The fight against corrosion from urea ammonium nitrate (UAN) solutions is a constant one with far-reaching impacts for the fertilizer industry. Solutions are important.

Not only is it important for UAN producers to preserve product quality for end-users, but they also want to protect manufacturing, distribution, storage and application assets. Equipment reliability leads to more online production time and ultimately more profit. Moreover, there are significant health, safety and environmental risks for producers and handlers when asset integrity is compromised.

Specialty chemical manufacturers know this, and they have been helping the industry maximise operations and mitigate risks for decades with UAN corrosion inhibition products. These solutions can be generally classified into ones that create a barrier between UAN and equipment (filmers) and ones that limit the electrochemical corrosion process between the anode and cathode (corrosion inhibitors).

Both are effective to fight specific corrosion mechanisms, but is there a solution more equipped to fight all corrosion mechanisms and better help meet the needs of producers and end-users? A US-based, industrial water and process treatment company thinks so.

Athlon Solutions has been delivering long-term successful corrosion inhibition with a patented product that provides both anodic and cathodic protection, is non-foaming and non-precipitating, and includes the benefit of preserving product quality with a secondary inhibitor that sequesters iron as the product is transported and stored.

The company’s AG-GUARD® product line is used to treat more than 70% of the UAN manufacturing capacity in the US.

The challenges of traditional solutions

The most common problems in the UAN storage and supply chain are generally caused by general corrosion, pitting corrosion, discoloration of the UAN and sludge precipitation for end-users.

There are potential solutions for each, but the traditional ones (filmers and general corrosion inhibitors) are either not able to fight all corrosion mechanisms or create other challenges with product quality.

To better understand the limitations of traditional solutions, UAN corrosion issues should be reviewed.
Cathodic and/or anodic protection.

Cathodic protection, which can require cathodic reaction: in environments where the pH < 7 (acidic), higher alloy with increased resistance.

Coatings, such as paints or metallic plating, galvanising and better storage and transportation materials with resistance to the environment.

Anodic/oxidation reaction: the anodic reaction is the oxidation reaction, where: M = M^+ + e^-

Cathodic reaction: in environments where the pH < 7 (acidic), hydrogen ions are reduced: 2H^+ + 2e^- = H_2

Corrosion reaction: in environments where the pH ≥ 7 (alkaline), the cathodic process is the reduction of dissolved oxygen, which leads to uniform corrosion:

\[ \text{O}_2 + \text{2H}_2 \text{O} + 4\text{e}^- = 4\text{OH}^- \]

With general corrosion, the second and third reactions listed above create a uniform distribution of cathodic reactants over the metal’s surface. The cathode and anode locations are random and changing, meaning there is a uniform impact across the metal’s exposed surface.

The traditional solutions to prevent or limit general corrosion are as follows:

- Thicker and stronger materials (higher alloys). These provide longer life, but do not stop corrosion. They just prolong the corrosion process.
- Coatings, such as paints or metallic plating, galvanising and anodising. However, poor application can lead to accelerated pitting corrosion at breaks in the coatings.
- Cathodic (and anodic) protection, which can require significant CAPEX, includes the following:
  - Sacrificial metal acting as the anode instead of the metal you want to protect.
  - Impressed current cathodic protection (ICCP) for large structures, where anodes are connected to a DC power source to drive a protective electrochemical reaction.
- Corrosion inhibitors or modification of the environment, which require proper application, monitoring and CAPEX for an effective program.

**Pitting corrosion – causes and potential solutions**

Pitting corrosion is localised and focused on a small area, resulting in cavities, holes or pits on the metal’s surface. Many tank failures are a result of pitting corrosion, which can take the form of trough or sideways pits that rapidly compromise wall thickness.

NACE International identifies pitting as the most damaging form of corrosion, as it is difficult to detect, predict and prevent.

Pitting corrosion can be initiated when an aggressive chemical species (e.g. chlorides, ammonium nitrate solution) are present in an aqueous solution. These anions/salts will damage the passive film (oxide), so pitting can initiate at oxide breaks. Also, the material environment can set up a differential aeration cell, such as a water droplet on the surface of the steel, allowing corrosion pitting to initiate at the centre of the water droplet (i.e. anodic site).

The traditional solutions to prevent or limit pitting corrosion are as follows:

- Control of the environment (e.g. pH, chloride concentration and temperature).
- Better storage and transportation materials with resistance to the environment.
- Higher alloy with increased resistance.
- Cathodic and/or anodic protection.
- Application of a corrosion inhibitor.

**Discolouration of the UAN – causes and potential solution**

If it is not addressed with an iron sequestering agent, there is a costly risk of UAN discolouration from iron oxide, which starts with a rust colour, indicating that the corrosion process is occurring. Iron oxide will accumulate as sludge and turn the product to a red or an orange hue, which can lead to product waste and drive up operational costs due to the required cleaning, removing and disposal.

After unloading a vessel, such as a railcar or barge, often a chemical heel and/or thin films of UAN solution are left on the bottom and the walls of tanks and vessels, including around the drain fittings. While UAN is minimally corrosive as produced when it is a neutral pH solution, when the solution is allowed to sit and heat up, the ammonia portion can flash off leaving behind a low pH solution. This can create bloom rust and can lead to sludge formation and discoloured product.

Vessels are inspected and cleaned every few years, which can include sand blasting and pressure washing the surface of the vessel or tank. The intent is to remove all existing corrosion inhibitors and natural or chemical passivation surfaces. After cleaning, the vessels can remain unpassivated for extended periods of time, which can cause considerable bloom rust to form. Bulk corrosion inhibitors used in UAN solutions will need several months to establish a protective film or passivate the vessel’s surface. So even cleaned, inspected and repaired vessels still have the potential for UAN discolouration.

The solution to mitigate becomes a complex one, involving a UAN corrosion management program that includes inhibitors, regular maintenance and management of the transportation and storage equipment.

**Precipitation – causes and potential solution**

Due to iron sludge found not only in storage and transportation vessels, but also in application equipment, many corrosion precipitation problems can occur.

This includes under-deposit and pitting corrosion, discolouration of the UAN and failure of equipment, such as spray nozzles in fertilizer equipment and irrigation booms.
Performance testing has involved several types of market and their own suite of products. Below are some of the key testing parameters, findings and results:

Athlon Solutions has developed and tested the AG-GUARD technology against traditional corrosion inhibitors from the market and their own suite of products. Below are some of the key testing parameters, findings and results:

1. Performance testing has involved several types of market and inhouse products, including filmer corrosion inhibitors, anodic inhibitors and cathodic inhibitors.
2. Tests periods have ranged from short-term ones (e.g. four days) to long-term ones (e.g. 170 days).
3. Testing is performed on both acidified and unacidified coupons.

Filming corrosion inhibitors versus general corrosion inhibitors

As noted earlier, traditional corrosion protection can be grouped into these two groups – organic filming corrosion inhibitors and general corrosion inhibitors (anodic and cathodic), such as phosphate, zinc and molybdate.

Films are organic phosphate esters designed to protect the metal surface by forming a physical barrier between the UAN and the surface of the equipment. The key advantage is that once the filming amine forms, it can provide an effective barrier. The disadvantages are more numerous and include the following:

- Localised pitting, which can occur at a high rate if there is a break in the barrier.
- The filming agents cannot penetrate active corrosion cells with a protective iron oxide cap, meaning there is no under-deposit protection provided, and once started can go unchecked.
- Short lifespan does not provide adequate protection during transportation and storage.

Because filmers can cause foaming in the UAN solutions during storage and delivery, antifoam agents are also used as part of this corrosion solution. Generally, the antifoam is effective in UAN storage tanks at a plant. However, issues will arise during transportation and in field applications should any oil contamination occur, which causes a disruption in the protective barrier and an increase in corrosion rates. Generally, the antifoam is effective in UAN storage tanks at a plant. However, issues will arise during transportation and in field applications.

Traditional corrosion inhibitors do not require antifoam agents. They work by reducing or preventing the flow of electrons from the anode to the cathode during the electrochemical corrosion process. Phosphate, zinc and molybdate are inhibitors that are effective with the right program. There are, however, key disadvantages to general corrosion inhibitors:

- Without sequestering agents, phosphates can react with iron, calcium, magnesium and other contaminants to form deposits and precipitate in storage tanks and transportation vessels.
- If molybdate is used as a corrosion inhibitor, it acts as a passivating corrosion inhibitor to form complexes with insoluble Fe²⁺ ions, meaning it is not effective at preventing rust and sludge. This is especially true if large amounts of Fe²⁺ ions are present, such as in an off-spec vessel or storage tank. Acidic UAN solutions in contact with these formed complexes will result in sludge formation and corrosion.

Developing a new alternative

Athlon Solutions’ work with UAN manufacturers in the US over the past two decades has resulted in the development of a custom blended traditional corrosion inhibitor with a proprietary secondary inhibitor to provide anodic and cathodic protection. The secondary inhibitor also acts as a sequestering agent, preventing iron and other contaminants from depositing on the floors of tanks and vessels. Because this product is not a filming amine, the drawbacks of filmers do not occur.

The product also has the benefit of a high heat stability, allowing the inhibitors to continue providing corrosion protection across the supply chain throughout the transportation process. In high temperature areas, NH₄⁺ will flush off and pH depression will increase corrosion potential.

Molybdate and secondary inhibitor mechanisms

When it comes to under deposit corrosion inhibition, molybdate (MoO₄²⁻) is the key component. It migrates into the pit of the cavity under deposits to form a passive iron molybdate film. Molybdate specifically propagates into the pit cavity to stop corrosion through these reactions:

- 7MoO₄²⁻ + 8H⁺ => Mo₂O₇⁶⁻ + 4H₂O
- 8Mo₂O₇⁶⁻ + 2OH⁻ => 7MoO₄²⁻ + 1OH₂O

Molybdate is often used by itself as an anodic corrosion inhibitor, though it can be cost-prohibitive to reach treatment levels necessary when used by itself. Athlon Solutions’ research and testing has shown it to provide 5% inhibition at a dosage of 25 ppm in a 32% UAN solution. There are many inhibitors on the market that provide greater protection than molybdate as a standalone inhibitor.

Through testing a number of different inhibitors in varying blends for their synergistic effect on the corrosion inhibition of molybdate, Athlon Solutions developed the use of a patented secondary inhibitor to form a better and more complete corrosion inhibitor that lowered the overall mils per year (mpy) corrosion rate. Couple this with the secondary inhibitor’s ability to sequester iron and the elimination of the disadvantages of filmers, the company’s AG-GUARD product line was created.

Performance testing

Through its ongoing research and development efforts, Athlon Solutions has developed and tested the AG-GUARD technology against traditional corrosion inhibitors from the market and their own suite of products. Below are some of the key testing parameters, findings and results:

- Performance testing has involved several types of market and inhouse products, including filmer corrosion inhibitors, anodic inhibitors and cathodic inhibitors.
- Tests periods have ranged from short-term ones (e.g. four days) to long-term ones (e.g. 170 days).
- Testing is performed on both acidified and unacidified coupons.
Strict controls are always in place, including independent testing for metallurgical differences in coupons and passivation techniques and procedures.

Significant research has been focused on molybdate-based inhibitors due to its corrosion inhibition mechanisms.

Molybdate inhibitor testing included molybdate-only inhibitors from the market and molybdate blended with a secondary inhibitor.

To determine the best-suited secondary inhibitor for synergistic protection, candidates included standalone and blended solutions with varying concentrations of amines, imidazolines, sulfonates, phosphonates, inorganic/organic phosphates and miscellaneous inhibitors.

Molybdate-based inhibitors with a blended secondary inhibitor performed better than molybdate alone. For example, a repeated performance of one AG-GUARD product showed 97% inhibition with 2.3 mpy during a four-day test and 100% inhibition with 0.1 mpy during a 13-day test. Molybdate alone showed 37% inhibition with 36 mpy during four-day tests and 17% inhibition with 65 mpy during 13-day tests.

Filmers obtained low mpy corrosion rates in testing, but evidence of pitting was often seen compared to molybdate products with a secondary inhibitor, which lowered mpy corrosion rates and showed no signs of pitting.

Importance of an effective service program

UAN corrosion technology is best handled when a competent service representative can implement and maintain a program. This includes working with the operations and treatment teams to optimise products and applications to achieve increased reliability.

An effective UAN corrosion program will include the following:

- New tank ‘pre-passivation’ with inhibitors on producer and customer tanks and vessels.
- Tank inspection and cleaning with sand blasting, hydroblasting and other methods.
- Passivation of a cleaned tank (direct inhibitor coating versus ‘super-passivated’ UAN).
- Continuous passivation of product entering tank or vessel.
- Residual inhibitor testing in producer and customer tanks and vessels.
- Corrosion testing in tanks with coupons.
- Removal of any residual oil with skimmers.
- Routine on-site laboratory testing.
- Finished product with neutral pH UAN solution.
- Eliminate unnecessary contaminants (e.g. wash-down water and oil from entering UAN solution).

Conclusion

The fight against UAN corrosion in the fertilizer industry has been a long one. For many years, specialty chemical manufacturers have been helping the industry with traditional filmers and corrosion inhibitors. They are effective with the right treating strategy, but there are shortcomings with each. An effective technology blending molybdate with a secondary inhibitor offering anodic and cathodic protection and iron sequestration is giving the industry a superior solution in this long fight.
Effective water and process treating is imperative to successful ammonia and fertilizer plant operations. Large amounts of high pressure steam and high purity water are required in the production process.

Athlon Solutions has a long and successful track record in the following areas:

- RAW WATER PRETREATMENT
- COOLING WATER
- BOILER FEEDWATER
- PROCESS CONDENSATE
- CO₂ REMOVAL
- UAN CORROSION INHIBITION
- STEAM