Design Considerations for Generating Ammonia from Urea for NOx Control with SCRs

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ABSTRACT

The first U2A® (Urea to Ammonia) and AOD® (Ammonia on Demand) systems for generating ammonia from urea were installed in 2000. During the last six years of commercial operation, refinements to the operational design of the units have been developed. This paper addresses dew point calculations and the design considerations related to avoiding gas side corrosion in urea to ammonia generation plants. Additionally the paper presents data on formaldehyde related compounds that have been measured in an operating unit and methods for identifying formaldehyde related compounds and system water balance issues. . Hamon Research Cottrell and Wahlco Inc have installed more than 30 successfully operating units in the U.S. and in Europe with several additional units in the design and construction phase.

INTRODUCTION

The process entails feeding an aqueous urea solution to a hydrolyser where it is heated under pressure and decomposes to an ammonia gas mixture of ammonia, water and carbon dioxide. The reactor operating pressures and temperatures are selected such that during normal operation the concentration of these gases is in equilibrium with the composition of the solution in the reactor and equal to the conversion products of the feed composition. In a typical U2A reactor the feed solution is in range of 40 to 50% urea to water.

The initial U2A systems were designed for operating temperatures of 300 deg F and operating pressure of 60 to 80 psig with a urea feed concentration of 40%. Higher urea feed concentrations reduce the operating cost by decreasing the energy required to to evaporate the water in the feed solution. As the market matures higher temperature designs and higher 50% urea feed concentrations can reduce the capital cost of the system as well as reduce energy consumption.

Since the rate of hydrolysis of urea is increased with excess water, maintaining adequate water in the reactor liquid is essential to the U2A process. However, for 50% urea feed and above, the

1

potential for ammonia production rate to be slowed because of diminishing water for the reaction must be considered.

A secondary issue is the additional heat needed to maintain higher urea concentration in solution. At 40% urea concentration the requirements for heat tracing of the urea feed system are reduced but reactor energy consumption is increased.

This paper covers some of the design considerations to be taken into account to maintain water balance in the reactor. Previously published results of our studies on formaldehyde issues are reviewed in this paper because of current interest in the subject.[1] Dew point calculations for the U2A process and results are presented.

WATER BALANCE

At an operating temperature of 300-310 degrees F and operating pressure in the range of 60 to 80 psig the concentrations of ammonia and carbon dioxide held in the reactor liquid solution are relatively low. Assuming ideal gas behavior we can make use of Raoult's law[2] and Dalton's law[3] to understand the equilibrium of the solution.

Raoult's law states that the vapor pressure of each component in an ideal solution is related to the vapor pressure of the individual component and the mole fraction of the component present in the solution. When the solution is in chemical equilibrium, the total vapor pressure of the solution is:

$$P_{solution} = (P_1)_{pure}X_1 + (P_2)_{pure}X_2 \cdots\cdots$$

Where $(P_i)_{pure}$ is the vapor pressure of the pure component and X_i is the mole fraction of the component in solution.

For calculating the water balance of the U2A process, we treat the urea and ammonia carbamate dissolved in a reactor solution as has having zero vapor pressure.

Dalton's law states the total pressure of a mixture of gases is the sum of the partial pressures of each gas in the mixture. Dalton's law may be expressed as $P = P_A + P_B + \cdots$, where P_J is the partial pressure of the gas J, and P is the total pressure of the mixture

The partial pressure is defined as:

$$P_J = y_J P,$$

where y_J is the mole fraction of the gas J, the ratio of its amount in moles to the total number of moles of gas molecules present in the mixture. With this definition, the total pressure of a mixture of any kind of gases is the sum of their partial pressures.

$$P_{total} = P_1 + P_2 + P_3 \cdots\cdots = y_1 P_{total} + y_2 P_{total} + y_2 P_{total} + \cdots\cdots$$

Based on the above, the equilibrium concentration of urea-carbamate in the reactor solution can be estimated over a range of temperature. Figures 1 and 2 below show the estimated equilibrium urea-carbamate concentration for 40% and 50% urea feed solutions for typical operating pressures and temperatures for a U2A reactor.
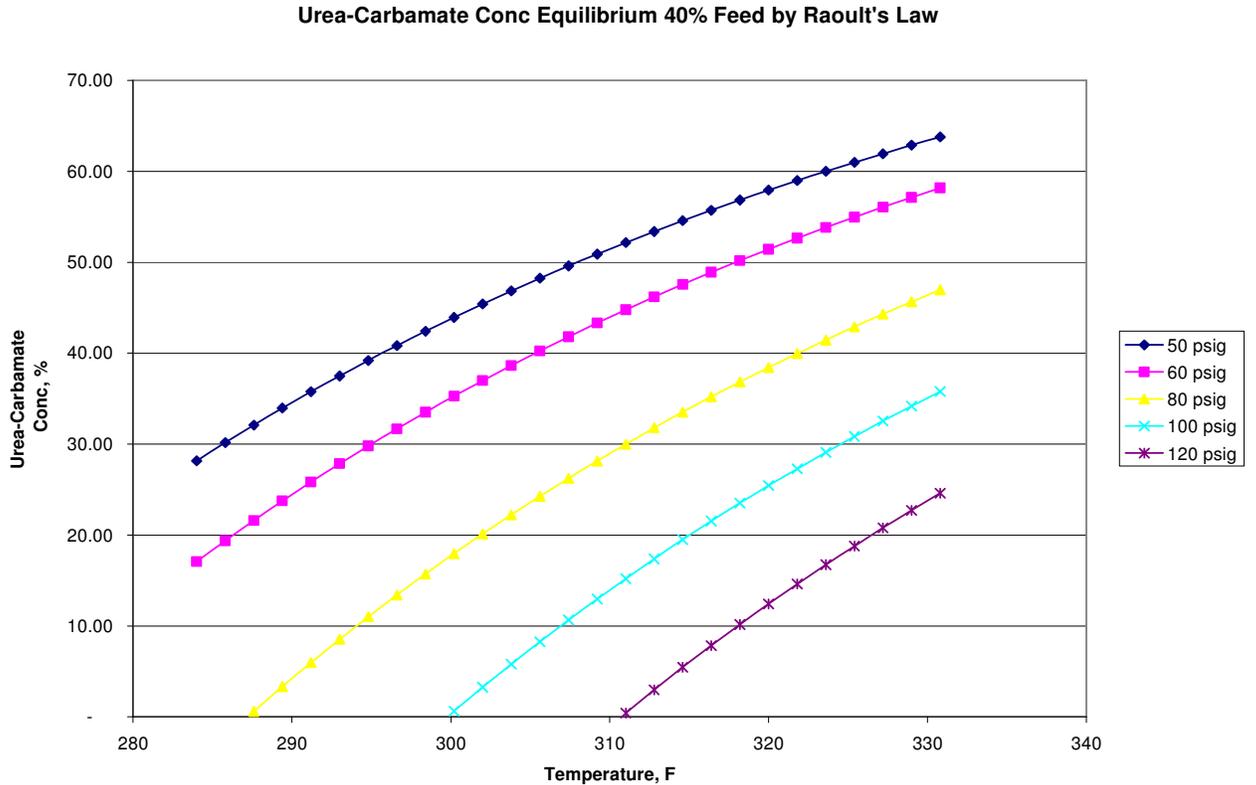
Urea-Carbamate Conc Equilibrium 40% Feed by Raoult's Law

Figure 1.   Urea-Carbamate Equilibrium Concentration for a 40%Urea Feed by Raoult's Law

These figures show that as the operating temperature of a reactor is increased the nominal operating pressure must be increased to keep excess water in the reactor in order to continue to promote the hydrolysis reaction.

For U2A reactors designed to operate at a maximum temperature of 315 deg F with a 40% urea feed concentration and operating pressure of 60 psig, Figure 1 shows the urea-carbamate concentration would be approximately 50% of the solution in the reactor. At minimum load (10%) and lower reactor temperatures the urea-carbamate concentration decreases to approximately 20%.

In most utility applications in cyclic service the typical control range is from about 33% to 100% load., in which case, the reactor liquor urea-carbamate concentration varies from 38% to 50% and excess water (62% to 50%) is maintained. For the commercial demonstration unit at Allegheny Energy, at a pressure of 80 psig, 36% urea feed and with typical maximum operating temperature of 295 deg F, the urea-carbamate concentration ranged from 15 to 25 %. During the first year of

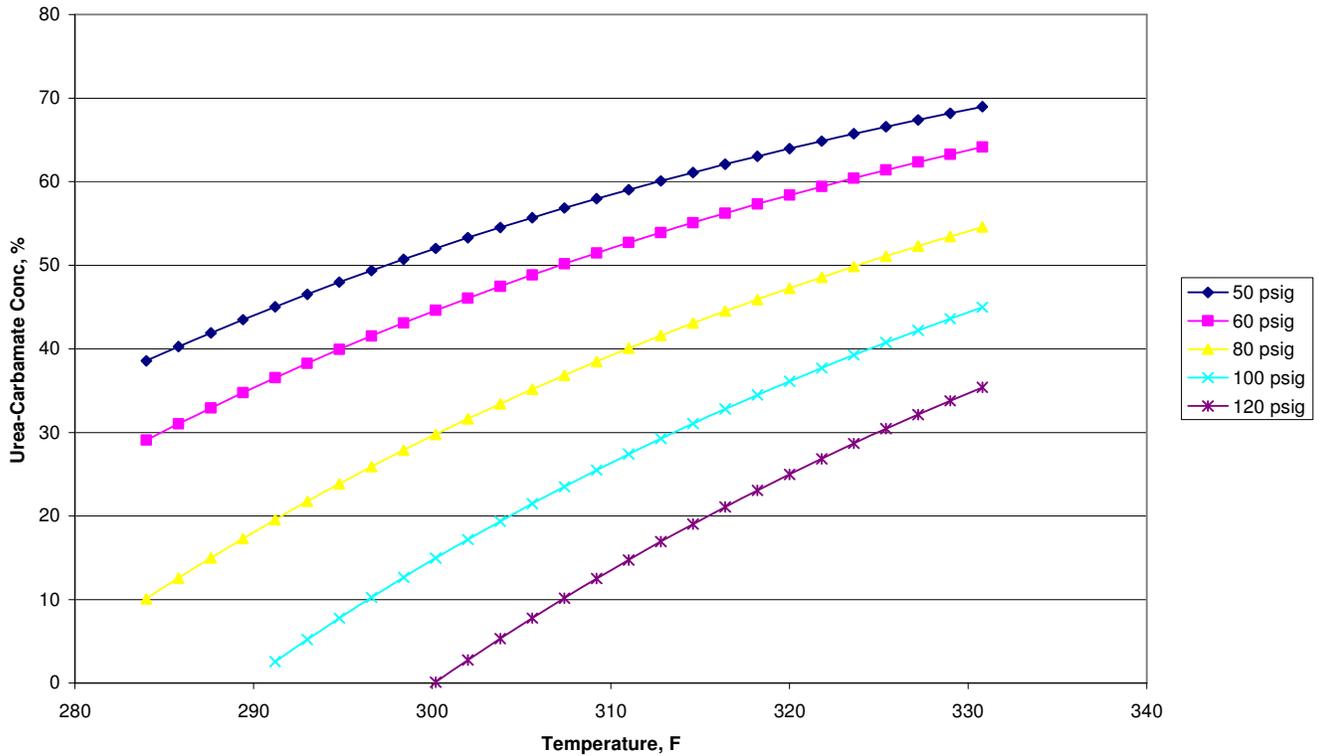**Urea-Carbamate Equilibrium Conc for 50% Feed by Raoult's Law**

Figure 2. Urea-Carbamate Equilibrium Concentration for a 50%Urea Feed by Raoult's Law

operation at the Wagner plant the measured concentration of urea, carbamate, and urea formaldehyde compounds ranged from 44 to 57 % operating with temperatures up to 305 deg F with 40% feed solutions.   Both of these units were typically daily cycling boilers and field measurements are in good agreement with the estimate water balance.

At reduced operating pressures urea-carbamate concentration will increase while water decreases to the limit of insufficient water.   In that case, the rate of the hydrolysis reaction will also decrease and higher temperature operation will be needed to maintain ammonia production.   For this situation, the reactor operating pressure needs to be increased while also considering the pressure effect on product gas dew point temperature as discussed in the next section.

U2A® REACTORS: DEW POINT

Dew Point Considerations
The U2A reactor should be set up to operate with a pressure for which the dew point is less than the normal minimum operating temperature, as condensation products increase general corrosion rates in the system. Corrosion allowances included in the normal design allow for extended
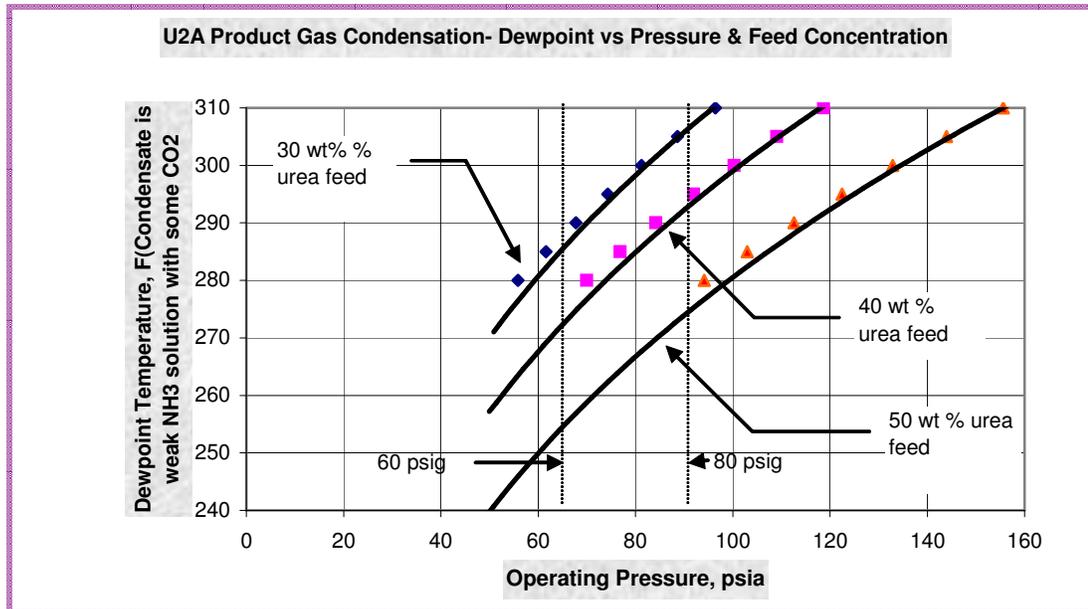
4

Figure 3: Dew point of U2A product gas

operation below the dew point, but it is recommended to maintain operations above the dew point. Phase equilibrium considerations on the NH_3-CO_2-H_2O gas system allow the determination of a dew point temperature as a function of pressure and concentration as explained below.

Dew Point Estimation for Gaseous Mixtures

The algorithm given at http://eies.njit.edu/~knoxd/che-611-g-org.doc[4] gives a procedure applicable for calculating dew point temperatures for condensation from a gas mixture of NH_3-CO_2-H_2O.

Equations for property estimation are found in the technical literature for NH_3-CO_2-H_2O and in articles specific for urea production and are valid for a wide range of temperatures and pressures including those experienced in the U2A system.[5,6,7,8,9,10]

For equilibrium of product gas with the reactor liquid, the determination of liquid phase concentrations assumes that the presence of urea, carbamate, and urea formaldehyde species (BMU/DMTU) in the liquid does NOT incorporate additional non-ideality, i.e. a solution of urea in water interacts with ammonia in the same manner as if only water were present in the liquid. To further refine these calculations activity coefficients for urea, and other ionic species in the liquid phase would have to be incorporated.

This algorithm as presented is:

"We are given T and y, and must solve for P and x. We start with our basic equation:

$$x_i \gamma_i P_i^{sat} = y_i \Phi_i P$$

5

where:

y_i is the concentration of component in the gas phase
Φ_i is the fugacity coefficient of component (function of y, P and T) i in the gas phase
P is the total pressure
x_i is the concentration of component i in the liquid phase
γ_i is the activity coefficient (function of x and T), of component i in the liquid phase
P_i^{sat} is the saturation vapor pressure of component i at temperature T.

P^{sat} is valid only when the components are below their critical state. Since ammonia is above critical temperature and pressure, fugacity equations incorporating f_i have to be used. An iterative solution was developed using MATLAB 6.5 resulting in the data shown in Figure 3.

Dew Points without Fugacity

Dew points were also estimated more simply using Raoult's Law without fugacity considerations. The results of both are compared with water dew points in the following Figure 4. As would be expected the dew points of the U2A product take gas are less than pure water. When we consider fugacity to account for the interaction between water, ammonia and carbon dioxide, slightly higher dew points are estimated.
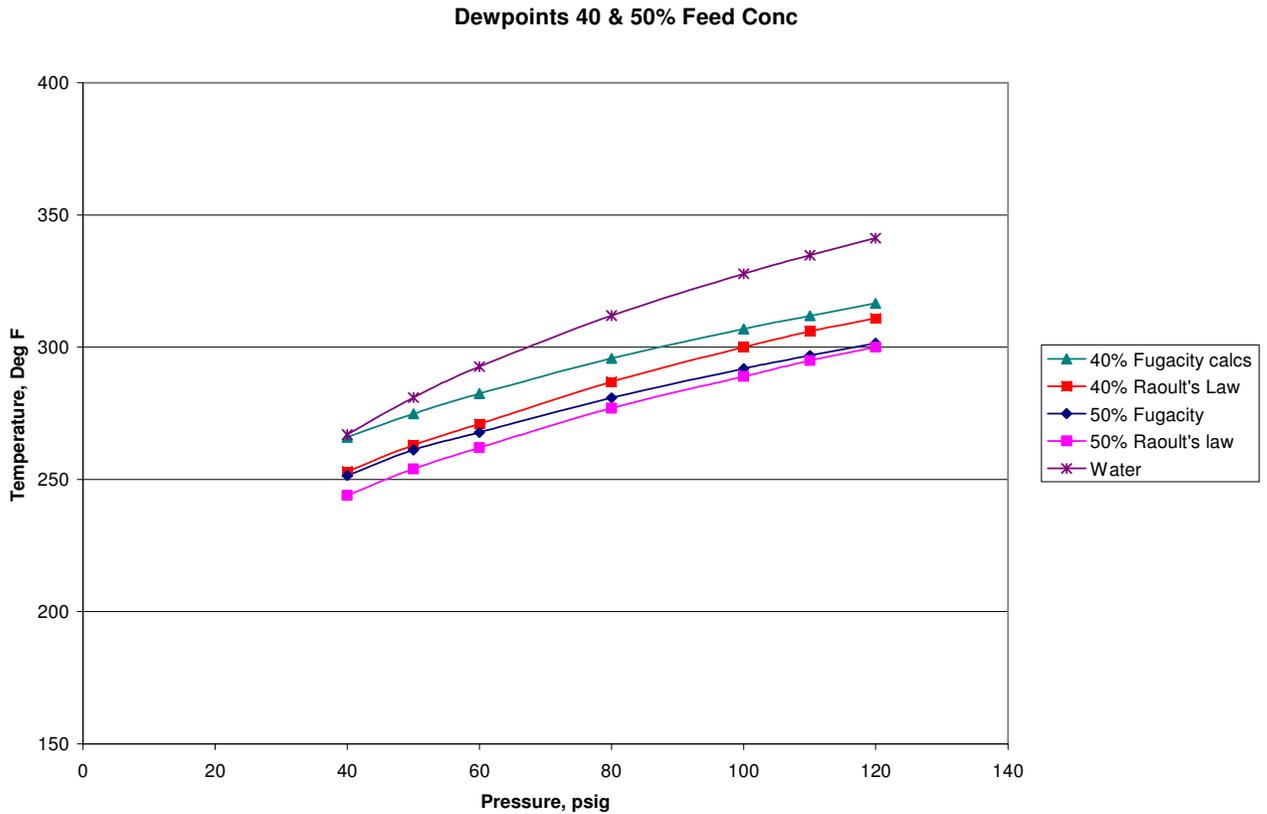
Dewpoints 40 & 50% Feed Conc

Figure 4 Dew points for 40% and 50% Urea Feeds

6

U2A Reactor Operating Environment

The U2A reactor operates with a controlled constant liquid level, resulting in a fixed liquid space and vapor space as shown below in Figure 5. The pressure in the reactor is controlled at nominally 60 to 80 psig while the temperature varies with production rate from 250 to 315 °F.

The reactor liquid typically contains from 15-50% urea, 0-18% higher urea derivatives, and 3-6% ammonia. At temperatures above 250°F, any ammonium carbamate in the liquid formed immediately decomposes to ammonia and carbon dioxide and hence very small concentrations (1-2%) of ammonium carbamate will be present in the reactor liquor. The balance is water.

When a U2A reactor is shutdown, the product gases that are trapped in the reactor start condensing on the reactor surface as it is cooling. This is especially true when cooling systems in the reactor reduce the liquid temperature from 300°F to 200°F in 20 minutes, and also true when the product gas finds any heat sinks/ cold surfaces in the piping or in the instrumentation. At lower temperatures, ammonium carbamate formation on surfaces may be favored.
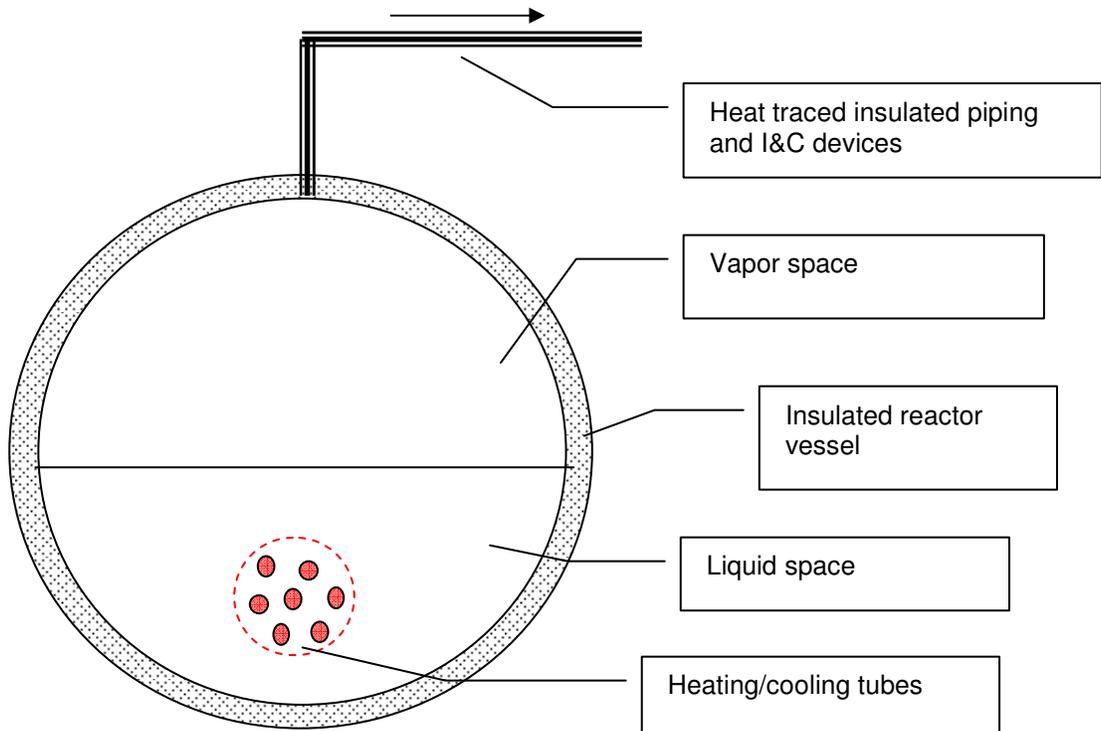

Figure 5, Reactor internals

From the chart in Figure 3, it can be deduced that if the product gas is at 80 psig (for 40 % urea solution feed), gas will not condense as long as it is above 296 °F. On the other hand, for a 50%

urea solution feed, the gas composition is different and this product (at 80 psig) will not begin condensing as long as the temperature is above 275 F.

At low loads, product gas temperatures (250-275°F) in the reactor can operate below the gas mixture dew points at the operating pressure of 80 psig. In this operating range, a weak ammoniacal solution in water condenses out of the gas stream whenever it comes in contact with colder surfaces. Inspection of reactor internals has shown such liquid condensation stains on the gas-side reactor surface. These condensing vapors on cold surfaces also contribute to the slightly higher corrosion rates on the gas side surfaces and therefore should be minimized where possible by adjusting operating pressures.

By designing U2A reactors to operate with gas side conditions to avoid dewpoints, and with temperatures less than 400 deg F, satisfactory corrosion rates of less than 3 mil/yr have been obtained with 316L SS materials for the reactor vessel and piping, and more specialized materials for some instrumentation and valving due to heat sink considerations

FORMALDEHYDE

The U2A process can be operated successfully with formaldehyde containing urea solution from solid urea deliveries as well as with formaldehyde free urea liquors.

While formaldehyde free urea liquors are available directly from urea manufacturing plants, most of the urea supplied to world markets contains formaldehyde (HCHO) as a surface conditioning agent added to minimize dusting of the prilled urea. Typical formaldehyde content is in the range of 0.1 to 0.4% by wt. The formaldehyde reacts with the urea to form methylolureas which are water soluble, especially at higher pH and breakdown with the release of formaldehyde vapor.[11]

Some specific experience related to formaldehyde and other urea compounds follows.

The formaldehyde vapor released from the U2A process is removed from the boiler flue gas at the SCR catalyst. This has been confirmed by previously reported results from the U2A process demonstration at AES/Alamitos plant.[1] Formaldehyde measured in the reactor solution after 1000 hours of operation, at 1117 mg/L matched the concentration in the feed calculated to be 1000 mg/L. The increase in formaldehyde in the flue gas (measured with and without injection) was also consistent with all the formaldehyde leaving the U2A reactor as vapor. A 96% reduction in formaldehyde emissions was measured across the SCR.

The U2A process avoids the formation of insoluble products by operating at a pH typically greater than 9. During the end of 2005 season shut down of the Allegheny/Harrison U2A plant a precipitate was obtained when the residual reactor solution was reduced below a pH of 7. Chemical analysis indicated that this was a mixture of urea and a urea formaldehyde compound. During any shutdown in which DI water is feed to lower the concentration of ammonia and urea in the reactor solution the pH should be maintained above 7.5.

At Constellation/Wagner Station crystallization of material in a static piping run after a shutdown led to further investigation of the composition of the reactor liquid and their solubility limits. A

simple piping modification followed which included elimination of dead legs and an increase in heat tracing temperatures to 150F.

Detailed analysis of samples taken at Wagner (from 50% feed) showed that they contained 45 - 55% solids of which 35-45% was urea and 7-10% was higher molecular weight urea derivatives including methlylene di-urea (MDU), dimethylene triuret (DMTU) which are related to the formaldehyde content as well as bi-methylene urea (BMU), biuret (BIU) and triuret (TRI) which were present in the HPLC analysis of the feed urea sample. At Wagner urea derivative compounds were found to be in range of 11 to 15% with a 40 % feed and reactor operating temperature of 305F.   All of these compounds are water soluble but reach their solubility limits at higher temperatures.

The HPLC analysis mentioned above for Wagner used a C-18 column and UV detection system to match the procedure for formaldehyde conditioned urea as reported from literature. The results obtained with this procedure for samples from Wagner are shown in figures 6 and 7. The chromatographs show the presence for MDU, BIU, BMU and TRI.
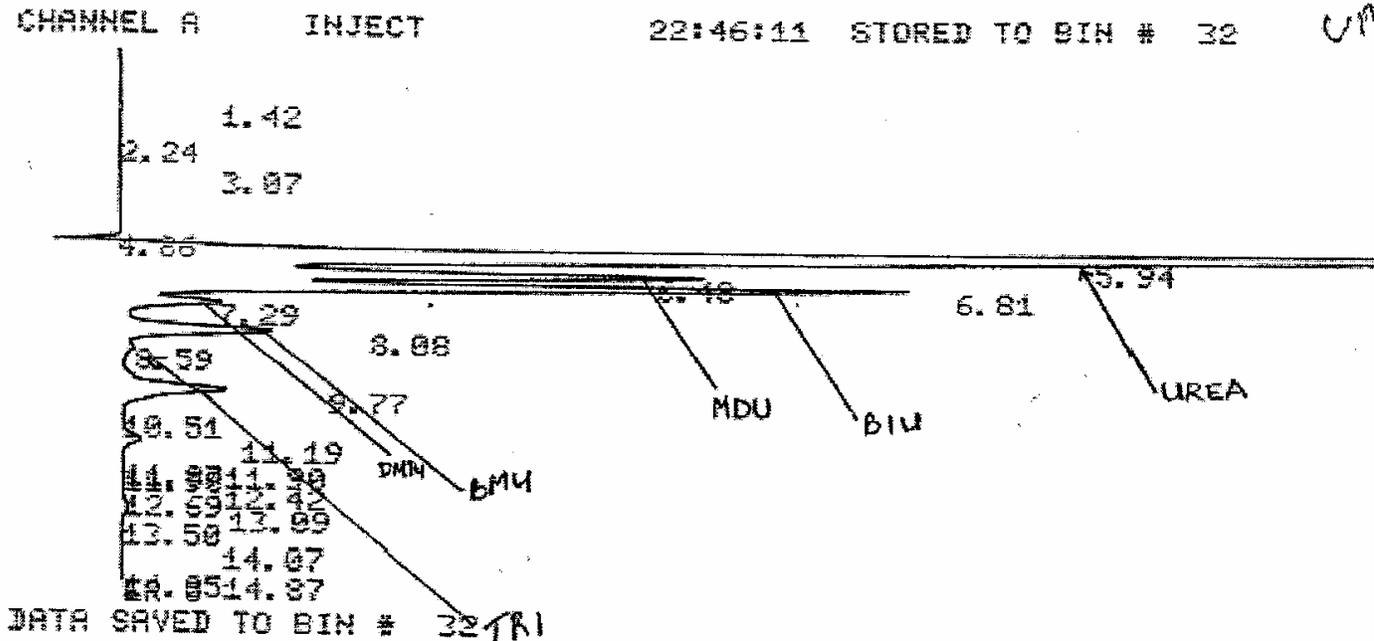

Figure 6, HPLC Analysis of the Urea Feed

Figure 7, HPLC of Precipitated Solids from Urea Reactor Solution

Reasons for the higher concentrations include the water balance issue as discussed above, along with conditions which favor accumulation of methylolurea compounds which along with biuret and similar urea related compounds have slower reaction paths in the eventual production of ammonia.

By the end of the first operating season at Wagner, approximately 100 tons of urea containing about 4500 lbs of formaldehyde was processed. At the end of the season the reactors were run with water feed only, resulting in a clean reactor with little or no residual materials as all of the urea related compounds were processed to ammonia.

CONCLUSIONS

The U2A process continues to be successfully operated at many utility plants. Since the first commercial operations in year 2000 EC&C Technologies, Inc. and its licensees Hamon Research-Cottrell and Wahlco, Inc. have broadened their fundamental understanding of the process and its applications.

Operating the U2A systems with consideration of water balance, operating pressure, temperature ranges, dew point and formaldehyde in the urea, the process is an efficient and reliable alternative to aqueous and anhydrous ammonia for utility NOx control.

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KEY WORDS

Urea. Ammonia, U2A, AOD, SCR