

Corrosion Damage Control On Urea Equipment

Daniel J. Benac, Dorothy Shaffer, and Johan Thoelen, BakerRisk, USA and Belgium, discuss the dangers of carbamate corrosion damage and the different mitigation methodologies available for urea equipment.

Urea plant equipment operates at elevated temperatures and is exposed to corrosive environments that can potentially limit its life. Awareness of the corrosion-related mechanisms that can damage the equipment used in urea plants is essential in developing an 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 specific mechanism and the rate of attack need to be understood in order to determine the remaining life expectancy of the equipment. For a proper risk-based inspection (RBI) programme or hazards analysis to be conducted, the appropriate



damage mechanisms must be identified so that the probability of failure can be determined in addressing reliability issues.^{1,2,3}

This article provides examples and discussion regarding the carbamate corrosion damage mechanisms related to urea process parameters, materials of construction and process equipment, and inspection methods and characterisation techniques to identify each form of damage.

Additionally, useful tips for considering potential mitigation methods are provided.



Figure 1. Failure of a urea reactor and release of the vessel head.

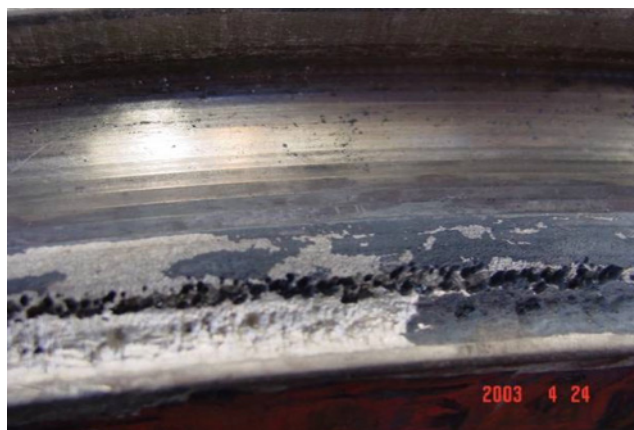


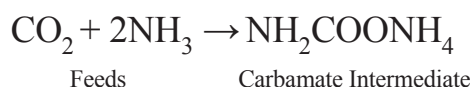
Figure 2. Crevice corrosion attack on a 25-22-22 high pressure stripper gasket surface.



Figure 3. Rupture of a deadleg in a carbamate line.

The urea process

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



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

The carbamate dehydrates (i.e., sheds a water molecule) to slowly form urea while it absorbs a small amount of the heat in the process. High pressure is required to keep the reactants in solution, as it mitigates decomposition of carbamate back to its components and increases yield. The high-pressure reaction section can range from 126 – 562 kg/cm₂g (1800 – 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.



The effluent from reactors will be a mixture of urea, carbamate, ammonia, and water. It can also include a lesser amount of ammonium carbonates – $(\text{NH}_4)_2\text{CO}_3$.

Urea equipment materials of construction

In an ideal world, the materials chosen for urea equipment would be impervious to deterioration effects from process conditions. In the real world, however, this is either impossible or cost prohibitive, so various types of equipment damage continue to occur. Most process equipment used in urea production is comprised of pressure vessels, piping, and storage tanks whose pressure boundaries are constructed from 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 specialised 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. Additionally, to control costs on the thick walls of pressure shells, cladding is typically used.

Zirconium and titanium are materials that react strongly with oxygen to form a corrosion protection layer, so they do not need the assistance of 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.

Typical materials of construction

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 corrosive conditions. Figure 1 shows a urea reactor that failed in 1992. It was determined that the weep holes had plugged and the corrosive attack of the multi-layer was unknown. After the stainless steel corroded through, urea entered and attacked the carbon steel layers. The 14 layers were compromised and could not withstand the pressure.^{6,7} Therefore, it is important



Figure 4. Carbamate condensate corrosion in type 316 UG plates.



Figure 5. Carbamate corrosion failure of a high-pressure scrubber.

that the weep holes are monitored, and a leak detection system is in place in case the liner fails.

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

Materials for urea production vary from those suitable for non-corrosive and utility services to those exposed to the rigors of the highly corrosive synthesis section. Materials include 316L to 316L urea grade UG, X2CrNiMo25-22-2, zirconium, titanium, and more specialised urea specific materials (Uremium 29, Safurex™, and others).⁸

Type 316L-urea grade, or 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, and 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, X2CrNiMo18-14-3, 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 – 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 – 0.15 mm/y (0.4 – 4 mpy (mils per year)) 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/y (300 mpy).

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

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 is designed to provide better corrosion resistance to the stripper conditions than 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.⁹ However, Figure 2 shows that crevice corrosion can occur at a gasket surface.

Other urea specific materials considered are Safurex™ 29Cr7Ni2MoN (UNS S32906) developed by Sandvik and preferred by Stamicarbon licensors, and DP28W (28Cr8Ni1Mo2W) UNS322808¹⁰ paper preferred by Toyo. Other alloys such as Uremium 29 (29Cr7Ni1MoN) UNS32906 are being utilised. Toyo Engineering Corporation (TEC) and Sumitomo Metal Ind., Ltd. (SMI) have jointly developed new duplex stainless steel DP28W™ for urea plants.

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

Although nickel-based alloys are resistant to many corrosives in alkaline solutions, when subjected to oxidising environments, nickel-based alloys are not suitable because of the formation in ammonia solutions of soluble Ni (NH₃)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 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 a reaction of ammonia and carbon dioxide at high pressures. A carbamate is a category of organic compounds that is formally derived from carbamic acid (NH₂COOH) 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 of more than 1000 mm/y. Higher temperatures and higher carbamate concentration increase the corrosion rates: the Arrhenius equation predicts that the corrosion rate doubles for every 10°C (18°F) increase in temperature. Higher temperatures and a low activation energy result in accelerated corrosion rates. Process licensors, company experience, or industry recommendations may set process limits to avoid aggressive carbamate corrosion conditions for the design materials.

The Arrhenius equation is:

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

Where:

- K : rate constant.
- A: pre-exponential factor.
- EA: activation energy.
- T: temperature.
- R: universal gas constant (= 8.314 J/mol-K).

In older plants with a reactor, this is 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 of more than 1000 mm/yr. In the urea synthesis section, points at which stronger carbamate concentrations can 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.¹⁰ Figure 3 shows that deadlegs can be particularly susceptible to accelerated attack, creating a risk for rupture of equipment.

Some of the ways carbamate corrosion can occur are described in this article.

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.

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 for 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

Where carbamate condenses in the vapour 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 4 and Figure 5 show an example of carbamate condensate corrosion.

In highly stressed regions with a carbamate solution condensing out a vapour phase, strain (or stress) induced intergranular racking (SIIC) may occur.¹¹

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, concentrates 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

Vapour areas in the high and medium pressure sections of the urea plant are at a risk of carbamate condensate corrosion:

- Vapour pipelines or piping or high spots that can trap vapours where steam tracing is inadequate or not in service.
- Areas where insulation is inadequate or may be damaged.
- Locations where attachments act as a heat sink such as lifting lugs, thermowells in vapour 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.

Mitigation options

- 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 CO₂ feed.
- 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, but the material is expensive.
- To minimise 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.¹²
- Evaluation of contaminants: online monitoring of nickel.

For prevention of flow-assisted attack

- Reduce velocity by changing the design – use multiple restriction orifices, increase the pipe diameter, or reduce 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.

Conclusion

Aggressive corrosion-related damage mechanisms are present in urea producing equipment. Understanding 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. **WF**

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