

Phil Bureman and Dr. Craig Myers

Take UAN Corrosion Seriously

If a tank leaks, you may be liable for water contamination in ground and surface water.



Figure 1. Collapsed storage tank.

Managing corrosion

UAN owes much of its popularity to its ability to mix easily with herbicides and other fertilizers, thus enabling a one-pass application on the farm. It also allows for improved safety versus anhydrous ammonia or dry ammonium nitrate. It is easy to handle and apply accurately, plus it is not so likely to be stolen for illegal use. Nevertheless, it is important to remember UAN can be corrosive to most metal surfaces when stored. When not properly managed, UAN corrosion can cause serious damage to pumps, pipelines, storage tanks, barges, rail cars, tank trucks, and agricultural equipment. UAN corrosion can cost UAN manufacturers, sellers and users in many ways, including damage to equipment and the cost of cleaning, removing, and disposing of UAN corrosion sludge.

For fluid fertilizer dealers, UAN corrosion can result in even more severe problems. For example, if a UAN tank leaks, or worse yet if it collapses (Figure 1), significant amounts of product and property could be lost; the dealer might

be liable for environmental and workplace safety violations, and the entire business and/or business reputation could be put at risk.

Why care?

The majority of UAN suppliers strive to produce high quality UAN that is only minimally corrosive. When manufactured and inhibited properly, UAN corrosivity can be minimized. However, when made improperly, UAN can corrode carbon steel very quickly. Fluid fertilizer dealers should be aware that many UAN producers and brokers have taken steps to reduce their exposure to the risk of UAN corrosion by installing tank liners, applying epoxy coatings, and replacing carbon steel piping with stainless steel.

In some cases, tank liners are applied simply to provide secondary containment as required by some state regulations. In other plants, UAN producers and brokers have learned through experience that upsets can result in significant damage to storage systems in a very short time. Such upsets are rare but they do happen. Corrosive properties

Summary: When there is a lack of attention and little effort on maintenance, corrosion caused by fertilizers (including UAN) can result in financial losses, environmental damage, and even loss of life. However, these potential risks can be greatly reduced with only a small amount of effort and minimal expense on the part of the dealer or grower.

in UAN are usually detected through sampling and testing and are corrected prior to shipment to any customer. However, in some facilities and terminals, no systems or few systems are in place to detect these corrosive properties. Since the results of UAN corrosion events may take some time to appear, the supplier may not always be aware that there is a problem. If corrosion in their facility can be minimized---for example by having tank liners, epoxy coatings, and stainless steel or plastic pipe in place---there may be less incentive for them to monitor corrosion quality.

Fluid fertilizer dealers should seek out quality UAN producers and brokers and ask what systems they have in place to ensure UAN quality. Dealers should ask producers and brokers about their sampling procedures and ability to promptly analyze those samples. Also, ask how these additional quality checks can help minimize risk and make them more money in the long term. UAN from better quality suppliers may cost a little more, but it is probably worth the higher price. Remember: If you never ask about

anything except nitrogen content and price, your supplier probably won't care about anything else either.

On the other hand, fluid fertilizer dealers and UAN bulk tank owners may not want to depend solely upon their UAN supplier to manage the corrosion that could occur in their equipment. The potential for UAN corrosivity can vary greatly from producer to producer, plant-to-plant, and even day-to-day in the same plant or terminal.

Before we discuss more about how to evaluate and minimize the corrosive quality of UAN you purchase, we must first understand more about why UAN is corrosive and the key corrosion mechanisms that occur when UAN is stored.

Excess ammonia

Of the components that make up UAN (urea, ammonium nitrate, water, and a small amount of ammonia), ammonium nitrate (AN) is the more corrosive component. AN's corrosive affect is buffered by the small amount of "excess" ammonia present; as little as 0.01 percent (100 ppm) to as much as 0.20 percent (2,000 ppm). Ammonia itself is not a corrosion inhibitor. But without this small amount of excess ammonia, UAN becomes extremely acidic and corrosion inhibitors cannot be applied cost effectively. One might wonder why extra ammonia is not always added to the UAN solution. It generally is not an issue of cost. Instead, excess ammonia content is usually limited by plant design and customer preference. Some UAN buyers prefer high ammonia levels in the UAN they purchase because their customers prefer that the UAN have a strong ammonia odor. Other buyers worry about odor complaints from neighbors if ammonia levels are too high during application. In addition, very high ammonia levels could be a safety hazard for personnel loading and unloading UAN. Furthermore, some herbicides and other tank mix products are sensitive to having too much ammonia in the UAN. With either preference, corrosion can be controlled as long as the ammonia

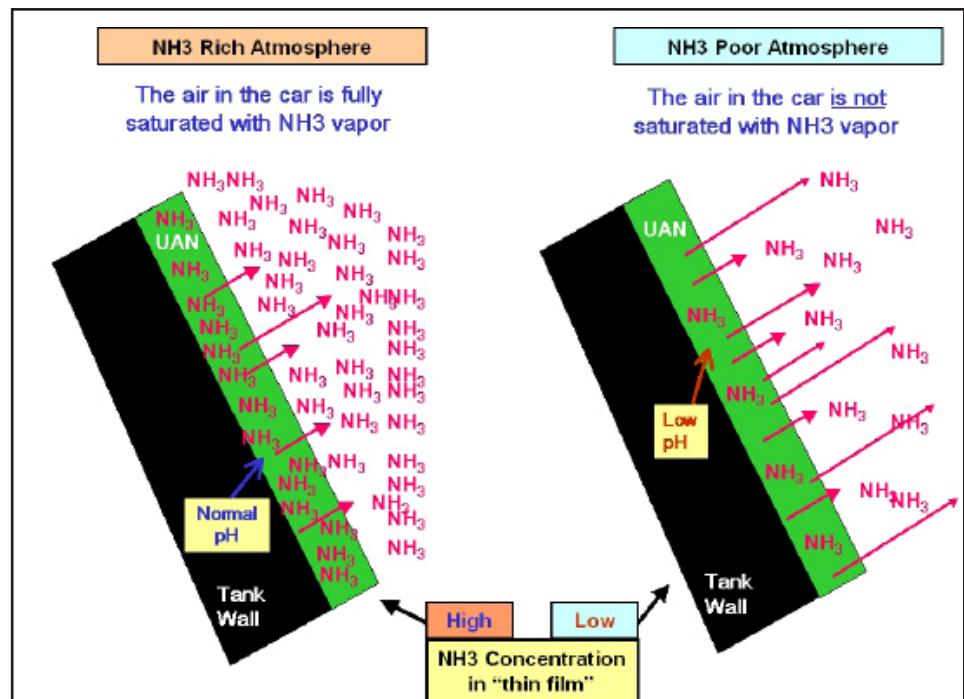


Figure 2. Example of how "thin UAN film corrosion" can occur.

stays in the UAN at adequate levels. The problem is there are many ways in which ammonia can be reduced to levels that no longer provide the buffering required.

For example, consider a rail car full of UAN, as depicted in Figure 2. When full, the ammonia quickly saturates the small vapor space above the liquid level in the car. Even when warm, no significant amount of ammonia is lost, so the UAN remains fairly non-corrosive. However, upon arrival at a customer site, when the tanker is emptied, a thin film of UAN is left on the tank wall. At the same time, fresh air (that contains no ammonia at all) is sucked into the tank. When this happens, the ammonia levels in the vapor space must be reestablished. The only source of ammonia is the "thin film" left on the tank wall. If there is very little ammonia available, such as when excess ammonia levels in the bulk UAN are less than 100 ppm to begin with, the corrosivity of the small amount of UAN remaining on the tank walls can increase dramatically.

Surface corrosion

As UAN levels in storage tanks drop during the season, this same corrosive "thin film" is formed on the vertical wall as fresh air comes

into the UAN storage tank. For this reason, fluid fertilizer dealers should ask about the typical excess ammonia provided by their UAN supplier. If there is a need to purchase a low ammonia product, the dealer should be aware that other steps may need to be taken to help minimize the impact of this low ammonia level.

The type of corrosion produced by low ammonia levels is called "surface corrosion." The good news is that surface corrosion initially is not very damaging to the steel. However, it does contribute to other problems.

In a simple demonstration, that can be done in one's own backyard, a steel corrosion coupon was put inside a well-sealed glass jar along with just enough UAN 32 to barely cover most of the coupon. In this example, an old coupon was used that happened to have a small corrosion spot on one side. The jar was sealed and left in the sun for 7 days (Figure 3) and during that time there was no sign of new corrosion. The jar was then opened to the air for about 3 hours and resealed and left overnight. The following morning, it was noted that severe corrosion had developed on the coupon (Figure 4). However, this generalized surface corrosion was not very damaging and was easily wiped off with a paper

towel. The amount of metal loss was small enough that even the original corrosion spot remained on the coupon (Figure 5).

Sludge

It has been determined that opening the jar resulted in the release of the ammonia from the UAN, which caused the corrosion that occurred on the surface of the coupon. The “Key Take Away” from this example is that although surface corrosion may not be very damaging, it does generate a large amount of corrosion sludge, and this sludge winds up on the tank floor! The reason this is important is that the generation of surface corrosion sludge leads to a major UAN corrosion mechanism called “under deposit corrosion.”

The chemistry that occurs with under deposit corrosion is complicated and a rigorous description is beyond the scope of this article. In brief, corrosion sludge prevents the normal flow of ions in the UAN solution and results in the formation of “pockets



Figure 3. Sealed jar left in sun for 7 days.

of corrosive ions” under the sludge on the tank floor. The buildup of corrosion sludge can also prevent corrosion inhibitors from accessing the steel under the sludge. The net result is the deep pitting that usually occurs on UAN tank bottoms. It is not unusual to see UAN pits as deep as a quarter inch develop in as little as 5 years when preventive measures are not taken. Examples of UAN sludge buildup and the resulting pitting corrosion are shown below in Figures 6, 7, 8 and 9.

Managing UAN corrosion

Fluid fertilizer dealers who handle

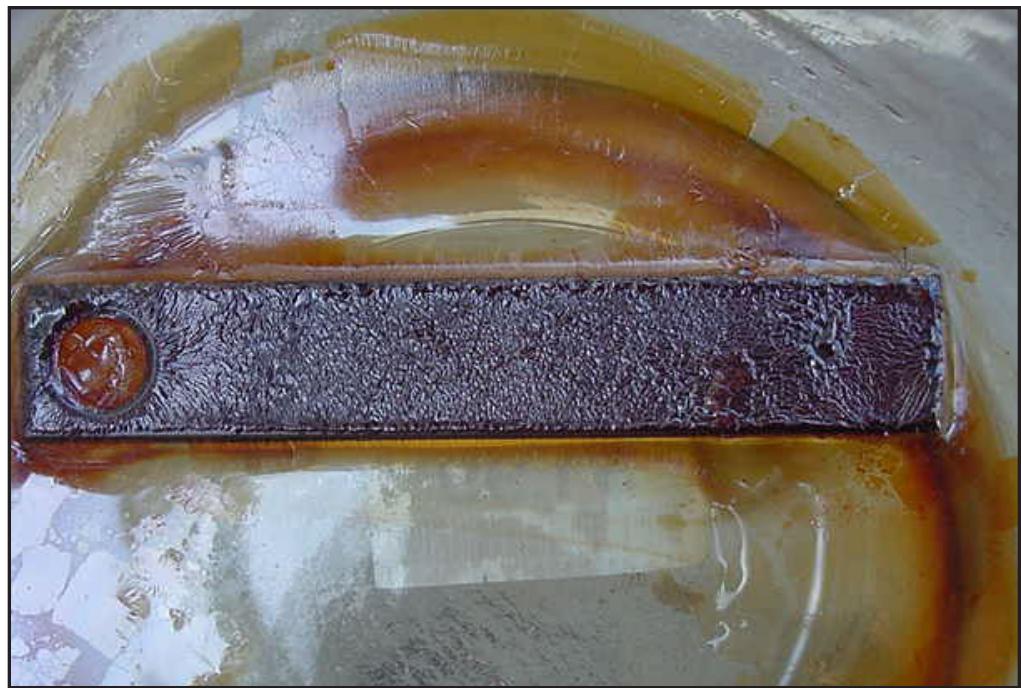


Figure 4. Severe corrosion developed on coupon after loss of ammonia.



Figure 5. Surface corrosion initially results in minimal damage.

UAN should assume a more active role managing UAN corrosion. There are mechanical, operational, and chemical means to do so, and all three areas should be considered at any UAN handling facility.

Mechanical

- Drain and clean UAN storage tanks at least every two years. This will remove the surface corrosion sludge that leads to the more damaging “under deposit or pitting type corrosion.”
- Never leave small puddles or “heels” of UAN in storage tanks for long periods of time. As in the rail car example cited above, this UAN can easily be stripped of the buffering ammonia and this results in acidity in the UAN and severe corrosion.
- Avoid leaving puddles of UAN

in steel piping. Blowing them clear with air just flashes off any remaining ammonia buffer, leaving thin films of acidic UAN on the pipe wall. Instead, consider a flush with aqua ammonia or, where practical, install corrosion- resistant pipe such as plastic or stainless steel.

- Secure the dome covers on all empty tanks or tankers that hold or transport UAN. This is particularly important for trucks and rail cars because it helps prevent the loss of excess ammonia. Dealers who carelessly leave this equipment open to the atmosphere increase the cost that all dealers pay for UAN transport and storage.
- Install a recirculation header in storage tanks. Corrosion sludge is bad, but sludge that does not move is even worse, as this



Figure 6. UAN tank sludge.

allows for the buildup of “pockets of corrosive ions” under the corrosion sludge. Many UAN producers now have adopted a best practice of installing an inlet recirculation pipe across the entire diameter of their tank bottom. This header pipe has several outlet spouts that point toward the floor at a 45° angle. Recirculation of the UAN allows

tank sludge to keep moving across the tank bottom. This helps to greatly reduce pitting corrosion.

- Some new tank builders are now recommending installation of a sloped tank bottom with a center outlet. This design is great for corrosion prevention, as sludge is constantly removed from the tank so buildup is always minimal.



Figure 7. Pitting under UAN tank sludge.



Figure 8. UAN rail car sludge.

- Consider installing a tank liner or applying a protective coating. Evaluate these options carefully, as these components can also fail, potentially resulting in an even larger problem.

Operational

- Check the pH of incoming UAN. Measurement of pH is a good indication of how much excess ammonia is contained in the UAN. Most producers ship product with a pH above 7.0. A pH as low as 6.5 is quite acceptable, but much below that there is a risk of stressing all the corrosion management systems. Discuss with your supplier a desire to receive product with a pH no lower than 6.5. UAN purchasers can check the pH of incoming UAN with something as inexpensive as pH paper tape (less than \$50), or consider the purchase of a pH meter (less than \$500). This is highly recommended if you are purchasing imported product, which has been known to lose



Figure 9. Pitting under UAN rail car sludge.

excess ammonia during the long transport time.

- If available, ask the supplier to include excess ammonia levels on the Certificate of Analysis for each load. Excess ammonia should be no less than 0.010 weight percent (100 ppm), and preferably should be at least 0.020 to 0.050 weight percent (200-500 ppm).
- Another important quality of the UAN is known as the AN/Urea Ratio. This is a simple mathematical calculation of the

weight percent of ammonium nitrate divided by the weight percent of urea. In UAN 32, this ratio is typically something like $45\%/35\% = 1.28$ AN/Urea Ratio. The AN/Urea Ratio is important because it greatly affects the temperature at which UAN starts to salt out. UAN 32 typically has a salt-out temperature of about 30° F. But this is only true at the optimal AN/Urea ratio range of about 1.20 to 1.40. At ratios above 1.6 or below 1.0, UAN 32 could start to salt out at temperatures above 45° F or higher. This is important because salt-out means lost nitrogen content. In addition, both AN and urea salts form very aggressive corrosion cells, so they are not a good thing to have sitting at the bottom of a tank (it's like leaving rock salt on the driveway at home). Lastly, both AN and urea salts have a negative heat of solution. This means that large amounts of heat are needed to get these salts back into solution. This may not be a problem when purchasing UAN in the spring, when ambient temperatures are already well above 50° F, and the UAN is to be applied right away. But the AN/Urea Ratio should be considered if one plans to store UAN 32 during cold winter months. There is no easy way for UAN purchasers to measure this parameter, but local suppliers should be able to give customers some typical values, or possibly include this measurement on the Certificate of Analysis, if requested.

- Try to store only UAN 32. Contrary to what many believe, UAN 28 is more corrosive than UAN 32. Consider purchasing and storing only UAN 32, and then if needed, dilute it with water to 28% just prior to application.
- Lastly, purchasing quality UAN from a trusted source is probably worth a higher price.

As detailed above, purchasers should monitor the product they receive and ask questions about the quality of the UAN being purchased. If suppliers can't tell buyers about the quality of the UAN being offered, they may not be monitoring it themselves.

Chemical

- Fluid fertilizer dealers should ask what type and how much corrosion inhibitor is being used in the UAN they purchase. It might be possible to request the treatment rate and brand of corrosion inhibitor be included on the Certificate of Analysis.
- If purchasing UAN from multiple suppliers or sites, it is possible to end up with UAN containing multiple inhibitors in your storage tanks. Although compatibility among different inhibitors is not an issue, these different inhibitors (now diluted) may not be as effective together as they were by themselves at full strength.
- Fluid fertilizer dealers should consider purchasing and applying their own corrosion inhibitor programs. Corrosion inhibitor chemicals are inexpensive, compared to the cost of UAN. Corrosion inhibitor programs typically cost \$0.60-\$0.70 per ton of treated UAN when purchasing in the small amounts likely to be needed by fluid fertilizer dealers. This cost could be much less if the inhibitor choice is matched to the one used by the UAN supplier. Most UAN corrosion inhibitors are easy to apply and safe to use. There are some products, however, which themselves are quite acidic and are inherently hazardous to handle and store. Be sure to discuss this question with potential inhibitor vendors.
- There are two basic types of UAN corrosion inhibitors. "Filmer" type inhibitors form a protective film on steel. "Passivator" type

inhibitors actually combine with the corrosion products when corrosion is initiated and stop corrosion by "sealing off" the corrosion cell. Both types have advantages and disadvantages and when applied correctly either type will greatly reduce UAN corrosion. Some inhibitor formulations offer additional features such as sludge dispersants, metal chelants, anti-foam additives and tracer compounds. A sales engineer, educated in UAN corrosion inhibitors, can help you decide which type is best for your UAN.

Phil Bureman is Nalco's technical consultant for Chemicals and Biofuels and lives in Olathe, KS; pebureman@nalco.com and Dr. Craig Myers is a research scientist at Nalco's headquarters in Naperville, IL; cmyers1@nalco.com