

Urea to Ammonia (U₂A™) systems: Operation and Process Chemistry

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ABSTRACT

Hamon Research Cottrell and Wahlco, Inc., under license from EC&C Technologies have supplied U₂A™ systems with ammonia duty rated at various maximum capacities from 10 to 10,000lb/hr.

This paper describes the operation of a U₂A™ (Urea to ammonia) reactor sized for a rated capacity of 460 lb ammonia/ hr for a coal-fired power plant SCR. The constant pressure system allows a controlled response to changes in NO_x-load that is almost instantaneous. Data shows that this reactor was able to operate over loads ranging between 50 and 400 lb/hr ammonia. The U₂A™ reactor system demonstrated smooth start-up and shutdown characteristics and provided 98% availability during its first operating season.

Data analysis shows how low and high load operation influence composition of the equilibrium reactor solution. Sample analysis of the reactor liquid shows that speciation of the reactor liquid is the same as urea feed with levels of the reaction intermediates varying somewhat with load.

At the end of season, inspection of the reactors revealed that internal surfaces and tubes were clean and accumulation of residuals was nominal. The absence of significant residuals demonstrates the complete nature of the urea hydrolysis reaction in the U₂A™ system.

INTRODUCTION

The development of urea-to-ammonia technologies is in response to the greatly increased requirements for utilities to control NO_x 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, OSHA and additional restrictions by local authorities.

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

The Urea to Ammonia (U₂ATM) system uses urea as the feedstock chemical and thereby entirely avoids risks associated with the transportation and bulk storage of ammonia. Since the ammonia equivalence of urea is approximately 56%, urea provides a lower operating cost chemical compared to lower concentration aqueous ammonia and an economic alternative where use of anhydrous ammonia is not desirable.

COMMERCIAL EXPERIENCE

Utilities are increasingly adopting urea as the preferred alternative to ammonia for their SCR projects. At present, systems installed or in design represent a total ammonia capacity of approximately 25,000 lb/hr NH₃ serving 10,000 MWe in the U.S. and Europe on gas turbine and gas and coal fired boiler SCR systems. The first U₂ATM commercial installation has accumulated approximately 16,000 hours operation to date.

The scope of these installations includes urea storage, handling, urea solution preparation, solution feed and control system, hydrolysis reactors and ammonia flow control units for systems ranging from 10 lb/hr to 10,000 lb/hr ammonia.

PROCESS BACKGROUND

U₂ATM 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. U.S. Patent 6,077,491¹ was issued on June 20, 2000. Additional patents (US 6,322,762 B1, Nov. 27, 2001, US 6,436,359 B1, Aug. 20, 2002 and US 6,506,350 B2, Jan 14, 2003) have since been issued and other applications are pending.

In the Urea to Ammonia (U₂ATM) process, an aqueous solution of urea is converted to a gaseous product of ammonia, carbon dioxide and water vapor by thermal hydrolysis described by the following overall reaction:



The reaction occurs in two steps and overall is endothermic. The first reaction involves the production of ammonium carbamate from the combination of urea and water.

Ammonium carbamate then breaks down in the presence of a heat source to form carbon dioxide and ammonia, with the excess water leaving the system as vapor.

Both reactions take place in the liquid phase in the reactor. The break down of ammonium carbamate is pressure dependent. At the operating pressure of approximately 80 psig, the carbamate dissociates at 98°C (208°F). Above this temperature the reaction favors the formation of ammonia. Below this temperature, at times during shut down of the system, the ammonia and carbon dioxide gases will recombine to form ammonium carbamate.

The rate of generation of ammonia by this reaction can be described by the Arrhenius equation which is of the form

$$R = A * e^{\left(\frac{-E}{kT}\right)}$$

Where A is proportional to the number of moles of water and urea in the reactor, and E is the activation energy for the reaction. The concentration of urea in the reactor and the temperature of the reactor influence the generation rate of ammonia. Below 115°C (239°F) the reaction does not occur at significant rates. Since the overall reaction is endothermic it is easily controlled by regulating the heat added to the reactor which is operated at constant pressure.

The U₂A™ reactor itself is a kettle-reboiler style heat exchanger, normally rated at 300 psig and fitted with a closed steam tube bundle or heating elements for heat input. When using steam, heat is provided by a nominal 150-250 psig steam. U₂A™ reactors operate typically at 80 psig and 300° F.

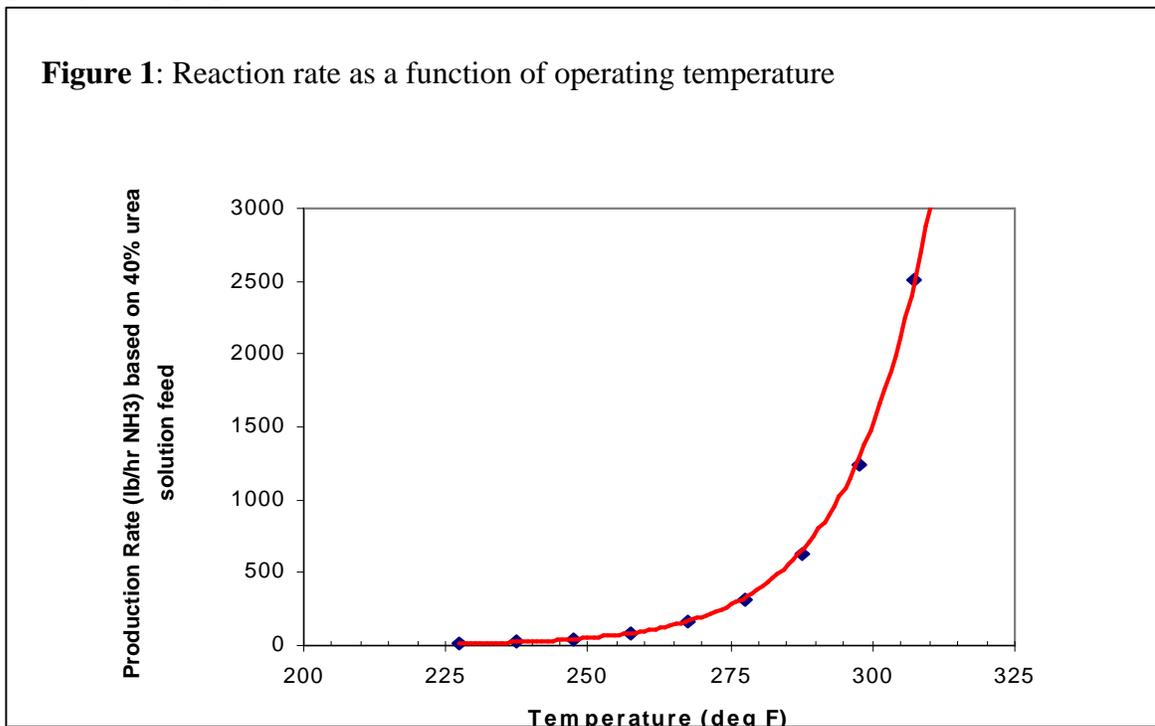
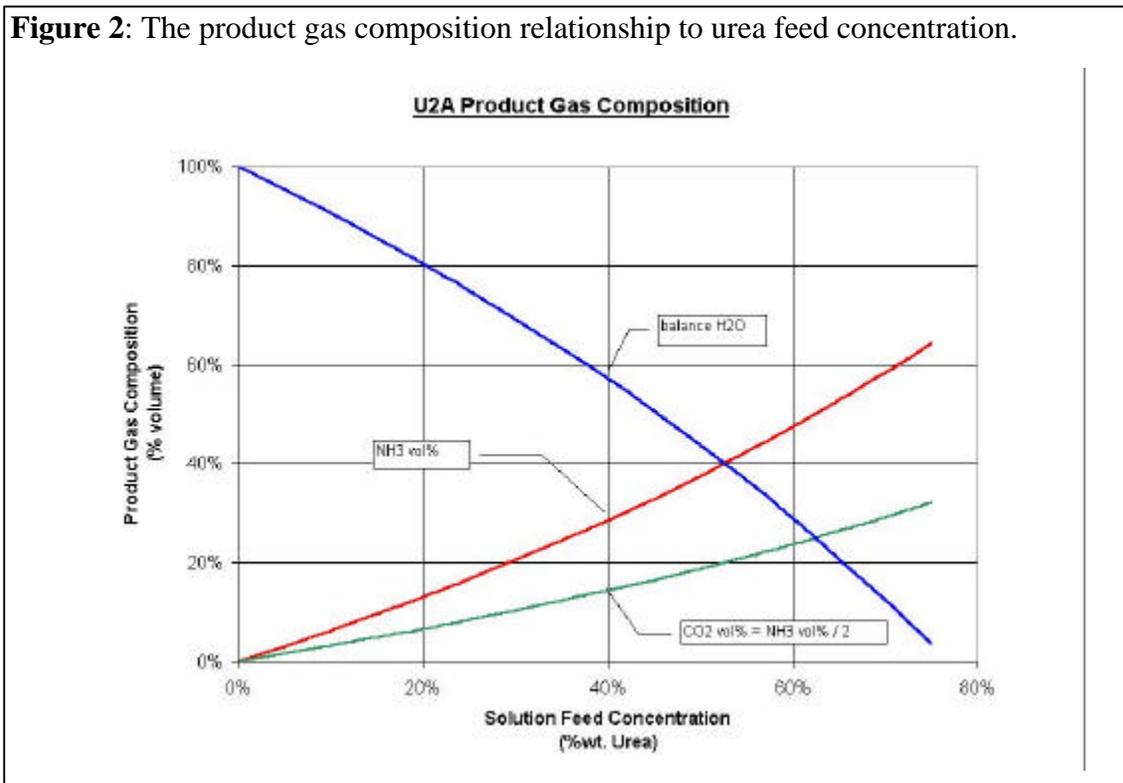


Figure 1 shows the exponential relationship between the operating temperature of the reactor and the relative production of ammonia. After a temperature threshold has been reached, the ammonia generation rate increases rapidly with temperature. Typically, the operating temperature cycles daily from high load operation at about 300 °F to low load operation at about 285 °F.

In practice, level and pressure are held constant, and temperature varies slowly. This provides a stable dynamic equilibrium and since the U₂A™ process operates 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 as shown in Figure 2.

Figure 2: The product gas composition relationship to urea feed concentration.



Two typical cases are outlined below.

Urea solution (wt%)	40%	50%
U ₂ A™ product gas	(vol%)	(vol%)
Ammonia	28.5%	37.5%
Carbon Dioxide	14.3%	18.7%
Water Vapor	57.2%	43.8%

Some optimization of the process is possible by operating with higher urea solution concentration. In addition to the heat requirements of the endothermic reaction, the process requires energy to process the excess water introduced with the urea solution. Therefore, operation at higher solution concentration reduces the energy requirements for the process. At the same time, the reaction rate versus temperature characteristic increases with higher urea concentration, allowing smaller reactors. These considerations are balanced against requirements for heat tracing to maintain proper temperatures in feed lines and other piping systems. An upper limit on feed concentration would be based on the need maintain excess water in the reactor for the hydrolysis reaction.

While the main components of U₂A™ product gas are ammonia, carbon dioxide and water vapor, trace amounts of HCHO are also present when formaldehyde conditioned urea is used. An earlier paper² discussing U₂A™ technology presented the results of tests which were also conducted specifically to determine the fate of small amounts (0.25% wt) of formaldehyde that are typically present in prill and granular urea. These tests had demonstrated that the formaldehyde is driven off to the flue gas and then destroyed across the SCR catalyst at 95% or higher removal efficiency.

One issue that has been raised regarding the fate of formaldehyde is the potential formation of urea-formaldehyde polymers. It is noted in the literature³ that the production of urea formaldehyde polymeric resins take place via acid promoted reactions that are favored at pH less than 5. The U₂A™ hydrolysis reactor operates at pH of 9 or higher in a range where polymerization does not take place.

The end of the season inspection for the reactors confirms the fate of formaldehyde in the U₂A™ process as little or no residual material remained after processing significant amounts of formaldehyde conditioned urea.

SYSTEM DESCRIPTION AND FIRST SEASON RESULTS

The installation for a 360 MW boiler was started up in June 2002. The scope included two dissolvers, reactor feed tank, circulation, feed pump and condensate skids and two 100% U₂A™ reactors.

Dry urea from trucks is fed directly to the dissolvers and all urea storage is in solution. DI water is used to make up the urea solutions batch wise in the truckload capacity dissolvers. The urea solution is then transferred to a reactor feed tank. The feed pump meters urea solution into the reactors (one operating and one on stand-by) which are heated using steam.

Operating Parameters

The U₂A system discussed here was designed for operation with 40 or 50% urea solution feed and 80 psig operating pressure and was sized such that it would give rated ammonia production at around 305 °F.

During initial start-up through June, the reactor operated with 50% urea solution and constant pressure at 60 psig. From July to September, the reactor was run with 40% urea solution feed and constant pressure at 80 psig, enabling direct comparison of reactor liquid properties with other U₂A™ installations which operate under similar conditions. In late September, the urea solution was gradually increased to 50% and the operating pressure was increased to 100 psig. The effects of these changes on the reaction temperature and reactor liquid properties were observed.

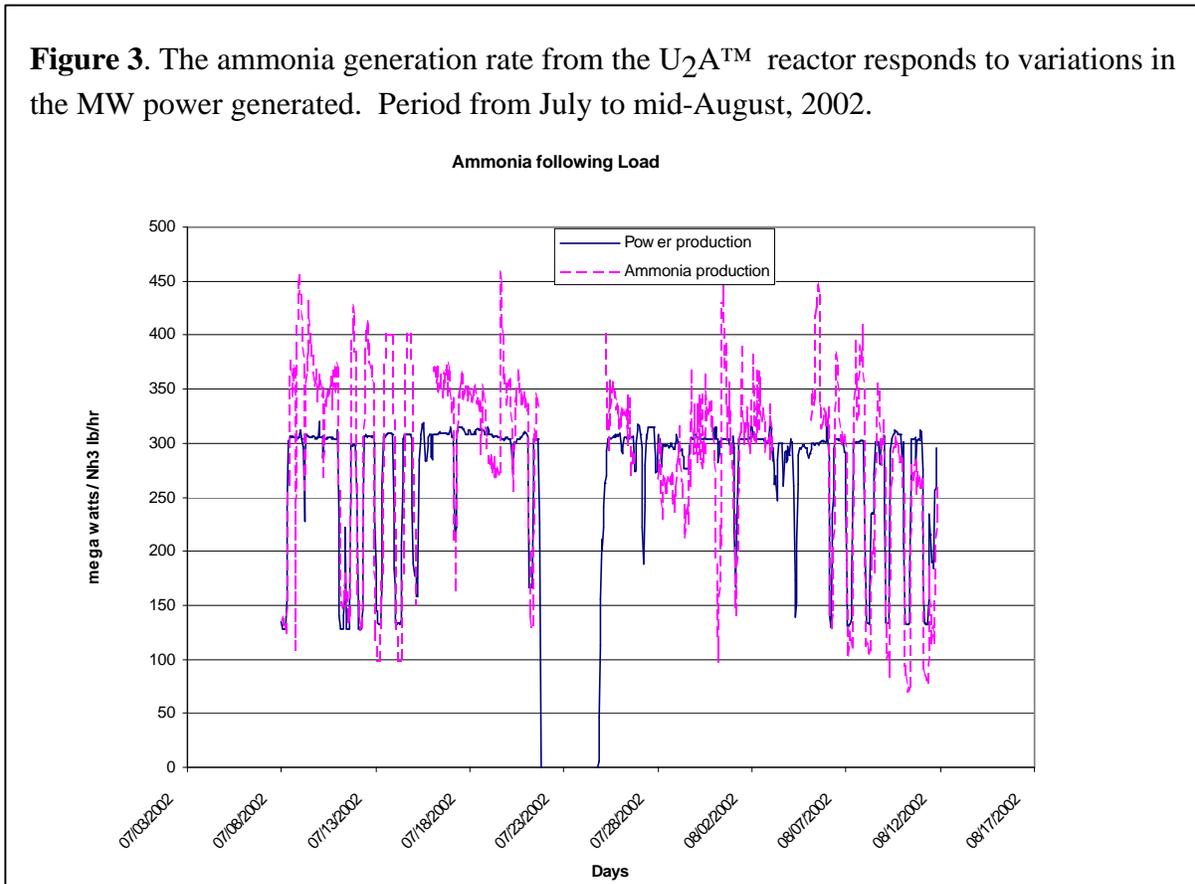
Overall Performance

The system was operated from the 1st week of June to the 1st week of October. After system check out, the initial start-up procedures were carried out in one day and performance tests were passed by June 21.

The boiler typically operates in cycling service with an estimated capacity factor of about 0.8. The system is designed for a peak load ammonia demand of 460 lb/hr but typical maximum demand for the first season was approximately 400 lb/hr.

Over the course of the first season, one reactor was operated for 80% of the time and the second reactor for the balance. During this time a total of 1,900,000 lbs of urea was processed in the two reactors, including 3 tons of formaldehyde (@0.3%).

Figure 3. The ammonia generation rate from the U₂A™ reactor responds to variations in the MW power generated. Period from July to mid-August, 2002.



During the 121 day operation season, the nominal availability of the U₂A™ system was 97.5% due to one 3 day U₂A™ outage. The U₂A™ outage occurred when solids were found to have crystallized out of solution in dead leg piping leading to the reactors. The pluggage was cleared with heat and heat tracing settings were increased. Subsequently the U₂A reactors operated for the remainder of the season without similar incident.

There were no SCR operational / control issues regarding ammonia supply as the system easily followed any boiler load or SCR demand change as shown in Figure 3.

Start-up

During commissioning, the reactor checkout is performed with de-ionized water. For initial start-ups, weak urea solution is fed to the vessel and the reactor liquid develops its equilibrium characteristics over the course of the first few days. During subsequent start-ups (from idle), the reactor already contains equilibrium solution.

As heat is input to the reactor, the solution temperature and pressure increases. Below about 225°F the reactor pressure develops based primarily on water vapor pressure. When the reactor reaches about 235°F, the urea thermal hydrolysis reaction begins and ammonia and carbon dioxide gases are generated which develops additional pressure.

At this point the system is placed under pressure control and the steam heat input is regulated to maintain constant reactor pressure which delivers product gas to an essentially constant pressure ammonia header. Downstream at the ammonia flow control station a control valve is modulated to meet the demand for ammonia as indicated by a 4 to 20 mA signal from the customer's control system. The urea feed to reactor is based on simple level control. The level control loop, the pressure control loop and the ammonia flow control loop are all independent of each other.

Figure 4 depicts start-up from cold conditions. During normal operation, half of the reactor volume is the liquid space (maintained via level control) and the rest is the vapor space. For the initial start-up, the liquid space in the reactor vessel was filled half with DI water and the rest with 50% urea solution to approximate an equilibrium solution. Since reaction rate increases with urea concentration, start up on full strength solution is not desirable, as pressure will build faster than temperature. With 25% urea solution in the reactor, the temperature was slowly ramped up to 240 F and the pressure rose to 80 psig before settling back to the set value of 60 psig. Now at constant pressure, the subsequent temperature rise depends only on the ammonia demand.

Figure 5 depicts the start-up of an already warm reactor containing equilibrium fluid. The reactor had been shut down due to an SCR issue and was being restarted. The reactor came up to the generating temperature of 240 °F in less than an hour. There is no initial pressure overshoot in this case in spite of the fact that the control set point was higher at 80 psig. The ammonia demand at that time as shown by the graph is 250 lb/hr. Again, the pressure is held constant while the temperature adjusts to the ammonia demand.

Figure 4: Reactor start-up from cold conditions

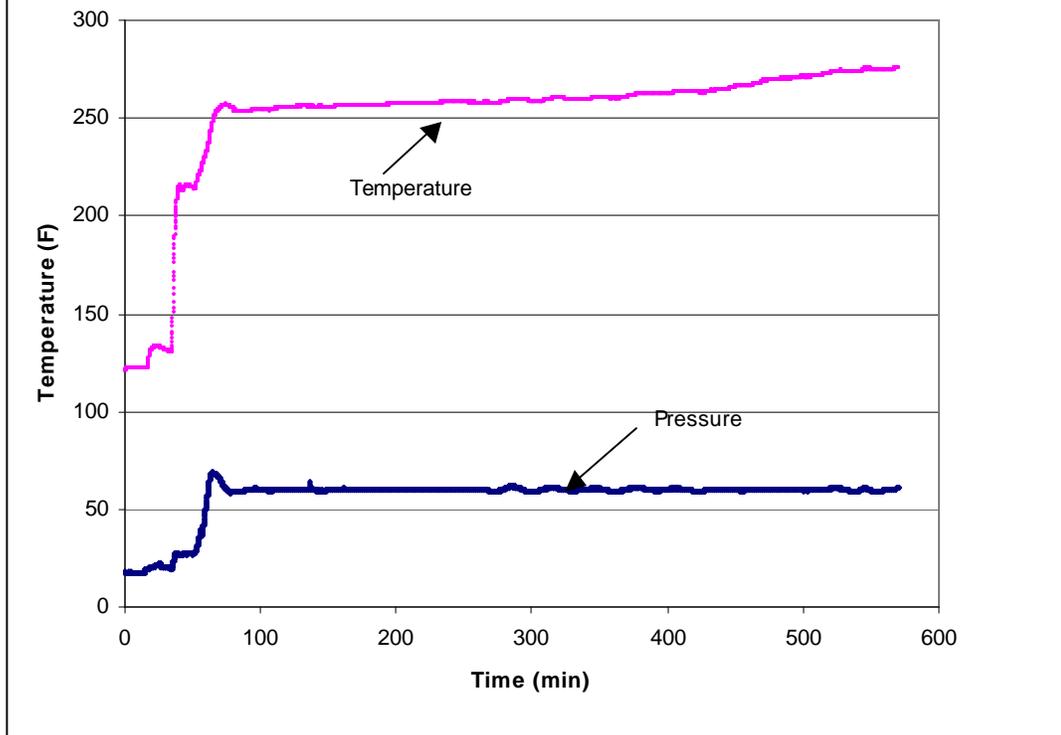
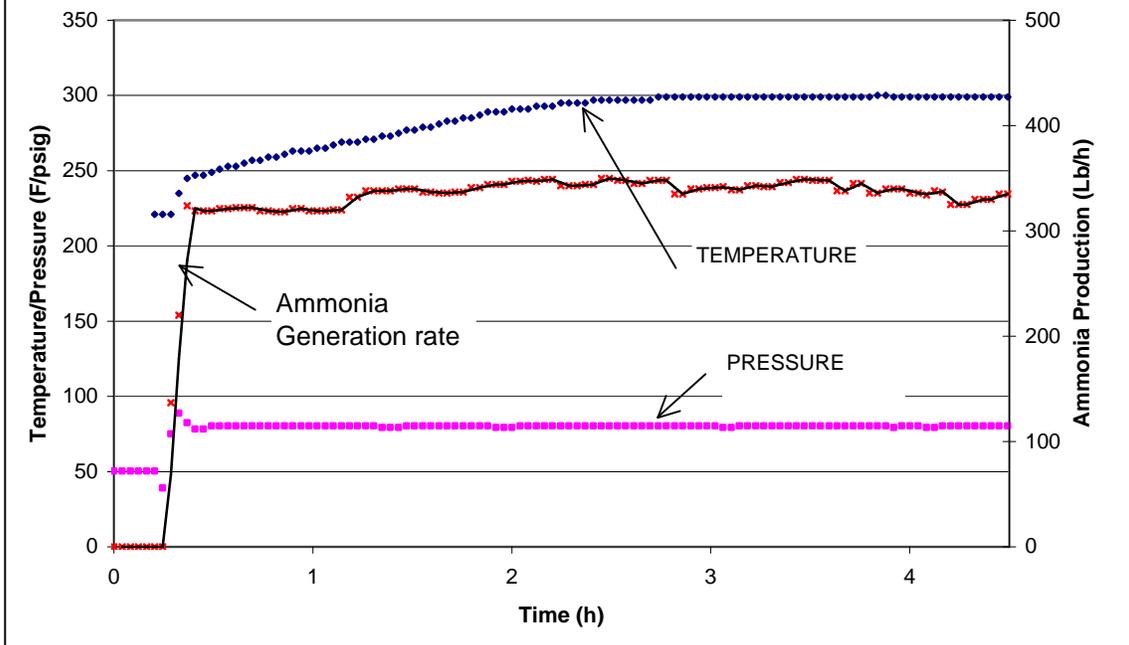


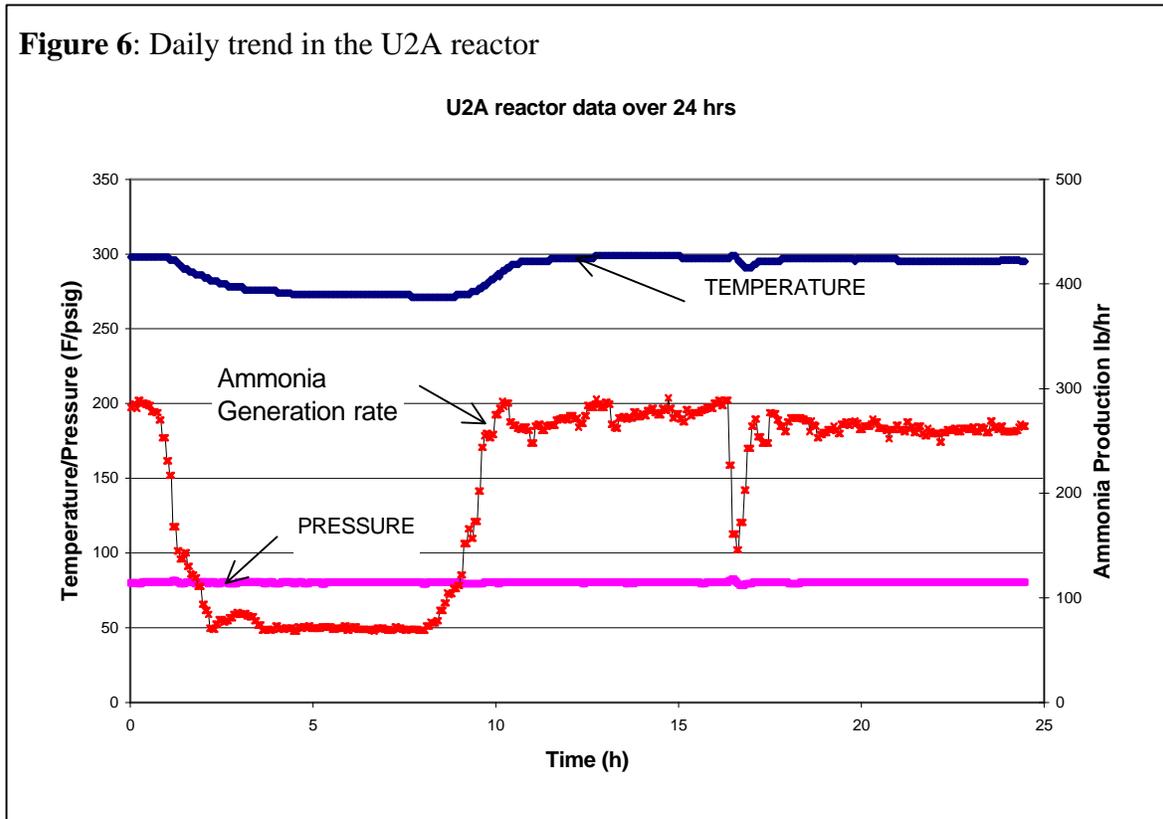
Figure 5: Reactor start-up from idle/warm conditions

Start-up of the U2A reactor from warm conditions



Normal operation

Figure 6: Daily trend in the U2A reactor

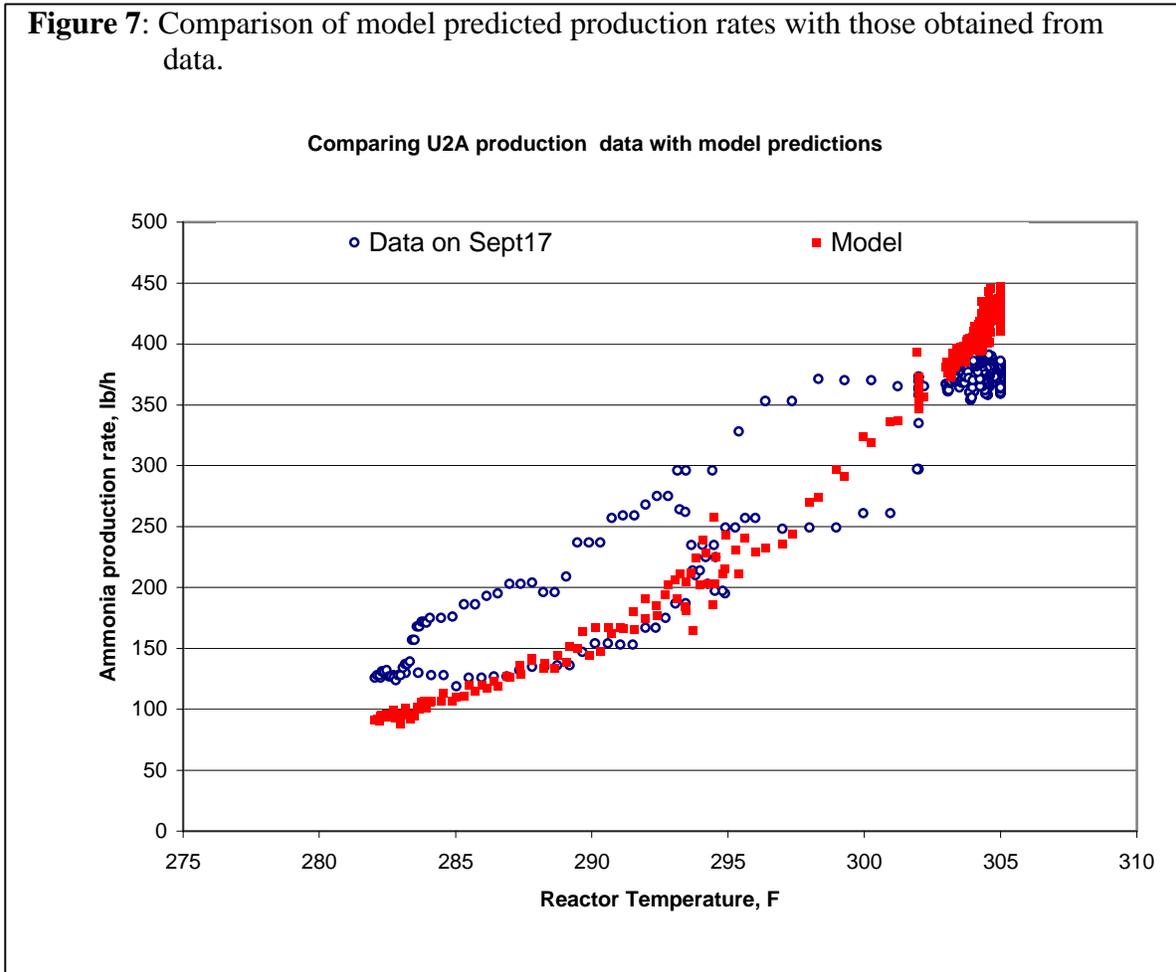


The graph depicts operation of the U₂ATM reactor over a 24 hour period. The ammonia demand correlates directly with the power consumption. Since power consumption is low in the early hours of the morning and high in the afternoon and evening, the ammonia production follows a similar trend. It can be observed that a 6: 1 ramp down was obtained in an hour. The reaction temperature dropped down 25 degrees to maintain the low production range. Again as demand increased, the temperature of the reactor increased due to increased steam supply and resulted in a 1:5 ramp up in a period of an hour. Under this kind of daily load fluctuations, the reactor operated continuously for a period of two and half months before a shutdown due to boiler leak. The instrumentation of the system enabled operation at constant pressure during that entire time.

The composition of the gas remains constant during these transitions in production rate. However the concentrations of ammonia, ammonium carbamate and the amount of water in the liquid phase change during the transition maintaining the vapor liquid equilibrium. At low production rates there is more ammonia (~3%) in the reactor liquid whereas at the higher production rates the concentration of ammonia drops to around 1-2%. Water concentration also drops off at higher production.

Comparison with model

Figure 7: Comparison of model predicted production rates with those obtained from data.



This chart compares the ammonia production rate versus temperature curves obtained from data with model predicted values from earlier units. One can observe that the data points which match best with the model values are the ones for which steady state has been achieved. When the reactor is in transient conditions there is a hysteresis type behavior with respect to the model depending on whether the points depict a ramp down or a ramp up phenomenon. The maximum ammonia production rate does not seem to exceed 400 lb/hr and is lower than the model predicted value at that temperature of 305 F. This was because of incorrect limits on the gas flow measurement device which were subsequently corrected.

End of season shut down

The seasonal shutdown procedures were designed to bring the tankage, urea solution piping, reactors, and product gas piping to a water (steam) only condition. Urea solution inventories were managed to run out by the 1st week of October. The system was shut down by adding DI water to the dissolver tanks to gradually dilute the remaining urea solution in the system until the reactor feed became water only.

The reactor was operated on water for a few days to ensure that all the urea chemicals had reacted and remaining ammonia was driven out of the system.

Remaining liquid was drained out and both reactors were subsequently opened for inspection, including removal of the tube bundle for inspection and cleaning. Care was taken to gather any residual material found and the “as-found” conditions were photographed.

The reactor shown in the following pictures had been in operation for approximately 100 days. Only a small amount of residual solids were found and the reactor interior surfaces were fairly clean. A thin layer of grime on the tubes was cleaned easily with steam.

The pictures provide confirmation that the formaldehyde content of the urea is driven off as vapor in the U₂ATM process, as previously demonstrated by testing at another site.

Figure 8: Some residual sediments from the reactor and light deposits on tube surfaces. The tube bundle was 75% out of the vessel at this time.



Figure 9: Reactor Tubes after steam cleaning



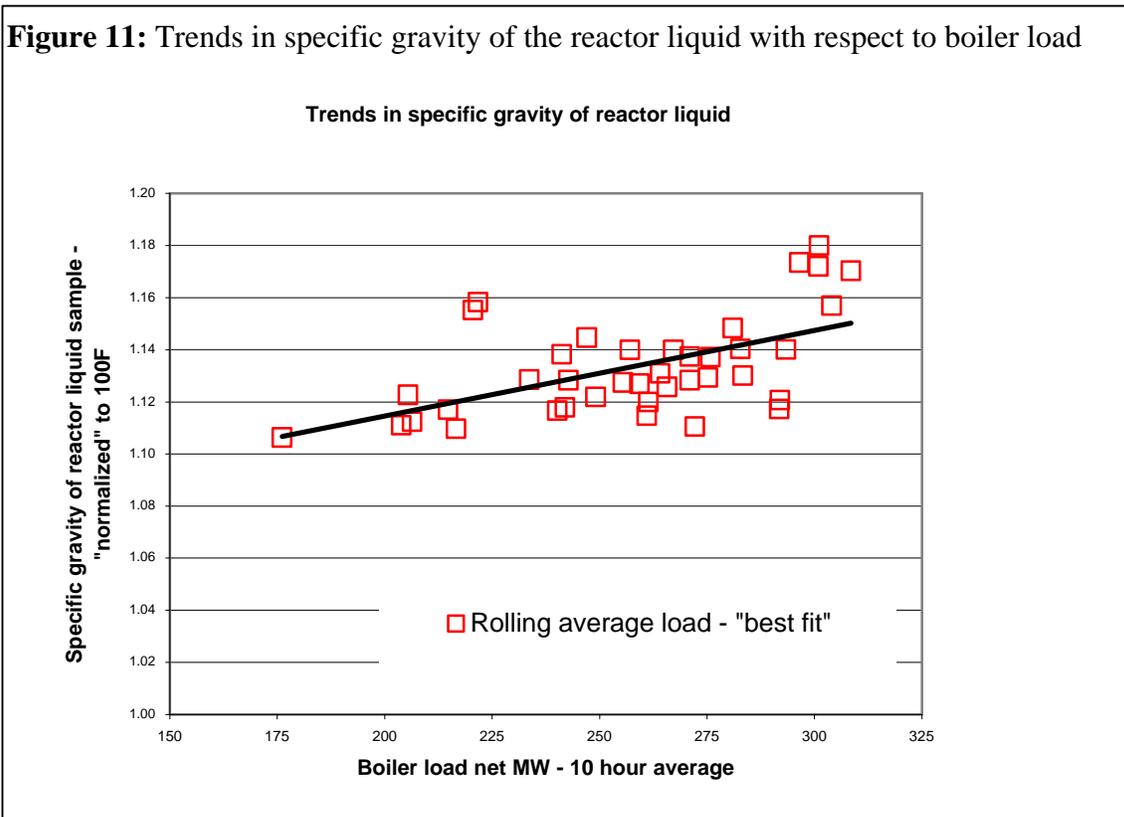
Figure 10: U2A reactor internal view after approximately 100 days operation. This reactor had processed 1,500,000 lb of urea containing about 4,500 lb of formaldehyde. This picture was taken immediately following removal of the tube bundle.



Chemical Analysis of Reactor Samples

Subsequent to a 3 day unplanned U₂A™ outage at the end of June when an external dead leg piping run was found plugged, reactor liquor samples were regularly drawn from the operating reactors and analyzed. It was observed that the specific gravity of the reactor liquid varied with time averaged operating load (and hence time averaged operating temperature). Figure 11 illustrates this trend in specific gravity. It was inferred that the relative amounts of urea, urea related chemicals and ammonium carbamate inside the reactor were varying as the overall reaction rate changed with ammonia demand. This led to a change in dissolved solids to water ratio in the reactor liquid affecting the specific gravity and solubility of the solution in the dead legs.

Figure 11: Trends in specific gravity of the reactor liquid with respect to boiler load



Analytical procedures

Urea was detected and quantified using HPLC (high performance liquid chromatography) separation in an amino column (25cm x 4.6 mm dia.), 10 μ pore size and a UV detector set at a wavelength of 200 nm. The retention time for urea is 10.5 min. In the second method, urea and urea derivatives were simultaneously detected using a C-18, 5 μ m column and a UV detector. This system matched the procedure for formaldehyde-conditioned ureas as reported from literature⁴ (Ind. Eng. Chem. Prod. Res. Dev., Vol. 24, No. 3, 1985). Urea, in this reference, was found to contain methylene di-urea (MDU), biuret (BIU), Dimethylenetriuret (DMTU), bi-methylene urea (BMU) and Triuret (TRI).

Total solid content was found by evaporating water at room temperature. Free ammonia and ammonium carbamate in the liquid was determined by wet chemistry methods, which quantify total NH_3 and carbamate. The presence (or absence) of carbamate was determined by acid digestion with evolution of CO_2 confirming carbamate.

Analytical Results

Solids slowly precipitated out of these samples, typically a few days after cooling to ambient conditions. Detailed analysis of these samples showed that they contained 45-55% of solids of which 35-45 % was urea and 7-10% was higher molecular weight urea derivatives like methylene di-urea (MDU), biuret (BIU), di-methylene triuret (DMTU), bi-methylene urea (BMU) and triuret (TRI). The pH of the samples varied between 9 and 10. These chemicals were present in HPLC analysis of the feed urea sample; therefore they were not alien to the system. Compare figures 12 and 13. Note that MDU and DMTU are related to the formaldehyde content of the base urea. The high solids content explains why they precipitated out of solution on cooling. The rest of the reactor liquid was composed of water (30 to 60%), and dissolved ammonia/ ammonium carbamate at 1 to 6%.

All the higher urea derivatives mentioned here undergo similar hydrolysis and decomposition reactions as urea in the reactor, resulting in ammonia, carbon dioxide, water and trace formaldehyde vapors. Their relative presence in the reactor liquid varied depending on the time average operating temperature inside the reactor. However when the ‘end of season ‘ shutdown was carried out, all the species in the reactor liquid reacted with excess quantities of DI water. This procedure reduced residues in the reactor, which was confirmed by the inspections.

Figure 12: This chromatograph was obtained by passing urea samples through a C-18 column in and HPLC and detecting by UV

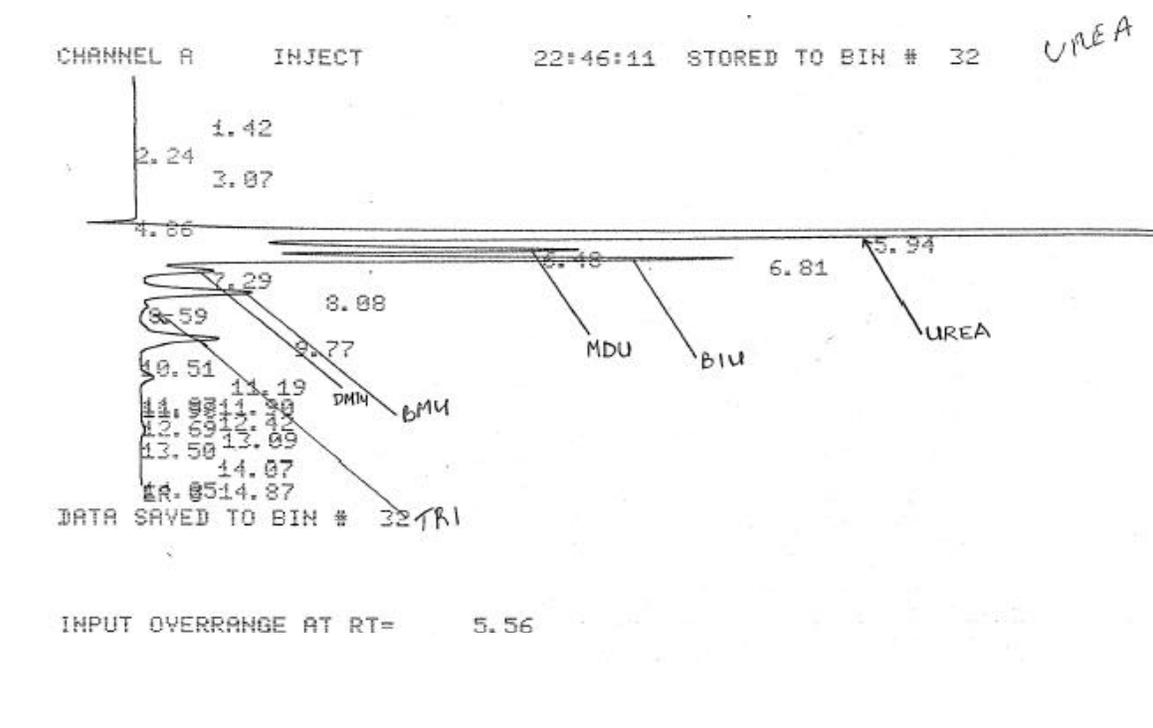
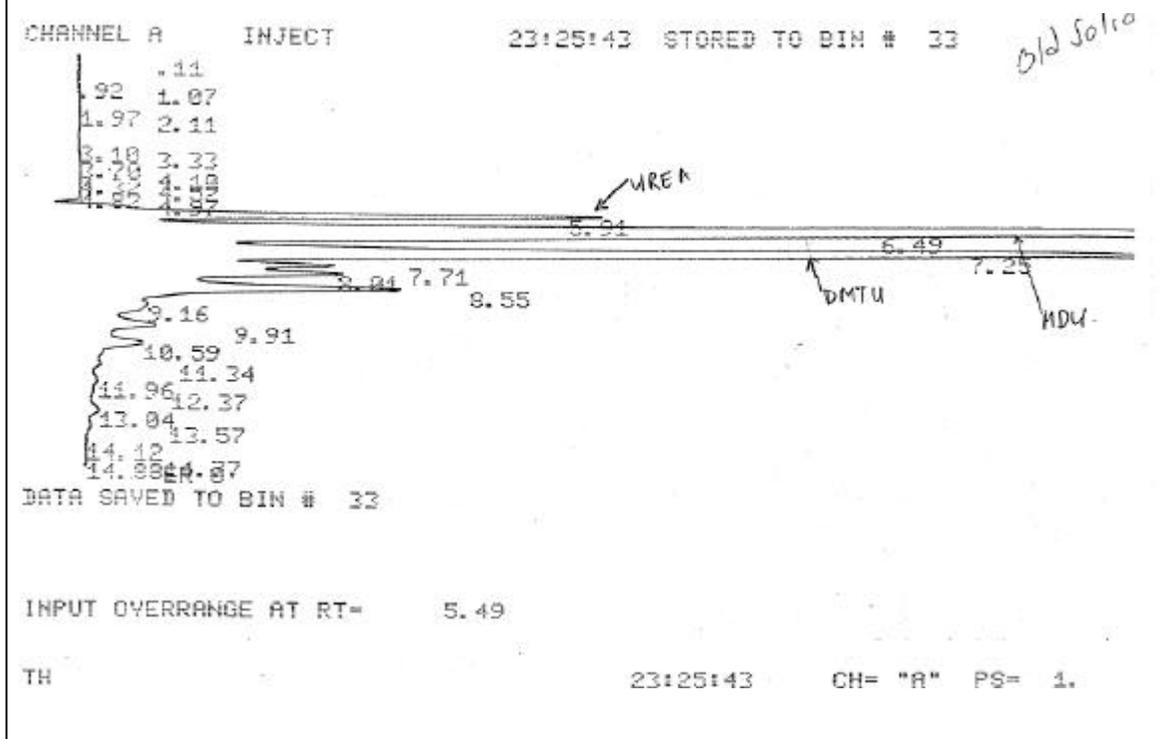


Figure 13: Chromatogram obtained when solids that precipitated from the reactor liquid samples on cooling were subjected to HPLC analysis



CONCLUSIONS

The reactor was successfully operated during its first season to meet the ammonia demands of the SCR providing 97.5% first season availability, with one unplanned shutdown. Some modifications were done to better control the system and improve its performance. The composition of solids of the reactor liquid initiated a thorough study of the system to identify conditions where the solids may precipitate out of solution. Some piping was redesigned to eliminate dead legs and heat tracing was increased. Some shutdown set points were changed so that the reactions were quenched in the system but not overcooled before the reactor was bottled up.

The decrease in operating temperature for 50% urea vs. 40 % urea as feed was confirmed as predicted from previous process models. It was found that changing the pressure from 60 to 80 to 100 psig did not have much effect on the operation of the reactor in so far as SCR operations are concerned.

A total of 1,900,000 lbs of urea was processed in the two reactors, including 3 tons of formaldehyde (@0.3%). On inspection after shutdown, only very nominal residue was found inside the reactors. It was therefore concluded that all the urea, urea derivatives and formaldehyde that are present inside the reactor during the operation are converted to the

gaseous products. The end of season operation with water only is allowed all these compounds to be driven off.

Hamon Research-Cottrell, Wahlco, and EC&C will continue to report on technical and operational details of our U₂A™ technology, with several additional major installations beginning operations in 2003.

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