ATI

Technical Data Sheet

Zirconium in Urea Applications

INTRODUCTION

Urea is one of the most important nitrogenous fertilizers, with the highest nitrogen content of common solid fertilizers. As a stable solid, it is safer and easier to transport than ammonia. In addition to fertilizer, urea is also used increasingly as a very effective additive to diesel fuel for NOx control, increasing the permissible engine operating temperature and thus the overall efficiency of the engine. Other uses of urea include the starting material for melamine production.

First artificially synthesized by Wöhler in 1829, modern production of urea is typically done in large scale plants using high pressure and temperature. The standard processes use ammonia and carbon dioxide as the feed materials, and therefore urea plants are usually connected to ammonia plants.

Urea synthesis is a two-step reaction, and parts of the process contain significant concentrations of the intermediate material, ammonium carbamate. At the temperature of production (approximately 160°C (320°F) and higher), ammonium carbamate is very corrosive to most materials. Although there are grades of stainless steel that have been specifically designed for use in urea plants, ammonium carbamate’s aggressive corrosiveness limits the maximum temperature and operating parameters that a plant may maintain.

One of the first uses for zirconium outside the nuclear industry was in urea production. Since that time, it has proved itself to be the ideal material for urea production, including the most aggressive parts of the plant.

CORROSION RESISTANCE

Zirconium has a very tenacious, naturally occurring, passive oxide layer that is virtually impervious to conditions inside a urea process plant. As compared to stainless steel, zirconium does not require any additional oxygen to be added to the process stream to remain resistant to corrosion. Additionally, zirconium has a much higher temperature capability in the urea process solution compared to other materials.

Compared to zirconium, many of the other common alloys in urea service compromise one desirable attribute for another. Stainless steel, the most common metal in a urea plant, requires passivation air to be injected into the process stream to maintain a passive corrosion resistant layer. Even with this layer, stainless steel will corrode somewhat, releasing Fe, Ni, and Cr ions into the process stream. Furthermore, stainless steel has a maximum temperature limitation of approximately 205°C (401°F), above which it experiences active corrosion.

Table 1. Corrosion Resistance of Zr

Material	Media	Temp.	Corrosion Rate
Zr702	50% Urea	Boiling	< 1
Zr702	45% Urea, 17 % Ammonia, 15% CO_2 10% Water	193	< 1

Titanium is also used frequently in urea processing applications due to its passivity in the urea processing environment. However the oxide layer of titanium is not nearly so hard and tenacious as that of zirconium, and it therefore suffers from localized erosion / corrosion on the inside of heat exchanger and stripper tubes tubes, specifically where the fluid velocity is high.

Zirconium is extremely well suited to the urea processing environment; it has a very high tolerance for variable plant conditions and compositions. Very little formal corrosion data has been generated for zirconium in this application beyond the numerous successful applications in operating plants. Numerous in-plant coupon tests have helped to confirm the operating plants’ experience.

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SUCCESS STORIES

Zirconium has been an important material in critical parts of urea plants for over 40 years. One of the original processes used a zirconium liner in the urea synthesis reactor that operated at temperatures as high as 220°C (428°F) without any problems. In another old process, zirconium heat exchangers that replaced poorly performing Hastelloy®, silver, and lead-lined equipment, were found to have no signs of corrosion after 20 years of service.

Zirconium has found extensive use in Snamprogetti's urea process, specifically in the high pressure stripper where corrosive conditions are most severe. Bimetallic tubes are stainless steel (25Cr, 22Ni, 2Mo) with a tight-fit zirconium liner inside that were developed to take advantage of zirconium's corrosion resistance to protect the inside of the tubes where the stripping action takes place. More than a decade of experience has clearly shown that zirconium is virtually impervious to the most corrosive conditions in the urea plant.

More recently, a stripper constructed of cladded zirconium and solid zirconium tubes was fabricated for the largest urea plant in the world to provide the ultimate in robust process performance. The use of zirconium, and the elimination of stainless steel from all of the interior wetted surfaces allow the elimination of passivation air addition to the stripper and the ability to increase the stripping temperature to at least 210 – 212°C (410 – 414°F), providing up to 15% added capacity. In addition to improved plant performance, this zirconium stripper will not have any of the ongoing maintenance concerns associated with stainless steel.

Another new development that is now available for Snamprogetti's urea producers is OmegaBond® Advanced Tubing. Using a zirconium liner that is metallurgically bonded to the inside of a titanium tube, OmegaBond® Tubing provides all of the benefits of a solid zirconium stripper along with the added benefit of being able to use a standard titanium clad stripper.

LIMITATIONS

Zirconium is highly resistant to corrosion in typical urea processing conditions. However, certain impurities are known to be deleterious to zirconium even in relatively low concentrations. Fluoride, in particular can cause rapid general attack on zirconium, especially in an acidic environment. Additionally, some metal ions (i.e., Cu or Fe3+) may promote the initiation of pitting in certain conditions.

SUMMARY

Zirconium has a long successful track record in solving very difficult corrosion problems in the urea industry. In an era where urea plants are expanding and "mega" plants with capacities approaching 5000 tpd are designed and built, plant downtime and corrosion issues in general are greatly magnified in their significance regarding process reliability and operation profitability. Increasing, process designers and operators are looking to zirconium to provide the materials performance necessary for these mega-plants.

By using zirconium, existing urea processes can perform at a higher level. Increasingly capacity, energy savings, reduction of corrosion products in the process stream, and elimination of the requirement for additional passivation air, and other environmental benefits in addition to longer equipment life may be possible with the proper application of zirconium.

For further information or questions about zirconium or OmegaBond® Tubing in urea applications, contact the Technical Services Division at ATI.

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