Stainless Steels and other Alloys in Urea Plants

UreaKnowHow.com
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1. Introduction

Special stainless steel grades must be used in the high pressure urea process to achieve long service life. The process conditions are highly corrosive and as the corrosion mechanism is complex, the development of suitable alloys has been concentrated in the past on refining existing grades by continuous improvement. The use of these special “urea grades" has resulted in low maintenance costs and long service life. Proper control of the process, as well as high pressure equipment manufactured with high quality products, is also needed for a long service life.

2. The traditional alloys

Over the last 30 years, two austenitic stainless grades have been dominant in urea plants with stripper technology. The lower alloyed version is a modified ASTM 316L (UNS No 31603), referred to as 316L MOD or 316L Urea Grade. It is modified to meet the requirement of a maximum 0.6 % ferrite and a maximum corrosion rate in the Huey test of 0.60 mm/year. Both are needed to provide the low corrosion rate for this type of alloy. The commercial version of 316L does not meet these requirements, as the alloy elements as per codes are too low in combination with too high carbon.
For the more corrosive areas, a higher alloyed material is needed. It is referred to as 25/22/2, which stands for the chromium, nickel and molybdenum contents. With a chromium content raised from 17 to 22%, and increased nickel content from 14 to 22%, corrosion resistance was further improved compared with 316L Urea Grade. Also, 25/22/2 alloy has an international designation UNS S 31050 (AISI 310) WSN 1.4465 or WSN 1.4466


Stainless Steel Sandvik tubes under fabrication

However, for use in the urea process, the impurities like sulphur, phosphorus and carbon have to be kept low, and as S31050 allows rather high impurity levels, it is not sufficient to specify the alloy by using only the UNS designation. As Sandvik was involved from the beginning in developing the

25/22/2 type, and thereafter made improvements to the composition, we believe that we produce the best 25/2212 version.

Corrosion and passivation

Urea is made by the reaction of ammonia and carbon dioxide under a pressure of 150-220 bar, in a reactor at temperatures in the range 170-200°C. The corrosive conditions are severe in all high pressure parts where the intermediate component ammonium carbamate is present. Several factors govern the corrosion of stainless steel in carbamate solutions.

Corrosivity is influenced by the amount of carbamate, but also by the ammonia/carbon dioxide ratio. Of utmost importance is the oxygen content. If there is no oxygen present, stain less steels will corrode actively at high rates, whereas only small amounts of oxygen are sufficient to keep them in the passive state. The amount of oxygen necessary is determined by the type of steel being used. For safety reasons, oxygen is added continuously to the feed. The effect of dissolved oxygen on the corrosion rate of different stainless alloys is illustrated in table 1 The table confirms the better performance of UNS No *31050 (25/2212),* which needs less oxygen to passivate and shows less loss of material in both the active and passive states. In operation, the oxygen addition must be much higher to ensure that there is a sufficient amount of oxygen in all parts of the plant.

Table 1: Effect of dissolved oxygen content on the corrosion rate of stainless steel alloys in urea solution.

O_2, *ppm*	Corrosion rate, *mm/year*	
	UNS No 31603	UNS No 31050
0,5	30-40 active [1]	10 active [1]
1	30-40 active [1]	10 active [1]
3	30-40 active [1]	0,03 passive [2]
5	0,12 passive [2]	0,03 passive [2]
7,3	0,12 passive [2]	0,03 passive [2]

Note: 1: Active corrosion, 2: The steel is in the passive state.

The urea synthesis is helped by an increase in temperature, which on the other hand will also increase the corrosion rate of metallic materials.

3. The new alloys

Safurex®

Safurex® is a duplex stainless steel grade exclusively developed by Sandvik Materials Technology and Stamicarbon for the Stamicarbon Urea process.

Sandvik Materials Technology is a world leading producer of high technology stainless steels, special alloy materials and advanced value-added products, developed in close cooperation with customers. Sandvik is a world leading producer of seamless stainless steel tubes and has total control over the entire production process from steel melt to the finished product. Their tubes are typically used within industries such as: chemical and petrochemical, oil and gas, power generation, fertilizer, pulp and paper and mechanical.
Sandvik Materials Technology has supplied quality products for high pressure urea service for more than 30 years. The best recognition for outstanding quality are that most plants in the world use our products and that the longest service record has been set with Sandvik 2RE69. The modern large scale urea plants are very efficient, in spite of the highly corrosive environments in the critical equipment. The high pressure and temperature in combination with toxic ammonia calls for best special stainless steel as Sandvik 3R60 Urea Grade (316L Urea Grade), Sandvik 2RE69 (25/22/2), Bimetallic tubes or Safurex®.
Sandvik manufactures and stocks tubes, pipes, fittings, bar, plates and welding consumables. The products conform to the specifications from leading licensees like Stamicarbon and Snamprogetti.

Stamicarbon is the technology leader in the urea industry, licensed more than 50% of all urea plants worldwide. Stamicarbon is continuously innovating the urea process with famous examples like the CO_2 HP stripper, pool condensation, 25-22-2 stainless steel and Safurex®.

Safurex® is a high alloy ferrite-austenite stainless steel, combining the good (stress) corrosion properties of the ferrite steel with the good ductility and weld-ability of austenitic steel.
The duplex structure results in high mechanical properties and, in combination with the low thermal expansion coefficient, results in great benefits with respect to the design and construction of the HP urea equipment. Not only savings in equipment weight but consequently also in costs are evident.
Safurex® is the standard material for Stamicarbon HP urea equipment, allowing the Stamicarbon urea plants, in case all wetted parts in the HP synthesis section are made in Safurex®, to run with very low and likely zero oxygen in the carbamate solution.

The good corrosion resistant properties of Safurex®, also in oxygen free carbamate solutions, have been demonstrated in elaborate laboratory testing and field experiences with Safurex® equipment and materials in service since already 1997.
All material forms (plates, forgings, heat-exchanger tubes, piping) and welding consumables needed to fabricate HP equipment and HP Piping in Safurex® are available and proven.
Also delivery time of these materials is comparable or better to other stainless steels grades.
SBN to date has fabricated more that 75 HP Urea equipment in Safurex® and the handling as well as the welding is not more difficult compared to the fully austenitic stainless steels grades traditionally used.
Safurex® has also improved resistance against stress corrosion cracking if exposed for chloride, which can occur with 316L Urea Grade and 2RE69 if chloride content is higher than recommended on the steam side in H.P. carbamate condenser. In practical terms, stress corrosion cracking is not a problem when using Safurex® in the H.P. carbamate condenser.

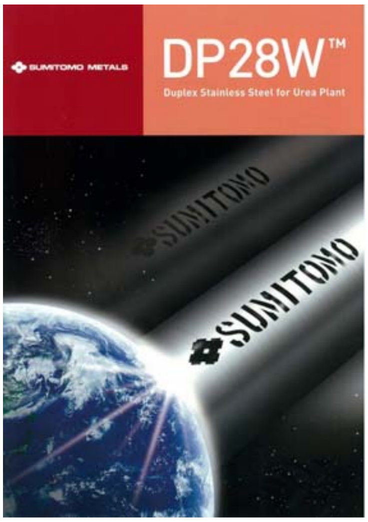
Safurex® HP stripper ready for shipment from SBN shop in Austria

The improve corrosion resistance means the oxygen addition can be reduced, which makes it possible for Stamicarbon to offer new and more cost effective plants. The operation becomes easier and the capital cost is reduced compared with the older design.

DP28W™

Another new super duplex, ferrite-austenite stainless steel DP28W™ has been developed by Sumitomo Metal Industries, Ltd. and Toyo Engineering Corporation (TEC) specifically for use in urea plants.

Sumitomo produces a wide range of steel products, including sheets and tubular products, and such non-ferrous metals as aluminum and titanium. Sumitomo is expanding its value chain by precisely responding to the diverse needs of customers in a huge variety of fields. In steel sheets, Sumitomo is leveraging their steel service center network in Japan and overseas to provide services, including procurement, storage, processing and just-in-time supply, mainly to automobile and home appliances manufacturers. In tubular products, Sumitomo is enhancing their functions as a total service provider by developing oil field services in addition to supplying tubular products to leading oil and gas companies through our Tubular Information Management System (TIMS), a proprietary SCM system.



TOYO Engineering Corporation has accumulated experience and expertise with petrochemical plants and with fertilizer and other chemical plants. TEC has developed their own technologies for building plants that produce environmentally-friendly, energy-conserving and high-quality products with impressive efficiency. Our experience is extensive, and encompasses ethylene, propylene, polymers and aromatics in the areas of petrochemical plants, urea, ammonia, methanol, and high-performance plastic materials. We have consistently offered state-of-the-art technologies in these areas, by improving proprietary technologies and collaborating with licensors of related technologies. TEC's market share in licensing urea plants is about 15% worldwide.

DP28W™ has an excellent corrosion resistance in urea-carbamate solutions, and high resistance to stress corrosion cracking in the chloride containing environments. Its properties are characterized as follows;

- Excellent resistance to general corrosion in urea-carbamate solutions
- High resistance to stress corrosion cracking
- Very high mechanical strength
- Good weldability
- Good formability

The corrosion properties in urea carbamate solution are being proved both in a pilot plant and commercial plants. Practical experience in this type of environment has shown that DP28W™ has highly corrosion resistance.
Duplex stainless steel, in particular DP28W™, has a big advantage in re-passivation properties because of high chromium and lower nickel content. DP28W™ has the ability to form the passive layer, that gives resistance to active corrosion, under the condition of very little dissolved oxygen. This excellent re-passivation property contributes to minimize the risk of active corrosion.
DP28W™ has good weldability. Chemical composition of DP28W™ has been designed to prevent sigma phase precipitation during thermal cycles and to exhibit excellent corrosion resistance in both the base metal and its weldment. Preheating or post weld heat treatment is not necessary. Interpass temperature shall be controlled below 150 ^{o}C. Matching filler metals have been developed for gas tungsten arc welding [GTAW] and electro slag welding [GESW].

DP28W™ has been applied mainly as internal parts of TEC's urea plants since 2002. In 2004, DP28W™ was nominated as one of the candidate materials of synthesis reactor of a total recycle plant in Japan which had been considered to be replaced. The owner had strong intention to operate a new reactor under the same operating condition as an existing reactor, which was fabricated with titanium. But for the materials to be nominated, the operating condition seemed to be very severe because titanium requires little amount of passivation air even at high temperature. After one year immersion test into the reactor, DP28W™ was selected because it showed the best result among candidate materials. The corrosion rate is far lower than titanium. The reactor that is fabricated with DP28W™ has started into operation successful since 2006 under the same operating conditions as the case for titanium.

4. NH_3 stripper

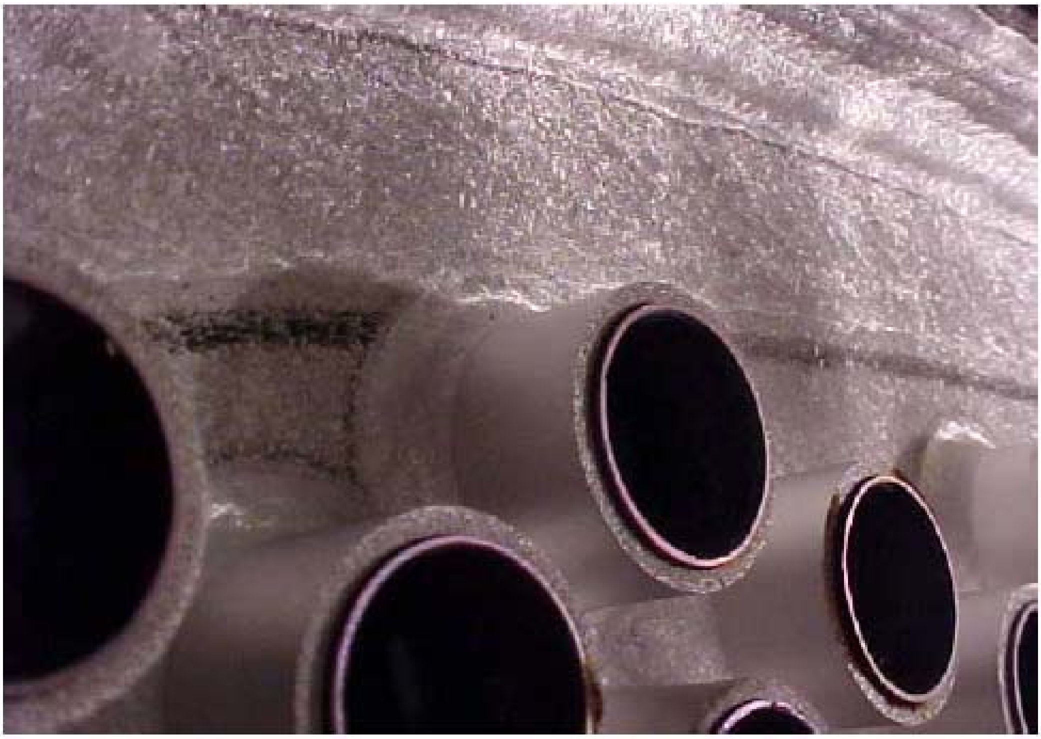
With the recent acquisition of Snamprogetti, the already considerable onshore activities of Saipem, traditionally focused on world-class construction, have found an excellent match and complement. The new combined Company now offers a complete range of project definition and execution services, from feasibility and front end studies to design, engineering, procurement and field construction (EPC), in virtually every world market, leveraging on its specialised skills across the most significant product lines in the oil, gas, refining, chemical and power industries. The new Saipem group is therefore a one-stop-shop to give life to the most complex and largest onshore projects in the world. Saipem's market share in urea licensing is about 35% worldwide.

In Saipem's NH_3 stripping urea process, the NH_3 stripper is a challenging High Pressure equipment item in terms of finding the right alloys to ensure a long lifetime. Whereas other high pressure equipment items can reach lifetimes of 20-25 years, the lifetime of the NH_3 stripper is max 10-15 years and this is only reachable by rotating the stripper after 6-8 years, so by re-installing the stripper upside down.

First Titanium was used as alloy protection against carbamate corrosion. Titanium has been used extensively in the urea industry and has many attributes that allow it to provide good service life. Although titanium does resist direct corrosion by ammonium carbamate, its oxide layer is prone to erosion. This leads to localized erosion where high fluid velocities abrade the protective layer. This phenomenon causes the tubes to wear at predictable rates. While titanium is not very sensitive to the urea chemical environment, the erosion leads to a limited lifetime in service. Some plant operators have extended titanium stripper life by tearing down and rebuilding the stripper after several years of service.

In order to utilize titanium in a urea stripper, the titanium tubes must be welded to a suitable substrate. Titanium cannot be successfully welded directly to ferrous alloys; specifically, a weldment made by joining two dissimilar metals results in a joint that can be expected to exhibit poor mechanical and corrosion performance. To avoid a dissimilar metal weldment, the interior surfaces of the stripper's upper and lower chambers and tubesheets are explosively clad with titanium. Cladding provides a titanium surface onto which the titanium tubes can be welded. A limitation in this configuration is that stainless steel cannot be used as the tubing material due to the incompatibility of the two metals during fusion welding. Previously, when re-tubing a titanium stripper, the choice of material has been limited to titanium, which historically has been subject to large swings in price and availability.

Saipem then introduced the Bimetallic stripper where the tubes were consisting of a zirconium tube in a 25/22/2 stainless tube. Zirconium is also an excellent alloy against carbamate corrosion and also does not face any erosion problems. However corrosion problems occurred in 25-22-2 stainless steel in the bottom of the stripper due to the high process temperatures (205-210 ^oC); adding extra air (oxygen) reduced the overall corrosion problems but could not result in a longer overall lifetime.



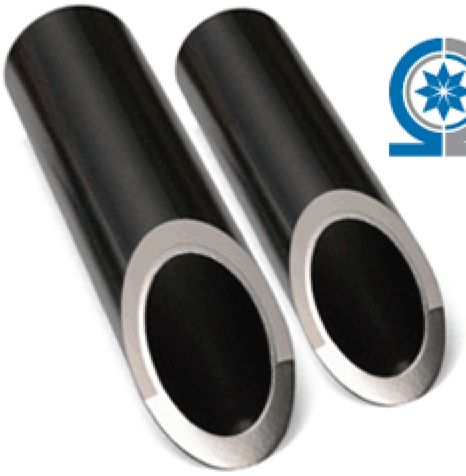
Corrosion at tubesheet weld overlay Bi-metallic NH_3 stripper at Safco, Saudi Arabia

Bi-metallic tubing is a large-scale adoption of zirconium that uses stainless steel as the material of construction for the structural component of the tubes with a mechanically fitted interior liner of zirconium. This design is intended to put the most corrosion-resistant material on the inside of the tubes where the greatest potential for corrosion exists. It allows the stainless steel jacket to bear the structural load and gives fabricators a stainless steel outer layer of tube to weld into a stainless steel tubesheet. Bi-metallic strippers have been employed at many urea plants and can be utilized, given careful adherence to known operating conditions and limitations. However, even with close adherence to proper operating conditions, the tubes at the bottom of the stripper will continue to suffer corrosion related issues due to the high temperature associated with the process.

A more robust solution over the current bi-metallic design is desired to ensure a higher factor of safety with respect to materials design and performance. For example, because the upper and lower stripper chambers and the tubesheets, in a typical bi-metallic unit, are manufactured from solid un-clad stainless steel, passivation air is still needed to prevent rapid corrosion. Furthermore, the lack of a true bond between the zirconium and stainless steel may allow carbamate solution to penetrate between the zirconium liner and the stainless steel outer tube. As this penetration is localized and occurs outside the bulk fluid flow, a crevice environment is created in which the media is not thoroughly oxygenated. In such cases, the isolated fluid becomes very corrosive to the stainless steel and is often times in a location where detection is difficult.

Now Saipem developed together with Ati Wah Chang the OmegaBond™ tubes.
Ati Wah Chang is part of the Allegheny Technologies Incorporated group of specialty metal manufacturers. Based in Pittsburgh, Pennsylvania, USA, Allegheny Technologies and its global resources have enabled Wah Chang to strengthen its position as one of the world's preeminent providers of strong, versatile, corrosion-resistant metals and a variety zirconium-based chemical products.
In 2004, ATI Wah Chang and Saipem began working together to jointly bring to market a new series of advanced tubing solutions for urea plants using Saipem's process technology. The result of this collaboration was OmegaBond™ advanced tubing technology which could enable urea and other chemical processing manufacturers to realize numerous benefits. Recognized benefits include: a reduction in corrosion-related down time, reduced maintenance related costs, potential energy

savings, and finally the technology should allow for more aggressive operating conditions with higher process yields.



This new tubing solution utilize solid-state joining technology where the interface between the two metals never reaches a molten state. By not allowing them to melt together, an alloy of the two does not form. Instead, the metals are plastically "forged" together at a temperature less than 50% of their melting points. The resultant joint has virtually no diffusion zone, no inter-metallic compounds, and no alloying. Likewise, the heat affected zone is negligible, if present at all.

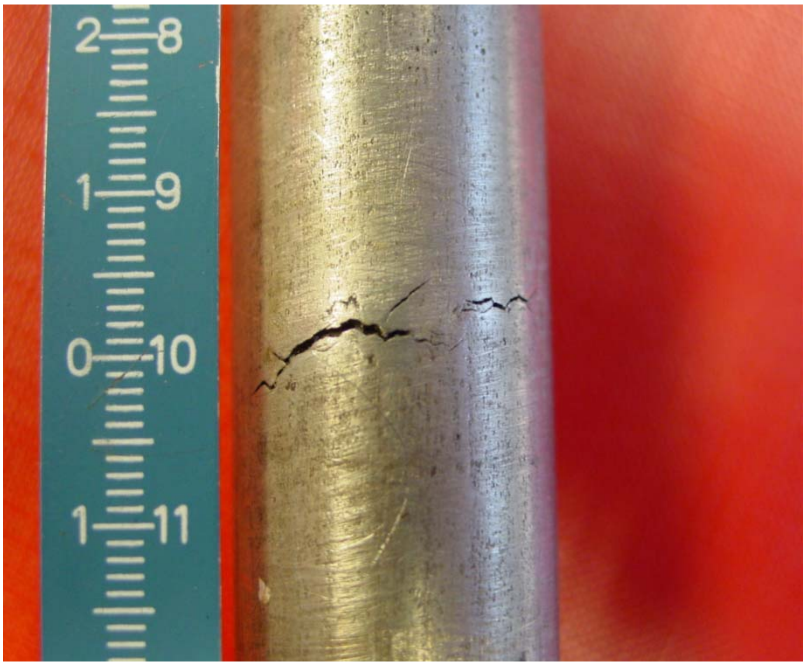
The two primary solid-state joining technologies in use in this development are extrusion bonding and inertia welding. Due to the lack of a significant transition zone or diffusion layer in either, both create high integrity, repeatable bonds that are strong and ductile. Likewise, the corrosion resistance should be the same as the parent metal.

OmegaBond™ tubes target to solve both the corrosion and erosion problems faces earlier in NH_3 strippers. The first NH_3 stripper with OmegaBond™ tubes will be in operation mid of 2009.

Agrium, USA has gained several years experience with Safurex® in their NH_3 stripper with good results proving that Safurex® has significant better corrosion resistance properties even at higher temperatures.

5. Chloride Stress corrosion cracking

With the traditional alloys 316L Urea Grade and 25/22/2 stainless steels several high pressure equipment items in urea plants suffered from chloride induced stress corrosion cracking problems.
Once some chlorides entered the cooling water, steam system or process side and had a chance to accumulate, cracks would show up in the stainless steel parts.



Cracks in a stainless steel tube

This crack formation could only be slowed down and would lead to an early and expensive high pressure equipment replacement project.
For this reason duplex was introduced in urea plants as duplex grades are better resistant against chloride stress corrosion cracking. Also Safurex® and DP28W™ are duplex grades and are therefore not sensitive for this kind of corrosion. The same is valid for Titanium and Zirconium.

References:

1. The special stainless steels from Sandvik Materials Technology for urea service, Mr. Knut Tersmeden, Business Development, Sandvik Materials Technology, 2006-11-29
2. Bi- Metallic Stripper Failure, Mr. Ali Al-Majed, Manager, Technical Support Dept. Saudi Arabian Fertilizer Co. (SAFCO), (SABIC Affiliate), Saudi Arabia, AFA 18th International Annual Technical Conference & Exhibition, 5-7 July 2005, Sheraton Hotel- Casablanca
3. DP 28W™, Duplex Stainless Steel for Urea Plant, Sumitomo Steel
4. ATI Wah Chang, Special Alloy Fabrication, Technical Data Sheet
5. Chlorides in urea plants, Mark Brouwer, Mechanical Paper May 2009 UreaKnowHow.com

Mark Brouwer was born on July 6, 1966 in Groningen, The Netherlands. He graduated in 1988 at the Technical University of Eindhoven at the faculty of Chemical Engineering. His thesis was about the production of ethylene by partial oxidation of natural gas.
After University Mark joined Military Services, Dutch Royal Navy where he was working at the Prins Maurits Laboratory of TNO in Rijswijk. In this period he was involved in Process simulation studies on the absorption of poisonous gasses on active carbon.

In 1990 he joined DSM, working for the Ethylene Plant No.4 as a Process Engineer. In these seven years he was involved in the Basic Engineering of a debottlenecking project at Stone & Webster in London and in the implementation of the DSM Extraction Styrene project (from Conceptual Engineering up to the successful start up) .

In 1997 he joined Stamicarbon, the Licensing subsidiary of DSM as Licensing Manager Urea Revamps. Later he became Manager Stamicarbon Services responsible for all Stamicarbon's activities in existing urea plants, such as After Sales, Plant Inspections, Debottlenecking Projects, Reselling projects etc. In these nearly twelve years he did visit nearly one hundred urea plants worldwide and was involved in numerous revamp, relocation, debottlenecking and grass root projects.

Since January 1, 2009, Mark Brouwer left Stamicarbon and started up UreaKnowHow.com.
UreaKnowHow.com is an independent group of urea specialists with an impressive number of years experience in designing, maintaining and operating urea plants. UreaKnowHow.com's mission is to support, facilitate and promote the exchange of technical information in the urea industry with the target to improve the performance and safety of urea plants.

Please feel welcome at UreaKnowHow.com, the website where the urea industry meets.

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features

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