

# **U<sub>2</sub>A<sup>TM</sup> Urea-to-Ammonia “State of the Technology”**

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## **ABSTRACT**

This paper reviews the state of the technology for U<sub>2</sub>A<sup>TM</sup> (Urea-to- Ammonia) with an emphasis on the test results from the AES demonstration, noting confirmation of key technical and operational details for the U<sub>2</sub>A<sup>TM</sup> process.

## **INTRODUCTION**

Utilities are increasingly adopting urea as the preferred alternative to anhydrous ammonia for their SCR projects. Utilities and A/E firms have shown keen interest in technology for urea-to-ammonia conversion. Several major utilities have committed projects to the urea-to-ammonia alternative and other major utilities have confirmed decisions to use urea and are actively evaluating systems for current and future projects.

After detail technical and economic evaluation, the EC&C Technologies U<sub>2</sub>A<sup>TM</sup> system has been adopted for utility systems representing more than 8000 MW capacities.

The development of interest in urea-to-ammonia technologies is in response to the greatly increased requirements for utilities to control NO<sub>x</sub> emissions and their implementation of SCR projects that require ammonia as the reducing agent at the catalyst.

Anhydrous ammonia is regarded as a hazardous and toxic chemical and is subject to strict regulations imposed by the EPA as well as OSHA.

Aqueous ammonia, although less concentrated, poses similar risks, and is also becoming increasingly regulated or subject to restrictions by local authorities. The use of aqueous ammonia as an alternative to anhydrous, significantly increases operating costs for chemical and energy, and increases transport and storage requirements. This is increasingly true as more dilute aqueous solutions are considered.

The Urea to Ammonia (U<sub>2</sub>A<sup>TM</sup>) system uses urea as the feedstock chemical and thereby entirely avoids risks associated with the transportation and storage of ammonia. The process transforms urea solution to an ammonia gas mixture that meets the dynamic requirements of the NO<sub>x</sub> control system.

The ammonia equivalence of urea is approximately 50%. This makes it a lower operating cost chemical compared to aqueous ammonia and overall the best economic alternative where use of anhydrous ammonia is not desirable.

## **PROCESS**

### **Process Development and U.S. Patent**

U2A™ technology was developed by Emission Control & Chemical Technologies (EC&C) under grant sponsorship from the EPA's SBIR program.

As a result of the successful development work, EC&C made its initial filing with the U.S. Patent office on March 21, 1997. The patent was allowed in 1999 and issued as U.S. Patent 6,077,491 on June 20, 2000. Additional applications on the technology are pending

The earlier filing date and the strength of the patent claims provide strong protection for the U2A™ technology against competing processes.

### **Process Description**

In the U2A™ process (U.S. Patent 6,077,491) urea solution is heated under controlled conditions to drive the thermal hydrolysis of urea to produce a product gas containing ammonia, carbon dioxide and water vapor. U2A™ is a once through process in which the hydrolysis reactor comes to a dynamic equilibrium with a water-rich reactor liquid compared to the feed solution.

The U2A™ reactor is a kettle-reboiler style “BKU” heat exchanger constructed from 316L stainless to ASME code requirements. The vessel is rated at 300 psig and is fitted with a closed steam U-coil for heat input. Heat is provided by a nominal 150-250 psig steam supply and the U2A™ reactors operate typically at 80 psig and 300° F.

The urea hydrolysis reaction proceeds from urea solution (excess water) to ammonium carbamate and then to ammonia, carbon dioxide and water vapor according to the following:



The overall reaction is endothermic and is easily controlled by regulating the heat input such that the reactor operates at constant gas pressure, which simplifies the control system to three primary PID loops. A demand signal based on NOx control requirements regulates flow of ammonia gas to the process via a flow control valve. A level controller adjusts urea solution feed to maintain constant liquid level in the reactor. A constant gas pressure of product gas is maintained by controlling the steam input to the heating coils.

## U2A™ Operations at AES/Alamitos

The first commercial scale U2A™ system was started up in October 2000 at AES Alamitos station to provide ammonia to their existing SCR as a full-scale demonstration project. The operation at AES Alamitos was a complete success, leading to formal acceptance by AES and a contract for permanent installation of two U2A™ reactors at their Huntington Beach Station for operation starting in the summer of 2001.

The U2A™ reactor at AES/Alamitos operated for approximately 1500 hours following system load in fully automatic controlled operation to meet SCR process demand requirements. During the operation of the unit, NO<sub>x</sub> reduction ranged from 87-95% and was always in compliance. Procedures for start-up, shutdown, and idle mode were demonstrated. In side-by-side tests at full load, the U2A™ system demonstrated equivalent performance vs. the original aqueous ammonia system in place at Alamitos.

The reaction kinetics for U2A™, well understood at the pilot scale, were confirmed at Alamitos at full scale where the reactor operated within a few degrees of the predicted operating temperature vs. specific reaction rate. Predictive models support the designs for the U2A™ reactor and allow close prediction of reactor performance for various feed concentrations, temperature and pressures.

Operating time at Alamitos was sufficient to allow for quantitative and qualitative analysis of the expected residual from dissolved solids in the urea solution feed. This analysis together with physical inspection confirmed the suitability of materials of construction, the calculated requirements for periodic blowdown (annual or semi-annual), and the absence of accumulated organic materials (including carbon) in the reactor.

Tests were also conducted specifically to determine the fate of small amounts (0.2%wt) of formaldehyde that are typically present in prill and granular urea. These tests demonstrated that the formaldehyde is driven off to the flue gas and then destroyed across the SCR catalyst at removal levels of 90-95%.

Figure 1 Photograph of the AES Installation



## **U2A™ Urea-to-Ammonia “State of the Technology”**

The U2A™ process is discussed below.

### ***U2A™ Typical System Operation***

#### **Urea Receiving and Storage**

Dry urea is received by either rail or truck delivery and transferred to bulk storage. For small capacity systems, commercial urea solutions can be used in lieu of dry urea.

#### **Urea Solution Preparation**

Urea is transferred from dry storage (or direct from delivery) to a dissolver tank. It is mixed with heated de-ionized water to make up a urea solution of nominal 40-50% concentration. The urea solution from the dissolvers is transferred to a feed tank.

#### **Urea Reactor**

Solution is pumped from the feed tank to the hydrolysis reactor to maintain a constant level in the reactor.

The hydrolysis reactor is a "kettle reboiler" type vessel designed to operate at up to 300 psig at 400°F. Normal operation is at 80 psig and approximately 300°F.

The reactor is operated at constant pressure and a PID control loop is used to control the feed rate of steam to the hydrolysis reactor to provide heat input to the endothermic reaction.

#### **Start Up and Normal Operation**

During commissioning, the reactor checkout is performed with de-ionized water. During initial start-up, urea solution is fed to the vessel and the reactor liquid is brought up to its equilibrium concentration during initial operations. During subsequent start-ups (from idle), the reactor already contains a near equilibrium solution.

As heat is input to the reactor, the solution temperature and pressure increases. When the reactor reaches about 235°F, the urea thermal hydrolysis reaction begins and ammonia and carbon dioxide gases are generated.

The pressure set point for the reactor is determined by consideration of the design rate for NH<sub>3</sub> production (a function of the temperature, solution feed concentration and reactor volume) and the equilibrium for the ammonia-water phase equilibrium at the design temperature and pressure (boiling point). The pressure must be set at a value above the boiling pressure in order that the desired reaction temperature can be achieved.

After start-up, the steam heat input continues in automatic control to maintain the gas pressure constant at the set operating pressure. The control valve on the product

ammonia gas line is opened or closed to match the required demand for ammonia as indicated by a 4 to 20 mA signal from the customer's control system.

### Equilibrium Conditions

During normal operations the U2A™ reactor operates at near equilibrium conditions and the composition of the gases leaving the reactor and the feed composition closely matches the stoichiometric relationships of the urea hydrolysis reaction.

The composition of the reactor liquid contains water, dissolved urea, dissolved carbon dioxide and ammonia at a solution strength determined approximately by the phase equilibrium relationships for aqueous ammonia. The solution pH is typically 10.5.

At equilibrium the reactor liquid contains:

Ammonia - approximately 3% to 5% determined by phase equilibria

Carbon Dioxide - approximately 1% determined by solubility

Urea/Carbamate reaction intermediates – approximately 20%

Water - balance

### Ramp up

When process demand for ammonia increases, the pressure control system increases the heat input to the reactor. As the temperature in the reactor rises, the rate of urea decomposition increases and ammonia can be withdrawn from the reactor at a faster rate while maintaining reactor pressure. The steam supply requirement and heat transfer equipment are sized to provide for a rate of increase in ammonia supply that is faster than the maximum ramp rate specified for the NOx control process.

### Ramp down

Reduced demand from ammonia is satisfied by reduction in the heat input to the reactor, again at constant pressure. As the demand decreases the reactor temperature gradually decreases.

### Normal shutdown

In a normal shutdown, urea solution feed is left on and heat input to the reactor is stopped. Residual heat in the reactor continues to evolve ammonia carbon dioxide and water vapor, which are bled off to the process. During the bleed off, the reactor pressure and temperature decrease. When the reactor temperature decreases to 240° F, the unit can be placed in idle mode, containing equilibrium solution for a subsequent restart. For

extended shutdowns or for servicing, the unit can be feed with DI water only and the urea/carbamate content of the reactor can be completely exhausted, such that the reactor will contains only water and blowdown materials.

#### Fast Shutdown

Auxiliary reactor cooling via the internal heat exchanger and/or from optional external coolers can be used to reduce the time required to cool the reactor and is used in certain upset conditions where ammonia gases can not flow to the flue.

#### Periodic Blowdown

A manually operated blowdown line is provided that can be used to drain off reactor solution in order to purge contaminants in the solution in the reactor. Based on using high purity DI water and typical urea (containing 20 ppm ash) blowdown requirements can be scheduled annually or semi-annually depending on load factor.

#### Ammonia Gas Delivery

The product gas is discharged through heat traced piping into the flue gas stream. The product gas line is maintained at a temperature above 300° F in order to avoid water condensation or reformation of ammonium carbamate solids.

### ***Reactor sizing***

In general, the following procedure is followed when sizing a U2A™ reactor:

The design basis includes the peak ammonia generation rate and the steam quality and cooling water available.

Specify a net liquid volume for the reactor vessel based on the reaction rate vs. temperature models, which define a specific ammonia production rate for the “boiling” temperature of the solution at the selected operating pressure.

Specify a vapor freeboard volume for the reactor vessel.

Specify a heat duty with allowance for ramping to meet the process dynamics.

Specify a cooling duty that satisfies the shutdown procedure time-temperature-pressure models.

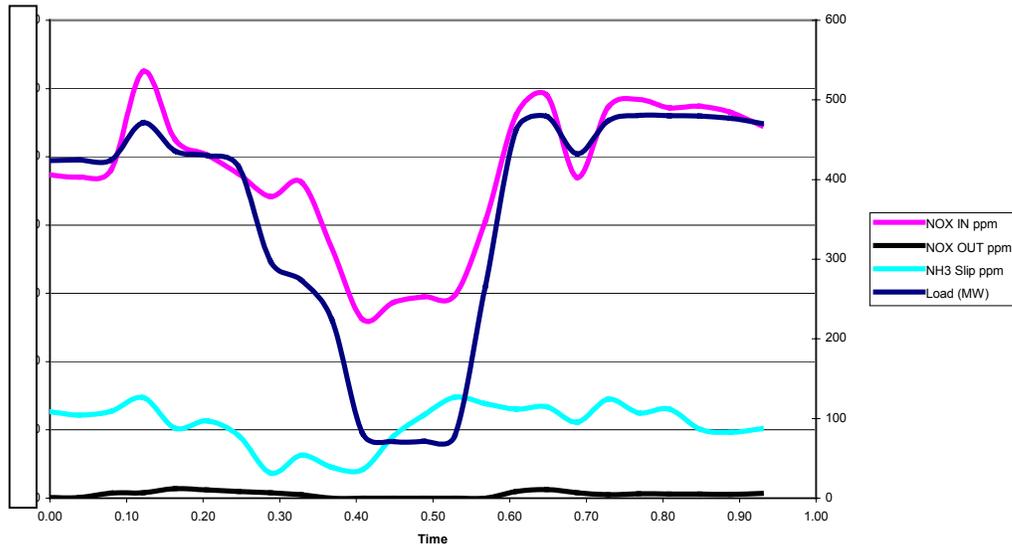
Determine the design of the heat transfer bundle to satisfy both the heating and cooling duty with the steam quality and cooling water given. For each specific case, either the heat duty or the cooling duty may control the design of the heat transfer bundle.

The sizing models for the design of the reactor were first developed during pilot demonstration work and are now confirmed from the operations at AES.

### AES Demonstration Results

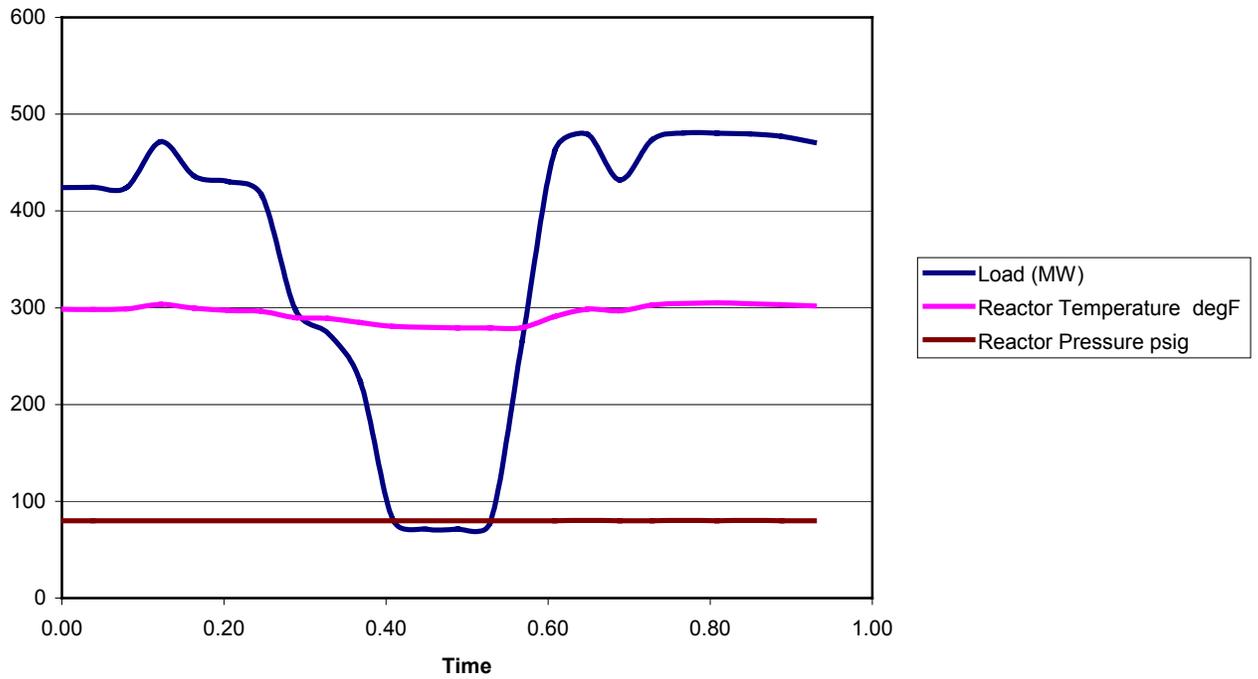
Test data representing operation of boiler and NOx SCR system (data points are hourly averaged information).

Figure 2 AES Operating Data, Load Scale Shown, the NOx and NH3 Slip Scale are suppressed.



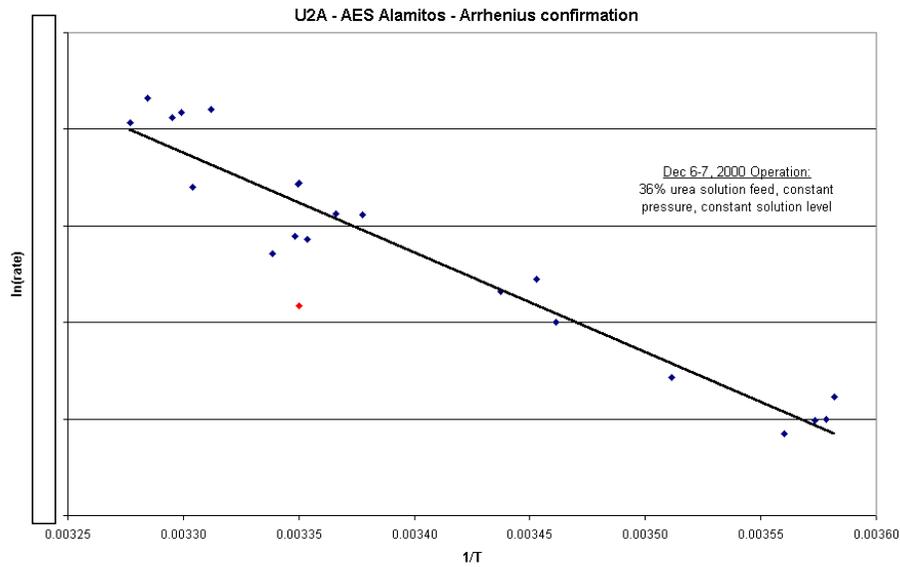
During this period the plant was operated to minimize NOx emissions to maximize the generation of NOx credits

Figure 3 AES Operating Data- Reactor Temperature and Pressure during Boiler Load Transition



**Ammonia Generation**

Figure 4 Reaction rate function of temperature

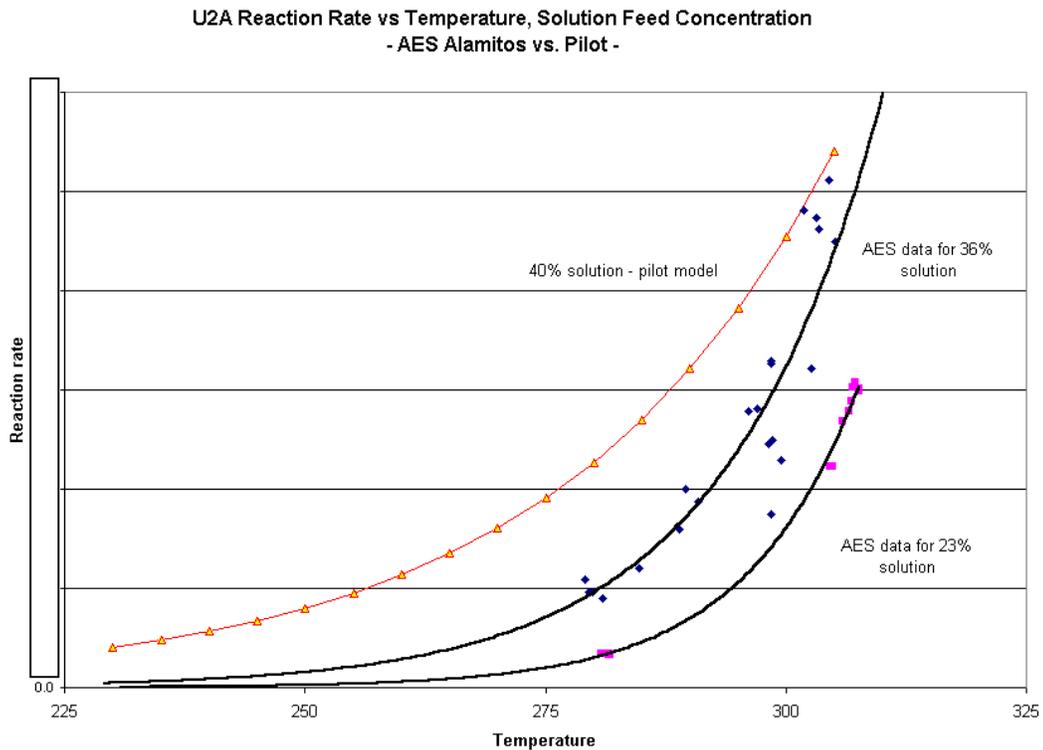


The U2A™ hydrolysis reaction is well represented by the Arrhenius relationships in which the log of the reaction rate is proportional to the inverse temperature.

### ***Reaction rate dependence on feed concentration***

The U2A™ reaction rate was observed at AES Alamitos for two solution concentrations and compared to pilot model correlations. The pilot correlation was run at 40% solution strength. There is a clear dependency of reaction rate on solution feed concentration.

Figure 5



### ***Correlation vs. pilot performance model and scale up***

The correlation showed good agreement between the operation of the AES reactor and the earlier pilot scale performance models. The AES data correlation will be used in reactor designs and while further scale up from this level does not require additional modeling, additional confirmation of the performance data will be obtained from the start-up of the larger reactors currently in construction.

### ***Product Gas Composition***

At the operating temperature and pressure of the reactor, the reactor gas contains ammonia, carbon dioxide and water vapor.

Since the U2A™ process operates at near equilibrium as a once-through process; the gas product leaving the reactor is at a known concentration that is the equivalent to the composition of the urea solution feed.

Urea solution concentration	wt%	40%	50%
U2A™ product gas			
Ammonia	vol%	28.5%	37.5%
Carbon Dioxide	vol%	14.3%	18.7%
Water Vapor	vol%	57.2%	43.8%

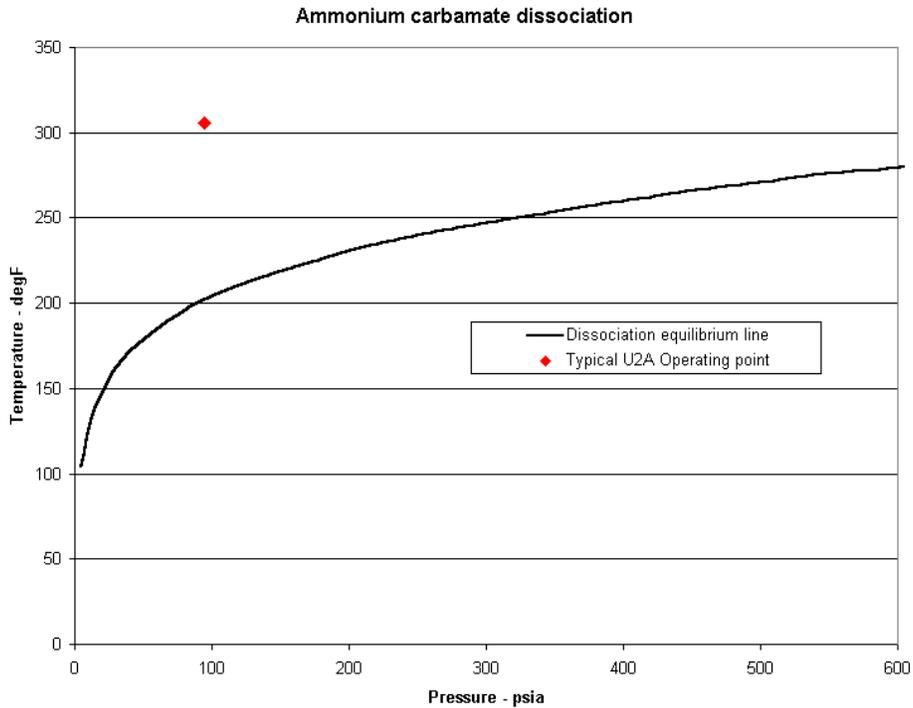
Operation with higher concentration urea solution reduces the throughput of water vapor through the system, while maintaining the volume proportion of ammonia to carbon dioxide at 2:1. The energy requirements for the process decreases while the reaction rate vs. temperature increases with higher urea concentration. With higher urea feed concentrations, more heat tracing is needed to prevent plugging of feed lines. In addition the feed concentration must have enough water to maintain excess water in the reactor for the hydrolysis reaction.

### **Ammonium Carbamate**

The product gas piping from the reactors to the point of use must be maintained at temperatures and pressures that avoid both condensation of water and formation of ammonium carbamate.

The dissociation of ammonium carbamate is described in the following chart, which is derived from reference data (Kirk-Othmer). The typical operating point for U2A™ is shown in the region of the chart where the equilibrium prevents reformation of carbamate. In the region below the equilibrium line carbamate will begin to form as a solid fume that can deposit on surfaces.

Figure 6



### *Non-flammable mixtures*

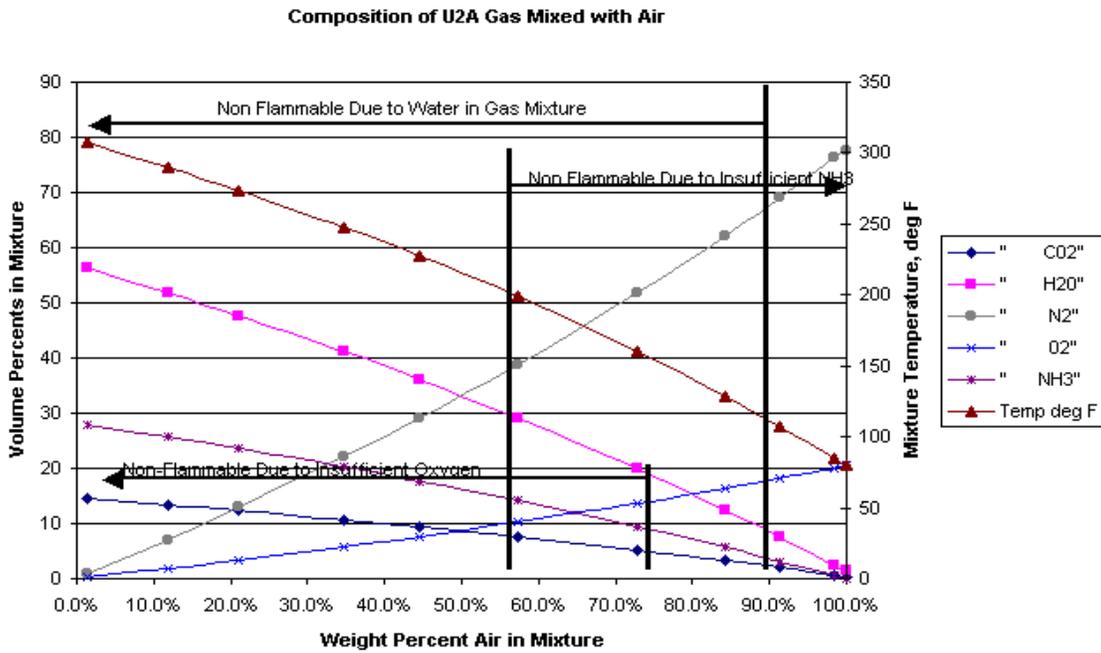
In most SCR systems, anhydrous or aqueous ammonia vapors are mixed with air to a point below the lower flammability limit of the mixture. Typically the mix is kept at less than 5% by weight ammonia in air.

The available data shows that all mixtures of the U2A™ product gas (for 40% urea solutions) with air are non-flammable.

The compositions of mixtures of the U2A™ gas (from 40% urea solutions) mixed with air (0 to 100 % by weight) are given in the graph shown below.

For mixtures with less than 75wt% air, the mixture is non-flammable due to the moisture content and due to insufficient oxygen to support combustion. For mixtures with greater than 57wt% air, the mixture is non-flammable due to insufficient ammonia. Since the regions overlap there is no mixture that is flammable. The temperature of the gas mixture is considered in setting the non-flammable region based on oxygen level.

Figure 7



## Process Control

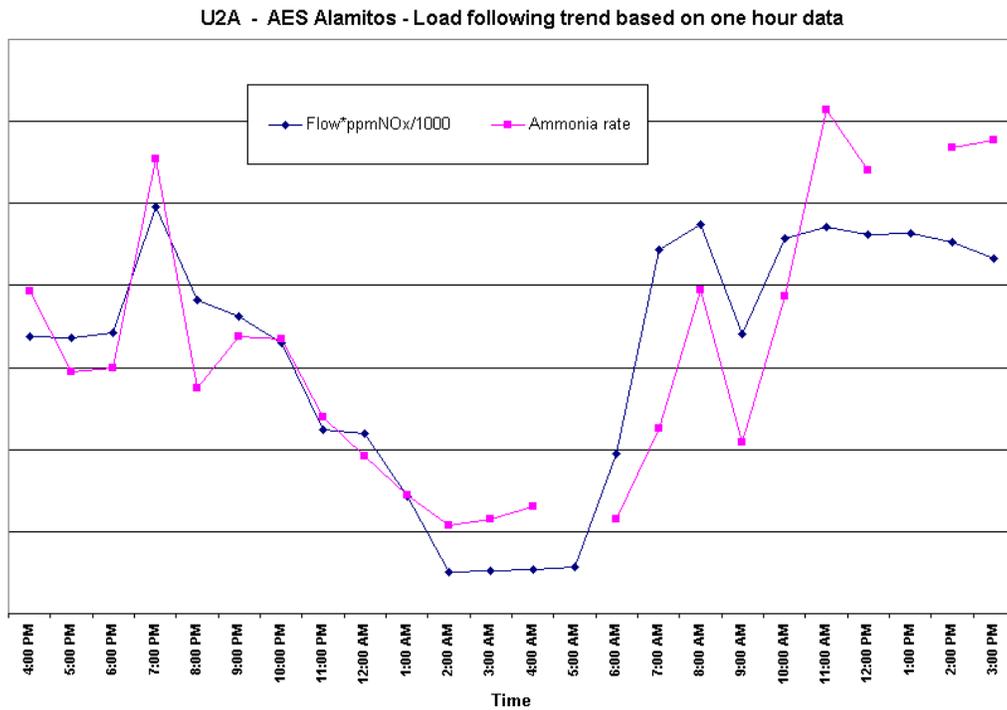
### Load Following

The U2A™ process was operated in fully automatic mode at AES Alamitos Unit #6. This unit operates as a swing load unit with the SCR system in service over the full load range.

During automatic operation, the U2A™ system delivered ammonia gas to the SCR ammonia flow control units in response to the NOx emissions control set points. At all times during U2A™ automatic control operation the NOx emissions and NH<sub>3</sub> were maintained within compliance set points determined in the plant DCS.

The following plot illustrates the load following trend over a turndown range of approximately 10:1.

Figure 8

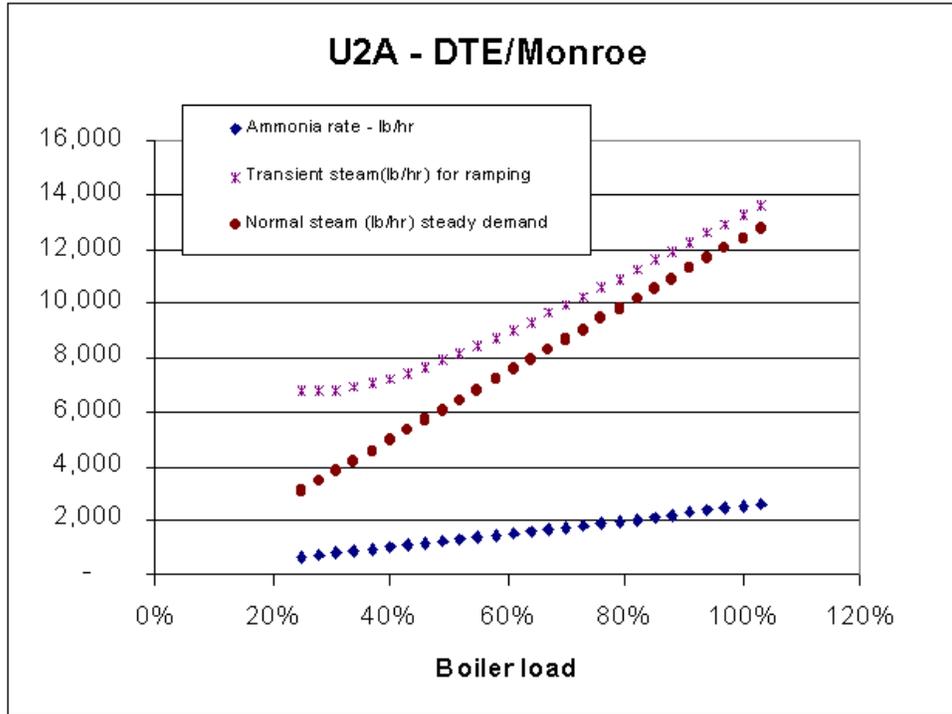


***Ramping***

The U2A™ process provides simple control and load following response including design to accommodate maximum ramping rates that are derived from consideration of the maximum rate of increase of boiler load, the flue gas mass flow vs. boiler load and the NOx concentration as a function of boiler load.

The heat exchanger design and the steam requirements consider the ramping rate requirement in the basic design, as is illustrated in the following example based on the system in design for the DTE/Monroe Station. Note that the requirements for steam flow during lower load operation compared to the steam capacity at full load will allow the system to ramp at rates much faster than the boiler will require.

Figure 9 Heat Input Requirements



The chart shows the expected steam consumption for one U2A™ reactor sized for 2500 lb/hr NH<sub>3</sub> based on:

Normal design per reactor of 2500 lb/hr ammonia from 40% urea solution at 100% load.

Assumption that ammonia demand is linear with boiler load.

Ramping is based on 75 lb/hr NH<sub>3</sub> per minute rate of change (3%/min).

Ramp rate applies across the entire load range shown.

Using 40% urea solution as the feed. Note that steam consumption can be reduced by feeding with 50% solution. Resulting consumption would be approximately 80%.

For one reactor at full load rating, expected steam consumption considering transient ramping requirements is 13,280-lb/hr of steam for 40% solution, and approximately 12,400 lb/hr normal.

This results in nominal steam consumption for four reactors of 49,600 lb/hr.

The mass balance submitted with a proposal will include a margin to account for steam pressure and/or temperature variation and to establish sizing for devices and piping. Steam loads for auxiliaries are determined separately.

## **Testing for SCAQMD**

SCAQMD set as an objective for the AES demonstration that tests be conducted to demonstrate that the existing SCR system could be operated at performance levels of NO<sub>x</sub> removal and show NH<sub>3</sub> slip than remained in conformance with the plant-operating permit.

### ***Flue gas testing at AES***

Stack tests at AES Alamitos were conducted by a certified third party testing firm in accordance with standard EPA methods, including:

NO<sub>x</sub>

NH<sub>3</sub>

Formaldehyde

The requirements of the SCAQMD were met. Liquid and residual samples were analyzed at a qualified third party laboratory. The test show comparable performance between aqueous ammonia and ammonia from U2A™. The test also showed that the ammonia from the urea feed to hydrolysis reactor was produced with a stoichiometric ratio of 1 as expected. The measured ratio was 1.02 based on averaged urea feed rates.

## **Reactor Inspection after Shutdown**

After approximately 1500 hours of operation the AES reactor was returned to the original assembly site at Wahlco for inspection prior to final shipment to its permanent location at AES/Huntington Beach.

### ***Visual inspection***

Visual inspection of internal surfaces of the reactor and heat exchange bundle were made prior to removal of the reactor heat exchange bundle for close inspection. After this inspection the unit was water washed and the surfaces inspected again.

The visual inspection revealed a thin coating of silt like residual materials on the wetted surfaces of the reactor and on the upper surfaces of the heat exchanger tubes. On surfaces where liquid had flowed, as the vessel was empty, rivulet patterns were shown.

Samples of this material were taken for chemical analysis and the total quantity of the material was estimated.

Water washing easily removed all materials from the steel surfaces leaving a smooth shiny appearance.

A consulting metallurgist was retained to participate in the inspection. His report confirms the suitability of the materials of construction for the service conditions.

### ***Residual material in the reactor***

Residual materials are expected from non-volatile trace contaminant materials in the water or in the urea.

### Total residuals

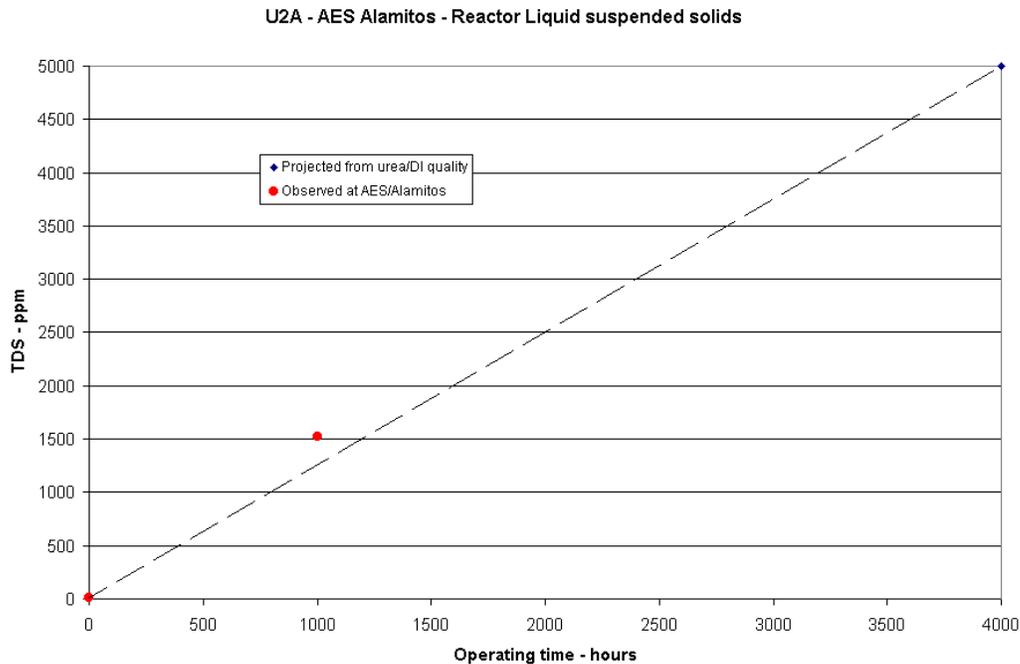
A total of approximately 25 to 50 lbs of brownish silt like particulate was found in the reactor. This amount is consistent with the buildup rate of suspended solids from the urea solution water quality. (Note that suspended solids are expected to reach about 0.5% after 4000 hours).

### Organics

The total residual solids were analyzed for a total organic content and found to contain 4% total organics. Based on 50 lb total residual this amounts to 2 lb of organic content after approximately 1500 hours operation.

The low organic content further confirms that formaldehyde does not accumulate in the U2A™ reactor and that no decomposition to carbon occurs. Both formaldehyde and carbon are discussed separately.

Figure 10.



### ***Materials of Construction – Metals Analysis of Residuals***

The reactor vessel and heat exchanger are constructed from 316L stainless steel. This material was used in earlier pilot reactor development and found to be suitable. As part of the AES demonstration the residual material was analyzed for Fe, Cr, Ni and other metals as follows:

A material balance was calculated considering the time that the reactor was exposed to urea/carbamate solution and the total silt content. This allows an estimate of the rate of corrosion with respect to the corrosion allowance considered for the vessel design, which is based on 316L for both the vessel and the heat exchanger tubes.

The calculated life of the 0.025” corrosion allowance in the vessel shell that results from this analysis is in the range of 20 years or more based on the Cr and Ni content of the residuals.

### **Urea Quality**

A typical urea specification lists:

<b><u>Urea Specification</u></b>	<b><u>Typical Analysis</u></b>	
Urea		99.0%
Moisture	0.3%max	0.15%
Biuret	1.2%max	1.0%
Formaldehyde		0.2%
Ash	20 ppm	15 ppm

The urea solution also must consider the TDS content of the water. DI water has a typical TDS content in the range 0.1 to 0.2 ppm.

### **Fate of Formaldehyde**

In the U2A™ process, urea solution is hydrolyzed under heat and pressure to form ammonia, carbon dioxide and water vapor in a once through process that is controlled to meet the process demands typically for SCR and SNCR NOx reduction processes.

Questions regarding the fate of formaldehyde, present in urea, were addressed during the operation of the U2A™ system at AES/Alamitos station.

The experience for U2A™ indicates that formaldehyde, though present in the urea feed solution, does not accumulate in the hydrolysis reactor, but instead is driven off to the flue gas stream where it is readily oxidized by the SCR catalyst.

### ***Formaldehyde in the flue gas***

Levels of formaldehyde were measured in the flue gas stream both before and after the SCR catalyst for operation of the system with the aqueous ammonia system and the U2A™ system.

A net reduction in formaldehyde concentration across the SCR catalyst was measured in the range of 85%-95%. This result was checked with and is consistent with the expectations of a major SCR catalyst supplier (Ceram/Frauenthal). The head of their technical department advises that they would expect SCR catalyst to oxidize formaldehyde at high efficiencies.

### ***No Carbon Formation***

The presence of carbon residuals has not been observed in U2A™. This has been apparent through observation of the process in the pilot development and has been confirmed after 1500 hours operation at AES Alamitos by testing of the equilibrium reactor liquids and the residual materials analyzed after shutdown of the system.

Accumulation of non-volatile organics would necessarily be sensitive to urea quality and water quality issues. Specifications for urea quality must exclude non-volatile organics.

Decomposition of organics to carbon via “coking” is of concern only at temperatures much higher than is practiced in the U2A™ process. .

### **References**

Cooper, H. B. H and Spencer, H. W., U.S. Patent 6,077,491 – Methods for the Production of Ammonia from Urea and/or Biuret, and Uses for NO<sub>x</sub> and/or Particulate Matter Removal.

Fenton, Donald L. et al., “Flammability Limits of Ammonia-Air Mixtures”, presented at IIAR 18<sup>th</sup> Annual Meeting, March 3-6,1996. (The paper is available from the International Institute of Ammonia Refrigeration, 1200 19<sup>th</sup> Street, N. W., Washington, D. C. 20036-2401.)