Corrosion Damage Mechanism Review and Mitigation Methodology for Urea Equipment[1]

Both well-known and not so common corrosion mechanisms found in Urea Plant piping and equipment can result in equipment failures and costly downtime. Examples of corrosion damage mechanisms are presented, including carbamate corrosion, and stress induced intergranular corrosion cracking. Discussion considers both short- and longer-term impacts, as those conditions affect the Mechanical Integrity planning and inspection management programs.

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Introduction

Urea plant equipment operates at elevated temperatures and is exposed to corrosive environments that can potentially result in life-limiting conditions. Awareness of the corrosion-related damage mechanisms that can damage equipment is essential in developing the appropriate solution for proper equipment inspection, damage mitigation, and failure prevention. The pertinent damage mechanisms can also provide input for fitness-for-service evaluations as the mechanism and rate of attack needs to be understood to determine the remaining life. For a proper risk-based inspection (RBI) program or during a hazards analysis, the appropriate damaged mechanisms need to be identified so that the probability of failure can be determined in addressing reliability issues [1,2,3].

The following two related but different damage mechanisms have been observed to affect urea equipment, and will be discussed in relation to

process variables, process equipment, and materials of construction:

- Carbamate Corrosion
- Stress-induced Intergranular Corrosion Cracking (SIIC)

This paper provides examples and discussion regarding these corrosion damage mechanisms related to urea process parameters, materials of construction and process equipment, and inspection methods and characterization techniques to identify each form of damage. Additionally, useful tips for considering potential mitigation methods are provided.

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The Urea Process

The steps of urea production occur as feeds are mixed either before or within the reactor where urea is formed. In urea production, CO_2 and NH_3 are individually brought to high pressure, are combined, and quickly react to generate carbamate and a large amount of heat.

$$\underset{\text{Feeds}}{CO_2 + 2NH_3} \Longrightarrow \underset{\text{Carbamate Intermediate}}{NH_2COONH_4}$$

For most processes, a small amount of oxygen is added to the CO_2 feed for materials passivation, usually in the form of air. A significant excess of NH_3 is used to ensure near complete conversion of the CO_2 in the temperature range of 135 ° to 200 °C (275 ° to 392 °F), for example in a 3.6:1 ratio. The ratio can vary from 4 for older designs to 3 for more modern designs. Higher ratios tend to be less aggressive. Excess ammonia also assists in conversion of carbamate into urea.

The carbamate dehydrates (in other words, sheds a water molecule) to form urea relatively slowly, absorbing a small amount of the heat in the process. High pressure is required to keep the reactants in solution and mitigates the decomposition of carbamate back to its components, thus increasing yield. The high-pressure reaction section can range from 126 to 562 kg/cm^{2}g (1800 to 8000 psig). The slow reaction time for the urea formation reaction requires a large reactor volume to increase the yield, which does not go to completion.

$$NH_2COONH_4 \Longrightarrow NH_2CONH_2 + H_2O$$

The effluent from reactors will be a mixture of urea, carbamate, ammonia, and water. It can include a lesser amount of ammonium carbonates $(NH_4)2CO_3$).

Urea Equipment Materials of Construction

In an ideal world, materials would be chosen that would be impervious to deterioration effects from process conditions. In the real world, this is either impossible or cost-prohibitive, so various types of equipment damage continue to occur. Most process equipment used in urea production are comprised of pressure vessels, piping, and storage tanks whose pressure boundaries are constructed of metallic materials. All materials of construction used in the urea industry are susceptible to degradation and various types of damage mechanisms. [4,5]

The carbamate intermediate is similar to a strong acid in its impact on materials and requires specialized metals to mitigate damage. Due to the harsh corrosion environments, stainless steels and specialty stainless steels are the most commonly used materials of construction for process equipment in the urea industry. These materials offer a suitable combination of strength and ductility and are capable of safely operating in the temperature ranges employed in the urea industry. Through the years, urea development work with austenitic and duplex stainless steels has improved the resistance to carbamate corrosion along with the use of special materials such as zirconium. To control costs on the thick walls of pressure shells, cladding is typically used.

Zirconium and titanium are reactive materials that react strongly with oxygen to form a corrosion protection layer, so they do not need passivation air. They are also resistant to Chloride SCC. However, titanium is relatively soft and is currently reserved for special situations; both of these specialty metals are expensive.

A discussion of typical materials of construction follows:

Carbon steel: Carbon steels are used in feed supplies and utilities but not in direct contact with carbamate because of the extremely high carbamate corrosion rates. Often on vessels and multi-layered vessels, a corrosion protective liner is used over a carbon steel pressure boundary with high tensile steels at times used in monowall high pressure equipment. This is often effective unless a situation develops where the liner is breached, and

the carbon steel is exposed to the corrosive condition.

Application of a leak detection system in case the liner fails is recommended.

Carbamate corrosion materials start with 316L to the more carbamate tolerant 316L Urea Grade UG, X2CrNiMo25-22-2, zirconium, titanium, and more specialized urea specific materials (Uremium 29, Safurex™, and others). [5]

Austenitic Stainless Steel 316L: Materials for urea production vary from those suitable for non-corrosive and utility services to those exposed to the rigors of highly corrosive synthesis section. Materials include 316L to the more carbamate tolerant 316L Urea Grade UG, X2CrNiMo25-22-2, zirconium, titanium, and more specialized urea specific materials (Uremium 29, Safurex™, and others). [6]

Type 316L-Urea Grade, aka 316L Modified (MOD), is the historical urea workhorse material with improved corrosion resistance. It is suitable for many areas, including most carbamate equipment in conventional plants. The low carbon content, combined with a well-balanced chemistry (low silicon and nickel content close to 14%) makes the alloy fully austenitic, free of intermetallic phase precipitations. The ferrite level is kept under 0.5% in the solution annealing and water quenched conditions.

Some designations include 1.4435, X2CrNi Mo18-14-3, 1.4404, and BC.01. According to one supplier, the alloy typically has low carbon (<0.03% C), 18% Cr, ~14% Ni, and 2.5% min Mo, with Si<0.5% and Mn between 1 and 2%. Stainless materials typically require a passivation step upon startup to secure a corrosion resistant chromium-oxide layer. If the oxide layer is maintained by oxygen feed, the stainless steel corrodes passively at low rates. Passive corrosion rates of 316L-UG are typically between 0.01 and 0.15 mm per year (0.4 and 4 MPY) on stream. If the passive layer is damaged (by erosion/corrosion, by surface contamination, or lack of oxygen to passivate the surface) active corrosion will set in and can reach values of 100 mm per year (300 MPY).

Active corrosion cannot be reversed online once started; once detected, the plant must be shut down and repassivated.

X2CrNiMo25-22-2 (referred to as "25-22-2"): The development of the austenitic 25-22-2 opened the doors for more severe but typically more efficient service conditions. This material is a higher-alloyed austenitic stainless steel and designed to provide better corrosion resistance to the stripper conditions than historical 316L-UG stainless steel. Likewise, under less severe service conditions, 25-22-2 shows better corrosion performance and less susceptibility to some of the typical damage mechanisms than standard 316L-UG. [7]

Certain duplex materials containing copper have good resistance, but care must be taken as others may not be suitable for urea service: use has also led to component failures, such as in stripper components.

Urea Specific Duplex Alloys: Other urea specific materials considered are Safurex™ 29Cr7Ni2MoN (UNS S32906) developed by Sandvik and preferred by Stamicarbon licensors and DP28W (28Cr8Ni1Mo2W) UNS322808 [8] paper preferred by Toyo. Other alloys such as Uremium 29 (29Cr7Ni1MoN) UNS32906 are being utilized. Toyo Engineering Corporation (TEC) and Sumitomo Metal Ind., Ltd. (SMI) have jointly developed new duplex stainless steel DP28WTM for urea plants.

Please note that while these alloys are resistant to carbamate corrosion and need minimal passivation, improper welding or handling can still introduce areas vulnerable to attack and damage mechanisms other than carbamate corrosion can apply such as flow-assisted corrosion.

The biggest advantage of duplex stainless steel is its excellent passivation property in urea-carbamate solution, which enhances reliability of

equipment and enables to reduce injection of passivation air. In the meantime, duplex stainless steel has some weakness in corrosion resistance in the heat affected zone (HAZ), which shows up in long-term operation.

Nickel-base alloys: Nickel base alloys are resistant to many corrosives in alkaline solutions; but in oxidizing environments, nickel-based alloys are not suitable because of the formation in ammonia-solutions of soluble Ni $(NH_3)_6$ which can result in accelerated corrosion. For example, the corrosion rate of one high nickel-based alloy (nearly 60%) in carbamate solutions has shown to be 2.2 mm/year (86 MPY.)

Carbamate Corrosion

A damage mechanism unique to Urea Plants is carbamate corrosion. Carbamate (short for ammonium carbamate) is produced in the urea process by reacting ammonia and carbon dioxide at high pressures. A carbamate is a category of organic compounds that is formally derived from carbamic acid (NH_2COOH) with highly aggressive corrosive properties for susceptible materials. Carbamate is an ammoniated form of carbamic acid with aggressively acidic corrosion properties that can result in general wall thinning of carbon steel and stainless-steel alloys, as well as other damage characteristics. Carbamate on carbon steel can have corrosion rates in excess of 25 mm/yr 1000 mpy. Higher temperatures and higher carbamate concentration increases the corrosion rates: the Arrhenius equation predicts that the corrosion rate doubles for every 10 ºC (18 ºF) increase in temperature. Higher tempertaures and a low activation energy result in accelerated corrosion rate. Process licensors, company experience, or industry recommendations may set process limits to avoid aggressive carbamate corrosion conditions for the design materials. The Arrehenius equation is:

$$k = A\ exp(-E_A/RT)$$

Where

k : rate constant

A : pre-exponential factor

E_A : activation energy

T : temperature

R : universal gas constant (= 8.314 J/mol-K)

In older plants with a reactor followed by a pressure letdown valve, the most severe corrosion conditions are in the reactor and valve. The drop in pressure helps in decomposing the carbamate and lowers the temperature in the medium pressure section of the plant.

In more modern plants, energy is saved by decomposing the carbamate, condensing it, and recycling to the reactors all in the high-pressure section, but at higher temperatures that have led to more resistant alloys.

The high acidity can result in general wall thinning of carbon steel. For example, carbamate on carbon steel can have corrosion rates in excess of 25 mm/yr 1000 mpy. In the urea synthesis section, points where stronger carbamate concentrations occur include mixers for ammonia and carbon dioxide, in the urea reactor, in recycle solutions, in the HP stripper/decomposer feeds, and in carbamate condensers.[9] Some of the ways the carbamate corrosion can occur are described below:

Flow-assisted Corrosion: Higher flow rates and velocities can remove protective passivation layers which will accelerate corrosion and result in flow-assisted attack (erosion corrosion) and carbamate corrosion.

Carbamate Cross Cut Corrosion: Even on more resistant materials, crosscut corrosion can occur where the tubes or bar stock are cut across the grain. In extruded materials, the variability of the microstructure can allow attack on the elongated grain boundaries deep into the metal, creating rough surfaces and tube end pitting (which interferes with tube plugging). Materials in special services (such as tight shutoff valves) benefit from "isotropic" fine grain boundaries which are consistent regardless of the face or cut. Safurex™ HIP is the tradename for a specialty material that is designed for resistance to crosscut corrosion. [3].

Carbamate Condensate Corrosion: Where carbamate condenses in the vapor space due to cold spots, carbamate condensate corrosion (also known as carbamate condensation corrosion), will occur as this process interferes with normal passivation and has higher corrosion rates. Figure 1 and Figure 2 show an example of carbamate condensate corrosion.

Strain/Stress Induced Intergranular Cracking (SIIC): In highly stressed regions with a carbamate solution condensing out a vapor phase, Strain (or Stress) Induced Intergranular Cracking (SIIC) may occur and is discussed in greater detail later in this article.

Figure 1. Carbamate Condensate Corrosion in Type 316 UG plates

Key Carbamate Corrosion Parameters:

- Lack of oxygen – reduces formation of passive film.
- Presence of carbamate
- High flow rates and velocities potentially remove protective films.
- High acidity – causes general wall thinning.
- Crevice formation, concentrating in cells with oxygen depletion.
- High stresses (strains) will promote Stress Corrosion Cracking
- Increased temperature increases corrosion.
- Iron or copper contamination
- Excessive ferrite in alloy or welds
- Cut ends.

Equipment Concerns:

Vapor areas in the high and medium pressure sections of the urea plant have a risk for carbamate condensate corrosion including:

- Vapor pipelines or piping or high spots that can trap vapors where steam tracing is inadequate or not in service,
- Areas where insulation is inadequate or damaged,
- Locations where attachments act as a heat sink such as lifting lugs, thermowells in vapor areas, or large flanges, for example at the top of the reactor.
- Most of the urea feed and high and medium process equipment, particularly where passivation is not maintained.
- Stripper exchanger tubes and ferrules
- Decomposers
- Condenser exchangers
- Drain lines.

Figure 2. Carbamate corrosion failure of a High-Pressure Scrubber

Mitigation Options:

- Passivity: Maintain oxygen levels for passivation**:** To maintain stainless steels in a passive state, it is necessary and recommended to add oxygen to the process (usually 0.4 - 0.6 volume percentage) in the CO_2 feed.

- Material Selection**:** Use higher-alloyed Austenitic or Duplex stainless steel (such as 25-22-2) or more resistant materials designed to provide better corrosion resistance to the stripper conditions than historical 316L-UG stainless steel. Zirconium bonded tubes are used in certain designs.
- Welding and Alloying**:** To minimize corrosion after repairs, it is recommended to select an electrode that will control the weldment to contain ferrite contents under 3%, even as low as <0.6 % ferrite Special electrodes for welding 316L UG for Urea service are available[10]
- Evaluation of contaminants: On-line monitoring of nickel.
- For prevention of flow-assisted attack:
  - Reduce velocity by changing the design—using multiple restriction orifices, increasing the pipe diameter, or reducing the flow rate.
  - Ensure control valves are properly designed where flashing conditions may create problems.
  - Where possible, improve the design to avoid turbulent flow (for instance, consider flow in baffles and impingement plates in heat exchangers).
  - Change to a more resistant material with increased hardness or one that is alloyed with increased corrosion resistance. Add hard facings on surfaces such as those used in valves and pumps.

Stress-induced Intergranular Corrosion Cracking (SIIC)

A damage mechanism unique to Urea Plants is carbamate Strain-Induced Intergranular Corrosion or Stress Induced Intergranular Cracking (SIIC), which are identical, as Stress and Strain are directly related by the elastic modulus of the material. "SIIC is an electro-chemical corrosion mechanism in combination with deformation (strain)." [3,11] Strain is induced primarily by pressure but also from thermal stresses in a liner which create plastic deformation at vapor (and upper liquid) areas. The strain is highest in conjunction with shutdowns that cool the reactor liner.

Based on Stamicarbon experience the splash area at the vapor liquid interface is typically the highest corrosion area with general thinning. However, carbamate condensate corrosion in the vapor space "cold spots" can accelerate wall loss in those areas.
The damage mechanism may also be known as Carbamate Condensation Cracking as it occurs with a liquid layer condensed from carbamate vapors, and Carbamate Stress Corrosion Cracking (SCC), since by definition SCC requires the presence of a tensile stress (either applied or residual) which will produce a localized tensile strain with a susceptible material in a specific aqueous environment. For simplicity, it will be referred to herein as SIIC.

This type of attack is a phenomenon that is usually found in the vapor space the reactor and scrubbers and gas piping after several years of operation. The following conditions are a prerequisite for occurrence of this damage mechanism:

- The presence of an electrolyte as a result of condensation of ammonium carbamate in the gas phase. In cases where the liquid level in the urea reactor is extremely high, these cracks are also observed in the liquid phase (so electrolyte is always present). The initial condensation regions of ammonium carbamate are particularly aggressive due to the absence of oxygen in the initial liquid phase.
- Plastic deformation (or strain) of the liner material. This deformation will always occur during high pressure and temperature cycles (especially during cooling down of the reactor when high tensile stresses occur in the liner). The stainless-steel liner has a lower thermal conductivity and high coefficient of thermal expansion than the carbon steel pressure boundary. While applied or residual compressive stresses are known to delay/inhibit most

forms of SCC, the tensile stress (either applied or residual) part of thermal cycles will promote SCC in the proper environments.

- The presence of minute levels of chlorides or sulfur will contribute to the damage.
- In initial construction, the liner thickness depends on the liner material used, the inner diameter of the vessel, and the size of the area which is affected by the overall and/or condensation corrosion. The original liner may be 12 mm or 0.5-inch thick. As service time and cycles accumulate, the liner will be reduced in thickness and the applied stresses (and therefore strains) will increase over time.
- Shaped liners such as in hemispherical heads or petals are more likely to have strain from bending process and/or from a gap in the that stresses the material against the pressure shell during cycling from ambient to high pressures.
- SIIC has been found in the bend of pipe elbows of vapor lines from the reactor and high-pressure stripper after several decades of service.

Figure 3. SIIC cracks near a circumferential weld in a hemispherical head of a urea reactor.

Repairs of vapor space liners:

If corrosion is limited to the upper portion, a partial replacement of the liner in this area can be possible.

All SIIC instances found occurred with 316L UG liners, though there are incidental field indicators of damage with 25-22-2 with poor welding practices or material quality. SIIC is often located near circumferential welds (likely due to higher strain in these areas). As vapor spaces will oxidize, resulting in a blue tint, an absence of blue tint may indicate potential cracking sites.

The SIIC cracking process is relatively slow, but frequent cycling can accelerate the damage. Be aware that when leaks occur, SIIC may also occur on the backside of the protective liner.

Key SIIC Parameters:

- Service time, temperature, pressure, and thermal cycles
- Large number/severity of thermal/pressure cycles
- Areas of internal condensation

Equipment Concerns:

- Areas in HP lined equipment in or near the vapor spaces particularly on cupped surfaces.
- Urea reactor, Figure 3 shows an example.
- HP stripper
- Condenser/Pool reactor
- HP Piping in two phase or vapor flows after a long time, likely related to startups/shutdown cycling .

Mitigation Options:

- Ensure a tight fit of liner parts.
- Do not use explosion cladding as this will increase strain.
- Monitor the liner thickness, especially in the condensate regions. Reduced liner thickness can increase the stresses in the liner and consequently result in cracking. The minimum required remaining liner thickness depends on the liner material used, the inner diameter of the vessel, and the size of the area that is affected by the overall and/or condensation corrosion.
- Inspect selected high-risk areas. If cracks are observed, these areas should be noted and reported in an inspection record for additional action or future monitoring.

- Take necessary action if a crack is found in a liner. The action level for actionable crack depth is typically a remaining thickness of 3 mm (0.12″) from the original 12 mm (or 0.5″) liner since it is known that the crack propagation is slow and mainly occurs during starts and stops of the synthesis.
- Inspect HP piping in aging facilities where plastic deformation and/or carbamate condensation may be taking place, such as elbows.
- Consider using an eddy current technique for inspection. [12]
- In case of clogging in the leak detection grooves, do not flush them with water.
- Avoid grinding on surfaces

Summary

Aggressive corrosion-related damage mechanisms are present in urea producing equipment. Having an understanding of these damage mechanisms and how operations or process conditions can affect equipment will help mitigate the occurrence of these damage mechanisms. Selecting the proper material and implementing the mitigation options mentioned in this article can help reduce the effects of Carbamate Corrosion and Strain-induced Intergranular Stress Cracking.

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