It should be noted that compressing the carbon dioxide from shift converter exit pressure to reactor pressure still must be charged to the urea plant (although having only one compressor in both plants reduces investment), and that heat recovery from the converter gas cannot be claimed for the urea process because it is normally recovered in the ammonia plant anyway.

Utility requirements claimed, on the basis of assuming typical consumption in the ammonia plant (based on conventional design) and subtracting this from the total for the integrated plants, are (per short ton of urea) 83 kilowatt-hours, 1040 pounds steam, and 24,000 gallons cooling water. This represents a considerable saving as compared even with the stripping processes. A 5 to 7 % reduction in combined investment is also claimed.

Although the process has some desirable features, tying the two products so closely together reduces flexibility. Moreover, there may in some cases be difficulty with the carbon balance; if there is too much carbon dioxide for combination with ammonia as urea (as perhaps with naphtha feedstock), an auxiliary carbon dioxide separation unit must be included. If there is not enough carbon dioxide (as perhaps in methane reforming), provision must be made to recover the excess ammonia as such or to utilize the equivalent excess hydrogen as fuel.

### Product Finishing

Removal of unreacted carbamate leaves a urea solution that must be concentrated before converting to the final solid form. Removal of the water, which amounts to about 25% of the solution after the third-stage decomposer-concentrator, has been a major problem in urea technology development. Without free ammonia present, heating the solution promotes decomposition, both to the original reactants (hydrolysis) and to biuret. Hydrolysis products can be recovered but the biuret goes on into the product where it is undesirable for some uses. Since biuret formation is a function both of temperature and retention time, the trend has been to evaporators that minimize the levels of these variables. Development effort has centered on the

film type, both falling film (air swept) and rising film (vacuum with high recirculation rate). The spinning disk, air-swept type is also effective but may not scale up as well as the others. The vacuum type has the disadvantage that volatilized ammonia (residual ammonia from the decomposers or ammonia formed by hydrolysis) is collected in the evaporator condensate and therefore may cause a water pollution problem (unless recovered), which usually is more troublesome than the air pollution resulting from use of an air-swept evaporator. The latter, however, requires a supply of dehumidified air reheated to about 140° C.

With good evaporator design and operation, biuret formation can be kept acceptably low. There is, however, some biuret already in the solution, formed mainly in the carbamate decomposers. This can vary with equipment design; the reboiler type of decomposer for example, is said (4) to give 0.5 to 0.6% biuret in the urea solution (based on urea content) as compared with 0.3 to 0.4% (typically) for other types. A good evaporator installation will add only 0.3 to 0.4% to this. A typical before-and-after analysis is (11):

	Before evaporation wt.%	After evaporation wt.%
Urea	73	99
Water	26.7	0.3
Biuret	0.3	0.7
Temperature	120° C.	140° C.

Very little biuret formation takes place during the prilling operation.

It should be noted that there is wide variation in reported values for biuret formation in the reactor-decomposer section of the plant. As low as 0.2% is claimed, with only 0.3% more in the evaporator to give 0.5% in the prilled product. Others report as high as 0.5% in the solution to the evaporator.

Getting the biuret content of prills under 1.0% has been a major accomplishment, but for technical-grade urea even this has not been considered low enough. As a result, the crystal remelt method—in which the urea solution is crystallized in a vacuum crystallizer and the crystals are centrifuged, dried, melted, and prilled—has been developed. The product contains only 0.25 to 0.35% biuret because the biuret in

solution does not cocrystallize with the urea. It is removed from the crystallizer in a purge stream of mother liquor that is generally fed back to the synthesis reactor where conditions are such that conversion back to urea takes place. The stream may go directly to the reactor or indirectly through the absorber system; SNAM feeds it back to the stripper (at synthesis pressure).

The crystal remelt method seems to be growing in popularity, even though investment is on the order of 8 to 10% higher than for evaporation-prilling.

Since reducing biuret content is expensive, there should be some clear-cut gain to offset the additional cost. The advantage or necessity of low biuret, however, is not at all clear, and several producers feel that its importance is exaggerated. There are three major types of products to consider.

1. *Fertilizer grade.* Although 0.9% is a typical specification, and most producers try to stay below 1.0%, there is good evidence that up to 2.5% is acceptable (with a few minor exceptions such as foliar spraying) (12).
2. *Feed grade.* In the United States, large quantities of urea "micropills" are used as a substitute for protein in animal feeds. For this use, high biuret is actually desirable; biuret has been shown to be superior to urea because it is less likely to be toxic to animals.
3. *Technical grade.* Industrial users have generally desired low-biuret urea for use in products such as plastics. There is some question, however, as to whether this is necessary. Impurities such as oil and iron salts are regarded by some to be much more detrimental and since the levels of these impurities, as well as that of biuret, are governed by plant operating conditions, biuret may have incurred guilt by association. In current practice, the iron and oil are removed by filtering the urea solution before evaporation, in some cases with air added in the decomposers to ensure oxidation of iron to the insoluble ferric form. With this purification, urea containing as much as 0.8% biuret has been sold as technical grade in the United States. In contrast, some producers install equipment both for evaporation-prilling and crystal remelt-prilling, as well as handling facilities

for crystals (0.1% biuret), in order to meet any customer demand that may be encountered.

Prilling the urea melt has become a fairly well standardized operation. Most producers prefer multiple spray heads rather than spinning baskets, apparently because a wider range of particle sizes (microprills to agricultural prills) is possible with the sprays. The main development probably has been use of a fluidized bed in the base of the tower, both to cool the product in a convenient way and to prevent sticking of prills on the tower bottom. Alternatively, a rake-type prill removal mechanism in a flat-bottom tower is preferred to the cone-bottom, gravity-flow type.

Some progress has been made in developing finishing equipment smaller in size than prilling tower installations and which gives a larger product granule. TVA has tested pan granulation on a pilot-plant scale (13), and Cominco has developed and is using a "spherodizer" type of operation (14).

The finished prills or granules should contain not more than 0.3% moisture for good storage properties. General specifications in the United States are:

	Composition, % by wt.						
	N	H <sub>2</sub> O	Biuret	NH <sub>3</sub>	Oil	Fe	Ash
Fert. grade <sup>a</sup>	46.3	0.3	0.9	0.015	— <sup>b</sup>	0.0002	— <sup>b</sup>
Tech. grade <sup>a</sup>	46.3	0.3	0.4	0.010	0.002	0.0001	0.002

<sup>a</sup>Unconditioned.

<sup>b</sup>Not specified.

Urea is often conditioned with clay, especially in humid areas. About 2.5% of a kaolin clay is normally used. Microprills for animal feeding are more subject to caking because of their smaller size; clay or cereal powder is used as conditioner, sometimes up to 10% by weight.

Adequate amounts of clay-type conditioners lower the nitrogen content of urea from about 46.3% to 45%. There are many materials claimed to be effective conditioners when added in such small amounts (less than 0.5%) that the resulting grade is 46% nitrogen. Among these are amines, aldehydes, ketones, fatty acids, acid amides, polymeric surfactants, oils, and waxes.

A dehumidified building is quite desirable when the product is stored in bulk in humid areas. Since

some ammonia is evolved in storage, ventilation of the building is necessary.

### Economic Considerations

Developments in the past decade or so have resulted in a major reduction in the cost of producing urea. Utility requirements have been reduced by recovering heat of carbamate condensation and by using feed gases to help strip out carbamate. Maintenance requirements have been reduced by better control of corrosion and by improved design of pumps and compressors. Finally, investment per ton of urea has been reduced by improved design and by building larger production units. Today urea is gaining at the expense of the major nitrogen fertilizer, ammonium nitrate, both because of its superior properties and because its production cost has been reduced to a comparable level even though the process is much more complicated.

Plant investment varies widely, of course, depending on location and bidding situation. In the United States, average battery limit investment (Gulf Coast location) appears to be as follows (7):

Capacity, short tons/day	Battery limit investment, U. S. \$
300	3,900,000
600	5,900,000
1200	9,000,000

The cost for the 200-ton-per-day, 75% solution plant being built by TVA is \$2,300,000 (battery limits).

For application in other areas, a factor should be applied. For example, plant cost in India and the Persian Gulf area is generally considered to be about 30% higher than in the United States.

Production cost for the smaller plants in the United States appears to average \$12 to \$13 per ton, including depreciation but excluding ammonia cost. An increase in plant size from 300 to 600 tons per day decreases production cost by about \$2 per ton, and going from 600 to 1000 tons per day gives a further reduction of about \$1.50 per ton. The main advantage of the larger plants, of course, is the lower investment per ton of urea and the resulting lower cash flow required to make the plant financially attractive. Single-train units as large as 1500 tons per day are planned and one was put into operation recently.

For the future, high-pressure decomposition may be favored because of the lower utility requirement, particularly in areas where energy cost is relatively high. So far, however, the conventional type has held its own in bidding situations in the United States. Whether this has been due to extraneous rather than intrinsic cost

factors remains to be seen.

The hot gas recycle and ammonia plant combination processes are farther away from realization but offer potential savings both in investment and operating cost. Several years probably will elapse, however, before they are proven commercially.

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