Several major utilities have shown a keen interest in urea-to-ammonia conversion technology and increasingly are adopting urea as a preferred alternative to the more toxic anhydrous and aqueous ammonia (NH₃) for selective catalytic reduction (SCR) systems. The development of urea-to-ammonia conversion technology is in direct response to the increased regulatory requirements imposed on utilities for the control of nitrogen oxides (NOₓ) emissions using SCR that requires NH₃ as the reducing agent. Anhydrous NH₃ is regarded as a hazardous and toxic chemical and is subject to stringent regulations imposed by the U.S. Environmental Protection Agency (EPA) and OSHA. Aqueous NH₃, although less concentrated, poses similar risks and is increasingly subject to restrictions by local authorities. EC&C Technologies Inc.’s On-Site Urea-to-Ammonia (U2A) conversion system uses urea as the feedstock chemical, thereby avoiding the risks associated with the transportation and storage of a hazardous chemical like NH₃. The patented conversion process transforms urea solution to an NH₃ gas mixture on site and on demand to meet the dynamic requirements of the NOₓ control system. Since 2000, EC&C’s U2A system has been adopted for utility systems representing more than 10,000 MW of capacity.

EC&C’s U2A system uses urea as the feedstock chemical, thereby avoiding the risks associated with the transportation and storage of a hazardous chemical like ammonia.

THE CHALLENGE
The development of the urea-to-ammonia conversion process began in 1989, with discussions between EC&C and a utility in the Los Angeles basin area on the subject of NOₓ removal and carbon dioxide (CO₂) recovery. The utility had concerns about using NH₃ for an SCR NOₓ control system that it was planning to install at a plant in a highly populated area. Around the same time, EC&C was approached to develop an alternative to NH₃ or urea, whose uses were covered by patents, for use in selective noncatalytic reduction (SNCR) applications. Dr. Hal Cooper, one of the founders of EC&C, suggested the use of ammonia carbamate. Since the cost of carbamate was prohibitive, a process for obtaining it by hydrolysis of urea was conceived. The disclosure for the process included the conversion of urea to NH₃. Dr. Herbert Spencer, also a founding partner of EC&C, had prior experience with SCR systems and accepted the challenge to develop Dr. Cooper’s initial conception into a process that could generate pressurized NH₃ on demand to match the requirements of an SCR NOₓ control system. In 1994, Drs. Cooper and Spencer submitted their first proposal to the EPA Small Business Innovation Research (SBIR) program. The initial proposal included two concepts: thermal hydrolysis of urea and an urease enzyme-based process. This first proposal was initially rejected, in part because one reviewer...
felt that the U.S. Department of Transportation should fund the development instead of EPA, since the process would have a major impact on reducing the risk of transporting NH₃.

RESPONDING TO THE CHALLENGE
In 1995, EC&C reworked its proposal and re-submitted it to the EPA SBIR program. The new proposal was accepted and EC&C was awarded a Phase I grant to further evaluate the concept. At that time, data on urea hydrolysis conversion rates for concentrated solutions of urea at elevated temperatures were not readily available in the literature, but within six months, the Phase I work developed the basic features of the U2A system, using the hydrolysis process. The enzyme process proved to be difficult to operate using a concentrated solution of urea.

After discussions with a local utility that used an SCR, one of the priorities was to make sure that the NH₃ generation system would have no potential for damaging the SCR catalysts. This directed EC&C’s work away from using any chemicals in the process that are potential poisons to SCR catalysts (e.g., phosphorus compounds). During the Phase I testing, a gas off-take control valve, pressure feedback control (to control heat input), and level control (to maintain the liquid level) were considered, but left to Phase II for testing. This simple control system is what has made the system a commercial success.

The control system decoupled the process from any NH₃ demand signal, treating the hydrolysis reactor like a heat exchanger rather than a process. The control scheme, along with the storage of the NH₃ in the reactor solution and gas reservoir in the reactor, makes the process very responsive to NH₃ demand.

Based on the Phase I results, a Phase II proposal was prepared and submitted to EPA. Phase II funding was obtained from EPA in 1996. The proposed Phase II work included constructing a small combustor and SCR system, where EC&C could demonstrate the ability of the U2A process to follow load changes and track variations in NOₓ levels. The Phase II work also included increasing the Phase I prototype by a scale of 10 to 1 to better develop the sizing criteria for commercial systems. For the Phase II tests, a 1-lb/hr NH₃ generation pilot unit and small SCR system were constructed. A water recycle system was also included in the initial concept (and is included in the subsequent patent disclosures) because EC&C did not know initially whether the system would achieve water balance. The Phase II pilot unit demonstrated, however, that the process could be operated on a continuous basis and that water balance could be achieved without installing a recycle system. Eliminating the recycle further simplified the process and the control system.

The Phase II work was successfully completed in May 1997 and provided the data and design basis for EC&C’s technology patents and co-licensing to Hamon Research-Cottrell Inc. and Wahlco Inc. This led to the first commercial demonstration in 2000 of a system capable of 400-lb/hr production at AES Corp.’s Alamitos plant in Long Beach, CA, and for much larger commercial units, including the reactors installed at Allegheny Energy Supply’s Harrison plant in Haywood, WV, to service 1800 MW of capacity.

FIRST COMMERCIAL DEMONSTRATION
The 400:1 scale up to the AES Alamitos commercial demonstration was a success. The project confirmed the technical viability of the U2A system in a commercial application and proved it is an economically attractive, reliable, and safe alternative to NH₃ for postcombustion NOₓ control strategies. The reactor, temporarily installed in parallel with an existing 29% aqueous system, operated for approximately 1500 hours from October 2000 to January 2001, over a range of 50–280 lb/hr of NH₃, following the system load in automatic controlled operation to meet SCR process demand. Overall turndown of the system was achieved across a better than 20:1 range. During operation, NOₓ reduction ranged from 87% to 98%. In side-by-side tests at full load, the U2A system demonstrated equivalent performance when compared to the original aqueous NH₃ system in place at Alamitos. The U2A reaction kinetics, well understood at the pilot scale, were confirmed with full-scale operation at Alamitos.

Operating time at Alamitos was sufficient to allow for quantitative and qualitative analysis of the expected residual from trace dissolved and suspended solids in the urea solution feed. This analysis, together with a physical inspection, confirmed the suitability of materials for construction, the calculated requirements for periodic blowdown, and the absence of accumulated organic materials in the U2A reactor. Typically, reactors are blown down at the end of an ozone season after every two years of continuous operation to remove any unevaporated materials for from the reactor. Based on the success of the Alamitos project, AES decided to transfer the reactor and technology to the company’s power plant in Huntington Beach, CA, to service Units 1 and 2 at the AES Huntington Beach installation.
A second U2A reactor, servicing Units 3 and 4, has since been installed to bring total NH₃ generation to 800 lb/hr to serve the SCRs installed on the four natural gas-fired units rated at 450 MW each. Huntington Beach has been in year-round operation since July 2001 (see Figure 1).

EC&C co-licensees Wahlco and Hamon have since been awarded many contracts from utilities in the United States and Europe for U2A systems, providing more than 20,000 lb/hr NH₃ capacity and serving more than 10,000 MW of utility generating capacity. EC&C licensees have installed or are in the process of installing more than 30 hydrolyzers for projects worldwide for both new installations and retrofits of anhydrous and aqueous NH₃ systems. Project NH₃ generation requirements range from 10 lb/hr to 5 t/hr.

**U2A PROCESS DESCRIPTION**

With EC&C’s U2A process, an aqueous solution of urea is converted to a pressurized gaseous product stream of NH₃, CO₂, and water vapor for use in the removal of NOₓ emissions from combustion flue-gas streams. Figure 2 shows...
the basic process and its control loops.

**Urea Solution**
The urea used in the U2A process can be supplied in either solid or liquid form. The design of the urea hydrolysis system is typically based on the use of dry urea in granular or prilled form. The dry urea is delivered by truck in quantities of 25 tons. It is then dissolved in deionized water to produce a 40–50% solution that is fed to the hydrolysis reactor. The urea solution can be prepared either on a batch basis or continuously.

Some utilities have chosen to receive a 70% urea liquid solution (available from urea manufacturers). Since the urea liquid is obtained before the prilling process, it can be more economical and has the side benefit of being free of trace formaldehyde. (Formaldehyde is used in the prilling process to harden the surface of the urea pellets. It decomposes in the U2A process, and tests conducted during the Alamitos demonstration showed that the SCR catalyst destroys 90% or more of the formaldehyde.)

For units where the urea solution is prepared on a batch basis, the batch dissolver is sized to dissolve and hold the volume of solution made from a truckload of urea or bulk bags. To prepare the solution, deionized water from the plant’s deionized water supply system is added to the batch dissolver first and recirculated with the urea transfer/circulation pump through the steam- or electric-heated urea solution heater, heating the deionized water to approximately 150 °F. The dry urea is then offloaded from the truck into the hot water. The solution is continuously recirculated with the urea transfer/circulation pump through the urea solution heater during this time to help dissolve the urea and to make up for the endothermic heat of the solution. Low-pressure steam, condensate from the reactor coils, or electricity is used to provide the heat used in the urea solution heater.

Most installations, including very large ones, typically store urea in liquid form on site. This avoids the risks and maintenance issues associated with a dry storage system.

**U2A Reactor**
The urea solution, in the range of 40–50% urea, is fed to the reactor. The reactor liquid level is monitored with a level transmitter/controller, which controls the feed rate to maintain a constant liquid level in the reactor. The feed rate is controlled using either a proportional pump or by controlling the rate of take-off from a pump equipped with a recirculation line. In the reactor, the urea is hydrolyzed to ammonium carbamate, which decomposes into NH₃ and CO₂. The overall reaction in the reactor is:

\[
\times H_2O + NH_2CONH_2 \rightarrow 2NH_3 + CO_2 + (\times 1) H_2O
\]

The excess water is evaporated. The reaction is endothermic and heat is required. The rate of NH₃ generation by this reaction is given by the Arrhenius equation:

\[
NH_3 \text{ generation} = Ae^{b/kT}
\]

where \( A \) is proportional to the number of moles of water and urea and \( b \) is the free energy for the reaction. The amount of urea solution in the reactor and the temperature of the reactor control the generation rate of NH₃. Below 115 °C (239 °F), the reaction rate is negligible. In the U2A process, the temperature is self-regulated by controlling the heat input into the reactor to maintain a constant pressure. The rate of increase in NH₃ generation can be rapid since (1) only small increases or decreases in the temperature of the reactor fluid are necessary to follow load, and (2) NH₃ is stored in the reactor and in the reactor solution, which is readily available. Increasing the reactor temperature from 140 °C to 158 °C, for example, increases NH₃ generation by 300%.

CO₂ is hydrophobic and quickly enters the vapor phase. The NH₃ and water concentration in the reactor liquid-phase concentrations are at dynamic equilibrium value with the NH₃ and water in the vapor phase, depending on the temperature and pressure of the system. In this dynamic equilibrium, the gas composition is the stoichiometric equivalent of the urea feed solution and is nearly constant, since temperature variations at most installations are on the order of 5% from the average reactor temperature.
The heat required for the reaction may be supplied in a number of ways, such as electrical external resistance heaters, internal electric bayonet heaters, or internal coils using steam or heat-transfer fluid. Generally, steam or electric heating is used to provide the energy input for the hydrolysis reaction. Steam pressures between 120 and 600 psig are used. The urea reactor requires approximately 4470 BTU of energy to generate 1 lb of NH₃ when the reactor is fed a 40% urea solution, and 3400 BTU to generate 1 lb of NH₃ at 50% urea solution. Additional heat input is also provided to handle the reactor heat losses and for urea dissolving (55 BTU/lb of NH₃). In comparison, the heat energy required to provide NH₃ from a 19% aqueous NH₃ solution is 5200 BTU/lb of NH₃.

The rate of NOₓ reduction with NH₃ from urea is the same as with aqueous or anhydrous NH₃. The SCR process equations are as follows:

(1) removal of NOₓ by NH₃ =

\[
\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 & \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O}
\end{align*}
\]

(2) removal of NOₓ by hydrolyzed urea =

\[
\begin{align*}
4\text{NO} + 2\text{CO(NH}_2\text{)}_2 + \text{O}_2 & \rightarrow 4\text{N}_2 + 4\text{H}_2\text{O} + 2\text{CO}_2 \\
2\text{NO}_2 + 2\text{CO(NH}_2\text{)}_2 + \text{O}_2 & \rightarrow 3\text{N}_2 + 4\text{H}_2\text{O} + 2\text{CO}_2
\end{align*}
\]

The reactor is designed to operate at temperatures of 170 °C and pressures of 120 psig (for a maximum pressure of 300 psig). The controls are configured to control the pressure in the reactor at a set point between 30 and 120 psig, depending on the required delivery pressure and to avoid condensation. The NH₃/CO₂/water vapor stream discharges from the top of the reactor and is routed in a pipeline to the distribution grid. The NH₃ flow rate in the feed line is controlled by an NH₃ demand set point signal from the SCR/ SNCR control system. This control can be completely independent of the U2A system, which controls itself locally by level and pressure. The NH₃ feed line is heat-traced to maintain a temperature above the condensation temperature of the product gas for the operating pressure. Since this product gas contains both CO₂ and NH₃, it can recombine to form solid ammonium carbonate and ammonia carbamate. EC&C licensees have learned to pay careful attention to heat-tracing requirements for both the direct product gas and diluted product gas streams to avoid the formation of carbamate compounds or condensation. The gas is noncombustible and does not require dilution for safety purposes, as is required with anhydrous NH₃. Some customers have been able to reduce system and operating costs by using the product gas directly without an air dilution system.

Large systems are typically installed with a water-cooling system that adds to the safety of the process by providing a...
means to cool the reactor solution to below the NH₃ generation temperature. It also provides a means to control the pressure that builds up in the reactor in the event of an instantaneous stop in gas offtake from the reactor. Some of the smaller systems have been installed without a water-cooling system. In these cases, a valve drains the hydrolysis reactor to the feed tank to control the reactor pressure during a fast shutdown of the reactor. A pressure safety valve on the reactor, set for 300 psig, discharges reactor liquid back into the solution feed tank or continuous dissolver. A minimum feed tank level is maintained sufficient to quench the relieved liquid solution to stop hydrolysis reactions.

A manually operated blowdown line is provided that can be used to drain off some or all of the reactor liquids to reduce the buildup of contaminants. The blowdown solution is transferred to the solution feed tank, dissolver, or a disposable tank, and contains urea, ammonium carbamate, and related chemicals in the solution.

COMMERCIAL INSTALLATIONS

Since the completion of the first commercial demonstration in 2000, the U2A system has become a widely accepted process to supply NH₃ for NOx control applications. A partial list of current operational installations is presented below.

AES/HUNTINGTON BEACH
NH₃ supply: 800 lb/hr
Application: SCR on four gas-fired 225-MW boilers located in Huntington Beach, CA
Project included relocating the reactor from AES Alamitos to AES Huntington Beach and providing an additional reactor to serve the SCRs on four gas-fired units. Each reactor serves two boiler units without redundancy or cross connection on the NH₃ header. Operational since July 2001. SCR operation is year-round.

ALLEGHENY ENERGY SUPPLY/HARRISON
NH₃ supply: 3700 lb/hr
Application: SCR on three coal-fired 684-MW boilers located in Haywood, WV.
The demonstration reactor was completed in September 2001. Operational since May 2002 for one unit; since May 2003 for all three boilers. SCR operation is seasonal.

DTE ENERGY/MONROE
NH₃ supply: Phase I: 2500–5000 lb/hr; Phase II: 10,000 lb/hr.
Application: SCR on four coal-fired 750-MW boilers located in Monroe, MI.
System uses 70% urea liquid, which is diluted to 40% on site and stored as solution. Operational since May 2003. SCR operation is seasonal.

CONSTELLATION POWER SOURCE GENERATION, BRANDON SHORES
NH₃ supply: 2350 lb/hr.
Application: SCR on two coal-fired 670-MW boilers located in Baltimore, MD.
System is designed to use dry urea for dissolving on site. Storage of the urea is at 50% urea solution that is fed to the reactor. Retrofit of aqueous NH₃ system used for one year and original anhydrous NH₃ system, which was never used. Operational since summer 2003. SCR operation is seasonal.

UNIVERSITY OF CALIFORNIA, LOS ANGELES (UCLA)
NH₃ supply: 21 lb/hr.
Application: SCR on two 29-MW simple-cycle turbines operating on a cogeneration plant located in Los Angeles, CA. System uses commercial urea solution. Retrofit of anhydrous NH₃ system located next to the new hospital at UCLA. Operational since July 2004. SCR operation is year-round (see Figure 3).

SUMMARY

The U2A process provides a controlled pressurized source of NH₃ whose flow rate can be adjusted to provide low NH₃ and NOx concentrations as effectively as an anhydrous NH₃ source. The process is commercially successful because it reduces the risks of transporting and storing NH₃, while meeting the requirements for commercial power plant operation. Several keys to the success of the patented U2A process include

- flexibility in source and supply of urea;
- simple control system for reactor and NH₃ supply;
- ability to respond rapidly to changes in power production and high turn-down ratios;
- ability to handle an instantaneous drop in NH₃ demand; and
- operating costs that are typically less than aqueous systems. NH₃ systems.

ABOUT EC&C TECHNOLOGIES

EC&C Technologies (www.ecctech.com) provides new and improved processes for purifying emissions from combustion processes with emphasis on those that recover useful products from stack gases, reduce or eliminate the use of toxic materials, and achieve ultra-high pollutant removal. Founded as a partnership between Drs. Hal B.H. Cooper and Herbert W. Spencer, III, in 1989, and located in Santa Clarita, CA, EC&C Technologies, which stands for Emission Control and Chemical Technologies, has several processes currently under development. EC&C licenses the supply and use of the technologies that it develops, and has granted exclusive co-licenses for U2A to Wahlco Inc. (www.wahlco.com) and Hamon Research-Cottrell Inc. (www.hamon-researchcottrell.com). This exclusive license allows use of the patented process in NOx reduction applications for stationary and mobile sources worldwide.

2005 HONORS & AWARDS

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Dr. Ramanan began his career with an Indian engineering firm shortly before the passage of 1977 Clean Air Act in India. He later advanced, becoming a project manager and general manager. In the late 1980s, he was a department manager of air quality consulting services with ENSR International. In 1991, he joined Mobil Oil, where he developed and implemented comprehensive plans to meet the 1990 Clean Air Act Amendments. In 2000, post-merger; Dr. Ramanan assumed his current position with ExxonMobil. Dr. Ramanan was awarded the Fellow Grade of Membership at the 2005 Annual Conference (see EM June 2005, p. 50).