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Best Practices for Corrosion Protection

***Matthias Walschburger, Knight Material Technologies,** debates best practices for corrosion protection during the production of fertilizer.*

Companies go to great lengths to minimise corrosion in fertilizer production, since success in this area contributes significantly to the durability and longevity of equipment and plant structure throughout all three operational phases: production, storage and handling processes.

Fertilizer production plants operate under various temperatures and pressures, handling highly corrosive raw materials such as sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), intermediates and by-products. Sulfuric, phosphoric, and nitric acid are the most essential minerals acids produced worldwide. Nitrogen is the most consumed nutrient in fertilizers, followed by phosphoric acid anhydride.

These plants produce sulfuric acid by combustion of sulfur with dry air to form sulfur dioxide (SO_2), followed by sulfur trioxide (SO_3) through a catalytic conversion. Finally, sulfuric acid is obtained after the absorption of sulfur trioxide in water in a sulfuric acid plant tower.

These conditions make the plants susceptible to significant levels of corrosion and abrasion. As a result, it is essential to understand and control these various chemical acids that form the root cause of corrosive conditions.

Understanding Fertilizer Plant Systems

Proper design of equipment and pipelines, including minimising crevices and ensuring good drainage, can reduce areas throughout the many places in a fertilizer production facility where corrosive substances might accumulate.

Consider the plant's absorption towers, which are typically constructed from carbon steel and lined with acid-resistant bricks to ensure durability and longevity. The use of alloy towers has become more prevalent in the fertilizer industry due, on one side, to the more controlled acid concentration in the process that works very well with alloy towers and their lighter weight, which reduces the need for more significant foundations and initial capital expenditure (CAPEX).

Despite their corrosion-resistant properties, specialised stainless silicon steels, like SX®, ZeCor®, or Saramet®, and high-cost nickel alloys are still vulnerable to harsh acidic conditions, especially when exposed to an acid concentration these alloys were not designed to withstand. Sulfuric acid, for instance, creates a corrosive cell on the metal surface, altering its internal morphology and degrading its physical, chemical, and mechanical properties.

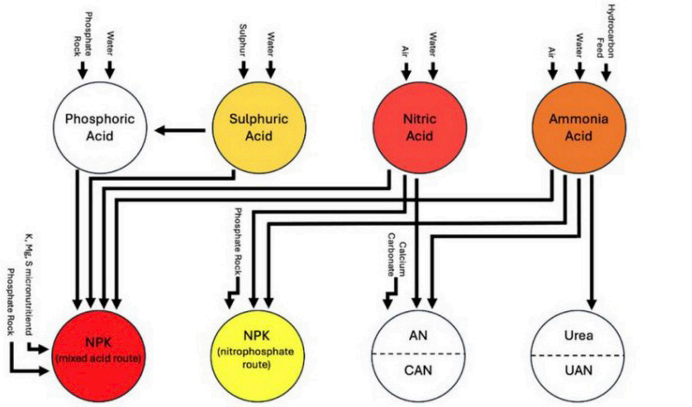

Figure 1. The main components used in the production of fertilizers.

A critical aspect of maintaining the integrity of alloy towers is conducting a thorough structural analysis. This analysis helps identify potential weaknesses that could lead to shell buckling above the packing level, especially in plants designed with the blower at the end of the process. One effective method to improve the structural stability of alloy towers is using structured packing, as it reduces pressure drop and, therefore, the compression stresses in the shell. This enhances the performance and operational life span of the alloy towers.

Figure 2. A carbon brick-lined vessel used in phosphoric acid vessels.

Managing Corrosive Acid Production

Plant systems must be able to withstand the wide variety of caustic and corrosive acids common in fertilizer production.

Nitric acid (HNO_3), most commonly used in fertilizer production, is a solution of nitrogen dioxide (NO_2) in water, which is a colourless to light-brown fuming liquid with an acrid suffocating odour. Nitric acid is the second most important industrial acid. It is a highly oxidising agent used widely beyond fertilizer production to manufacture chemicals, explosives, fertilizers, steel pickling and metal cleaning. It is corrosive to metals, forming flammable or explosive gases. Nitric acid also reacts violently with organic compounds.

The most commonly used steel in nitric acid towers is Type 304L stainless steel. This low-carbon austenitic stainless steel is preferred due to its good resistance to nitric acid corrosion, especially at 60–65% concentrations.

For more demanding conditions, such as higher temperatures or the presence of chlorides, more advanced materials may be used.

Phosphoric acid is mainly consumed during the manufacturing of phosphate fertilizers or for direct use as an acid in the food and beverage industry. When used in manufacturing fertilizer, representing 80% of its overall use, phosphoric acid requires a lower grade of purity than in the food and beverage industry. The production of fertilizers derived from phosphoric acid has increased significantly during the last 120 years because, among other things, of technical breakthroughs in the field of phosphoric acid and ammonium phosphate manufacturing. In addition, economies of scale have resulted in high-capacity plants, which produce a limited range of products at very competitive prices.

Phosphoric acid is commonly stored in rubber-lined steel tanks, although stainless steel, polyester and polyethylene-lined concrete are also used. The rubber linings used include neoprene, butyl and natural rubber. In transportation or shipment, ISO containers or tank carriers are lined with rubber, fluoropolymer, or polymer.

Considering a Wide Variety of Corrosion Resistant Materials in Use

The available literature offers a wide range of optimal materials and practices for handling these types of corrosive acids. While selecting corrosion protection materials might seem straightforward due to the known raw materials and products, the practical application of these systems is complex. The severe and varied working conditions and production environments require careful consideration when choosing and applying the appropriate corrosion protection to achieve the best, long-lasting outcomes.

Acid-resistant bricks, also known as acid-proof bricks, are made from unique ceramic materials that can withstand acidic environments. They are often used in linings for tanks, reactors, and other equipment.

Graphite and carbon bricks are highly effective for acid protection in industrial environments due to their excellent resistance to various corrosive chemicals. Carbon bricks are typically made from high-purity carbon materials, which provide superior resistance to acids such as hydrofluoric acid (HF), phosphoric acid, sulfuric acid, and hydrochloric acid (HCl).T hey are designed to withstand long-term exposure to highly acidic and high-temperature conditions.

Silicon Carbide (SiC)

Silicon carbide exhibits excellent resistance to a variety of acids, including hydrochloric acid, nitric acid, and sulfuric acid. This resistance is due to forming a thin, protective layer of silicon dioxide (SiO_2) on its surface, which acts as a barrier against further corrosion.

Epoxy Resins

Epoxy resins can offer good resistance to phosphoric acid, especially when cross-linked with suitable hardeners. However, their performance can degrade at higher temperatures and concentrations. Unique formulations and additives can enhance their resistance. The performance of Novolac epoxy resins exposed to concentrated sulfuric acid at medium temperatures using adequate modifiers is excellent.

Vinyl Ester Resins

Vinyl ester resins are highly valued in industrial applications for their excellent chemical resistance, particularly in acidic environments. They offer superior resistance to a wide range of acids, including strong acids and oxidising environments, even at higher temperatures. This makes them ideal for harsh chemical conditions, like phosphoric and nitric acid applications.

Phenolic resins

These resins are highly resistant to phosphoric and sulfuric acids. They are often used in tank linings and other applications requiring strong acid resistance and high temperatures. Vinyl ester resins are among the best choices for handling concentrated phosphoric acid and Novolac epoxy resins for sulfuric acid at 90°C. Phenolic resins can also be used; still, their performance may vary based on specific formulations and conditions.

Polyethylene

Both high-density (HDPE) and low-density (LDPE) polyethylene resins offer good resistance to phosphoric acid (85%) and sulfuric acid (70%) making them suitable for storage tanks and piping with limitations at higher temperatures.

Fluoropolymers

Polytetrafluoroethylene (PTFE—sometimes known as Teflon), ethylene tetrafluoroethylene (ETFE), fluorinated ethylene propylene (FEP), and perfluoroalkoxy (PFA) are highly resistant to a wide range of corrosive chemicals, including sulfuric and phosphoric acids. PTFE is often used in gaskets, seals, and linings for its excellent chemical resistance. Most of these fluoropolymers resist temperatures up to 260°C, crucial for maintaining performance in harsh chemical environments. In addition, these fluoropolymers offer superior wear resistance,impact toughness, and radiation resistance.

Asphalt

This material is not highly resistant to phosphoric or sulfuric acid, specifically when unmodified asphalt is used, and may degrade relatively quickly. However, it can be modified to improve its resistance. Polyphosphoric acid (PPA)—modified asphalt can offer better durability and resistance in such environments. PPA enhances the high-temperature performance of asphalt and can improve its resistance to chemical attack, including phosphoric acid.

Methods for Control

Companies, such as Knight Material Technologies can provide cost-effective solutions for controlling corrosion in fertilizer production facilities. This could include methods such as a membrane with a carbon brick lining to protect the membrane, or an advanced fluoropolymer lining as an alternative to traditional alloys (e.g., stainless steel vessels, towers, or reactors). Various ceramic, organic and polymeric coatings are also used to protect metal surfaces. However, these coatings can develop porosities, allowing hydrogen ions to penetrate and initiate corrosion. Advanced coatings offer improved protection by providing a more uniform and less porous barrier.

Coating steel with carefully formulated protective solutions and membranes in less severe corrosive environments can be a viable alternative. Additionally, cathodic or anodic protection methods, which involve applying a protective electrical current to the metal surface, can help to prevent corrosion and extend the service life of simple surface protection systems. This technique is particularly effective in environments where coatings alone are sufficient.

But what if corrosion, or depletion of the corrosion protective barrier, has evolved to the point where the steel shell of the equipment has been compromised? To combat this, Knight Material Technologies has developed an injection procedure in which technicians inject a corrosion-resistant resin into the voids created by the depleted membrane and fill those spaces to extend the service life of the equipment.

Conclusions: Conquering and Controlling Corrosive Effects

Adequate corrosion protection in fertilizer production is crucial for maintaining the integrity of processing equipment and ensuring continuous, cost-effective operations. By employing a combination of inhibitors, advanced coatings, cathodic and anodic protection, and selecting appropriate corrosion protection materials, the industry can mitigate the adverse effects of corrosion and enhance the longevity of its infrastructure.

Implementing a proper corrosion protection system extends the service life of the equipment and reduces maintenance costs, which can be substantial and may require facility shutdowns. The effectiveness of the protection system depends on the appropriate selection of materials, correct surface preparation, and the use of suitable application equipment and trained personnel. Therefore, choosing a protective solution that meets industry standards, such as those set by NACE or ASTM, is imperative.