Phil Bureman and Dr. Craig Myers, Nalco Water, USA, discuss the advantages of a comprehensive UAN corrosion management programme.

Liquid urea ammonium nitrate, known as UAN, has gained traction among farmers worldwide for good reason. As a water-based nitrogen fertilizer, UAN offers farmers convenience and efficacy in its application. In the field, UAN fertilizer enables farmers to precisely manage its application to crops. In addition, UAN offers growers three forms of nitrogen – nitrate (NO_3) for fast uptake, ammonia (NH_3) for intermediate crop growth and urea for long term nitrogen nutrition. UAN is typically sold as a 32% nitrogen content product (45% ammonium nitrate, 35% urea, and 20% water), referred to as UAN32.

Moreover, UAN is versatile. It blends easily with other liquid fertilizers such as phosphate, micronutrients, herbicides and pesticides. This versatility reduces the number of passes a farmer must make to apply nutrition to their crops. UAN also avoids the serious inhalation hazards posed by anhydrous ammonia, and unlike dry ammonium nitrate prills, UAN poses low risk of explosion.

But UAN does have a potential drawback – especially if not manufactured properly. UAN solution is corrosive, and it must be treated with a quality corrosion inhibitor, specifically formulated for UAN. In addition, the inhibitor must be applied at the correct treat rate and be properly blended with the UAN. Storage tanks, conveyances (pipelines, rail cars and barges), and agricultural equipment are vital to fertilizer businesses, enabling the storage, transportation and application of UAN. UAN can corrode carbon steel, which may jeopardise the structural integrity of equipment and lead to potential leaks or catastrophic failures (Figure 1).

UAN's composition and corrosive nature

UAN contains urea, ammonium nitrate, water, and a small amount of 'excess' ammonia. Of these, ammonium nitrate (AN) is the more corrosive component. Although ammonium nitrate has pronounced corrosive behaviour, the 'excess' ammonia in the solution can mitigate its effect. The term 'excess' refers to the ammonia concentration above the amount needed to form ammonium nitrate and urea. To maintain the solution's integrity and reduce its corrosive tendencies, the excess ammonia is typically kept above 0.01% by weight, or 100 ppm. However, for the best results, the concentration should be 0.02 – 0.05% by weight, or 200 – 500 ppm. Excessive ammonia levels can lead to odour complaints during spray application. The optimal pH for UAN is between 7.0 and 8.0. A pH value below this range will

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significantly increase the risk of damaging corrosion, particularly if the solution is exposed to high temperatures.

Challenges arise when ammonia levels diminish and pH levels drop. This is especially true when temperatures rise. A typical scenario that highlights the issue occurs when a rail car, once filled with UAN, gets emptied. This action leaves a thin layer of UAN on the side walls of the car, as well as a heel of UAN on the bottom. As the rail car gets emptied, an influx of ammonia-free air can swiftly transfer the ammonia out of the liquid phase and into the vapour space above. As a result, the pH drops rapidly, which then amplifies the corrosiveness of the UAN. Without a robust corrosion inhibitor in the UAN, rust build-up can occur at the bottom of the rail car. This kind of corrosion, created by dwindling ammonia levels, is called 'thin film surface corrosion.' The resulting corrosion sludge leads to under deposit corrosion on the rail car or tank bottoms, which can result in severe pitting if an effective corrosion inhibitor is not utilised. Pitting can threaten the structural integrity of storage tanks and rail cars. The potential for localised corrosion is particularly targeted to weld joints and the heat affected zone around the weld joints (Figure 2).

Figure 1. Collapsed storage tank due to catastrophic corrosion damage.

Figure 2. Example of severe pitting corrosion of a tank bottom and weld joint (where proper mechanical, operational, and chemical corrosion mitigation procedures were not followed).

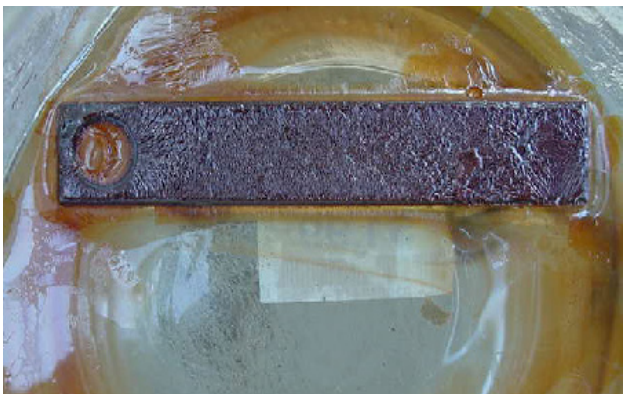

Figure 3. Thin film corrosion developed on coupon after loss of ammonia.

The corrosion described here can be demonstrated in a simple experiment. A 1010 carbon steel corrosion coupon was placed in a glass jar filled with just enough UAN32 (without a corrosion inhibitor) to cover it. After sealing the jar and leaving it in sunlight for seven days in high temperatures, no additional corrosion formed. However, after opening the jar for three hours and resealing it for the night, a thick uniform iron oxide (rust) layer formed on the steel by morning (Figure 3).
The corrosion occurred because ammonia escaped from the thin film of UAN on top of the coupon when the jar was open, resulting in a drop in pH levels. The corrosion product buildup (sludge) creates ideal conditions for localised under deposit corrosion to form. Inspections of tank floors readily show the importance of under deposit corrosion. Areas with solids accumulation, such as the bottom edge of lap welds, can show severe pitting, while the remaining plate surfaces remain without corrosion.

Another important property of UAN is the AN/urea ratio, as it pertains to both corrosion potential and fertilizer performance. UAN contains approximately 80% dissolved solids. If the ratio of AN and weight % urea is between 1.2 and 1.4, UAN32 starts to freeze at approximately 30°F.
However, the freeze point can rise significantly if the UAN is blended outside of the desired ratio. When this happens, salts of either ammonium nitrate or urea will form and drop out of solution. These salts can cause several problems:

- The AN and urea salts create powerful corrosion cells where they settle, which leads to severe pitting corrosion.
- The remaining solution loses nitrogen content, so it does not deliver the required nutrition.
- The remaining weak solution becomes much more corrosive:
  - UAN28 is about 20% more corrosive than UAN32.
  - UAN16 is about 35 – 40 times more corrosive than UAN32.

The fundamentals of UAN corrosion management

While UAN storage and transportation entails corrosion risks, fertilizer producers can manage the risks by focusing on the related mechanical, operational, and chemical factors.

Mechanical measures to minimise corrosion risk

To enhance the lifespan of storage infrastructure and reduce the corrosive impact of UAN, a proactive mechanical approach is necessary:

- Regular maintenance: drain and clean large storage tanks at a minimum of every five years. This routine

effectively removes the corrosion sludge that can lead to detrimental under deposit or pitting corrosion.

- Avoid UAN accumulation: ensure no small puddles or heels of UAN are left in storage tanks over prolonged periods. Stagnant UAN can lose its excess ammonia, causing acidic conditions and intensified corrosion. Be especially careful not to leave puddles of dilute UAN on metal surfaces (Figure 4).
- Optimise flow: install a recirculation header. Corrosion sludge buildup at the tank's base may lead to corrosive cell pockets. Many UAN producers counteract this by installing a recirculation pipe across the tank's diameter. Outfitted with 45° angled outlet spigots, this type of pipe encourages constant UAN movement, drastically reducing pitting corrosion. Thin film corrosion sludge sitting at a tank bottom is bad, but when that same sludge does not move, the impact can be devastating.

Figure 4. Example of corrosion that occured in a rail car heel with poorly inhibited UAN.

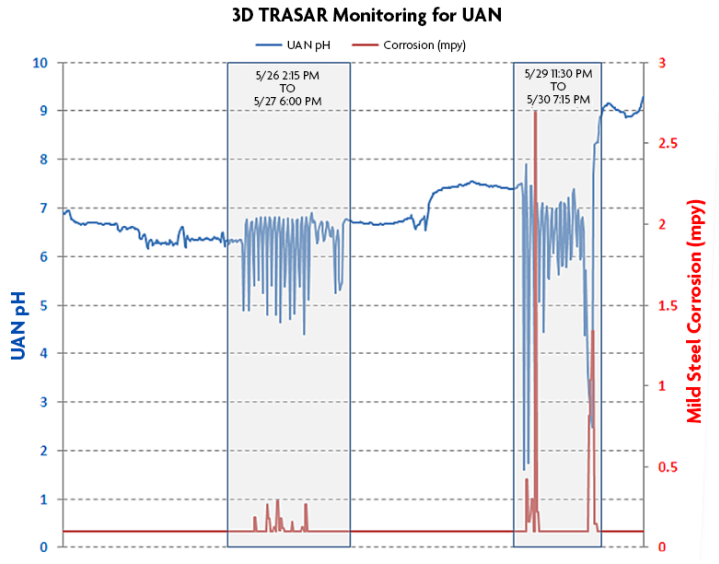

Figure 5. UAN process dynamics and pH excursions.

- Temperature regulation: aim to keep tank temperatures within the 10 – 47°C (50 – 110°F) range. High temperatures can speed up chemical reactions and the corrosion rate.

Operational measures to minimise corrosion risk

For effective UAN corrosion management, operational actions like the following are key:

- Monitor pH and ammonia: consistently gauge the pH of incoming UAN and watch for proper ammonia levels – both are pivotal quality indicators. Fertilizer distributors may want to ask their supplier to include excess ammonia levels on the certificate of analysis for each load of UAN
  - Understand UAN: know the AN to urea ratio – it signifies when UAN begins to salt out. This number is generally included on the certificate of analysis. From a storage perspective, UAN32 boasts an edge over UAN28 because it is less corrosive by nature.
- Monitor corrosion: use corrosion coupons at essential areas, such as the tank's mid-and-bottom levels to monitor long term corrosion. Utilise two sets – one for short-term quarterly assessments and another for annual reviews. Remember that under normal conditions, significant corrosion can take years to occur, but a severe pH upset can damage a tank within days.
- Prioritise quality: choose high-grade UAN from trustworthy producers.

Chemical measures to minimise corrosion risk

The right chemical measures can act as the first line of defense against UAN corrosion:

- Inhibitor insight: investigate the exact corrosion inhibitor type and amount in a UAN. Different UAN sources may use diverse inhibitors, so be wary when combining them. Chemical corrosion inhibitors all have a minimum effective dose. If UAN is combined from different producers that may use different inhibitors, the blend may not contain enough of any inhibitor to be effective.
- Which inhibitor and how much? Ask a UAN supplier for proof of performance information or their reason for choosing a particular corrosion inhibitor. Make sure the UAN supplier is using a well-regarded and high performing corrosion inhibitor designed specifically for use with UAN. In addition, ask what measures the UAN supplier is taking to ensure they are always adding the recommended amount of corrosion inhibitor. Corrosion tests run by the inhibitor supplier to prove material efficacy should be carried out with control over excess ammonia, temperature, and pH, to ensure reproducible and relevant results.

The benefits of digital monitoring

The process of manufacturing UAN by making and blending ammonia, ammonium nitrate and urea is extremely complicated. Typically, these complex processes are managed effectively and carefully, but occasional upsets can lead to variations in both quality and corrosivity. Continuous monitoring of key corrosion parameters, such as inhibitor levels, corrosion rates, pH levels and temperature, help mitigate potential challenges in asset protection and UAN product quality. Nalco Water has developed its 3D TRASAR™ technology for UAN corrosion management to provide 24/7 monitoring across all four of these critical parameters.

Along with regular on-site technical support from Nalco Water sales-and-service engineers, 3D TRASAR technology for UAN corrosion management helps fertilizer producers manufacture a high quality and minimally corrosive UAN product. This technology uses advanced chemical innovation and specially designed monitoring devices to detect problematic parameters and determine how to optimise performance.
Moreover, its internet-connected communication capabilities ensure that stakeholders stay informed in real time. The technology for UAN corrosion management works in concert with Nitrosolve inhibitor formulations.

One of the strengths of 3D TRASAR technology for UAN corrosion management is its ability to offer deep insights into UAN process dynamics and its correlation with corrosion rates. For instance, in Figure 5, two pH excursions with corresponding high corrosion rates were identified. In the first excursion, after receiving the alarm, operators discovered a faulty nitric acid valve causing bursts of acidic UAN. In this case, the valve was fixed, and the pH fluctuations in the mix tank were buffered in the main storage tank.

The second excursion occurred as a plant began shut-down procedures. The plant was unaware that the shutdown procedures caused negative effects until 3D TRASAR technology was implemented.
After implementing the system and receiving 24/7 monitoring, the plant identified the challenges and adjusted their practices to reduce corrosion disturbances. If these acidic events were not identified and addressed promptly, they could have dramatically increased corrosion in storage tanks and rail cars. A single major stress event can lead to significant corrosion damage.

Conclusion

UAN offers benefits to farmers as a versatile and efficient nitrogen solution. However, its corrosive nature must be properly managed to ensure long asset life for infrastructure like storage tanks, rail cars, pipelines and agricultural equipment. The complex nature of UAN demands a multifaceted approach to corrosion management, encompassing mechanical, operational and chemical strategies. These include regular maintenance, consistent monitoring, and the use of robust, proven corrosion inhibitors. Regular on-site support by engineers and advanced technologies for UAN corrosion management can offer fertilizer producers an effective strategy to manage UAN corrosion proactively. WF

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