The use of duplex stainless steels in the chemical process industry has expanded rapidly over the past few years. They are now used not only in chloride environments, where they are more resistant to SCC than austenitic stainless steels, but also in a wide variety of other demanding applications.

In DSM plants, duplex is used especially for chloride-containing process fluids and for ammonium carbamate solutions. The material has been found to offer good resistance to chloride SCC, although such corrosion can and does occur at pH values lower than 3 to 4. This we established both in the field and through CERT (constant extension rate testing).

In a strongly alkaline chloride-bearing solution, duplex SS gives excellent performance whilst a high-nickel alloy fails after about three years because of SCC. These findings are supported by drop evaporation tests.

In oxygen-free carbamate solutions, duplex has proved to be even more corrosion resistant than much more costly materials such as titanium and high-nickel alloys. In the high-pressure synthesis section of urea plants, duplex is an excellent alternative to traditional urea grades such as type AISI 316 L UG and X2CrNiMoCu 21 8 3 2. These are particularly prone to SCC on the steam side of heat exchangers when the boiler feedwater is contaminated with chlorides.

Fabrication of high-pressure vessels in duplex is not without difficulty, however. Also, the duplex must meet particular quality requirements to ensure proper performance in carbamate environments. These have meanwhile been defined in a DSM/Stamicarbon material standard. Use of duplex SS can offer significant cost savings. As a case in point, a condenser, which has given 12 years of satisfactory service, cost US $ 300,000. The same vessel in high-nickel alloy would have cost US $ 1,000,000.
Various types of duplexes have been used here including 22% Cr and 25% Cr grades like X2CrNiMoN 22 5 3 and X2CrNiMoCuN 25 7 3 2. For nitric acid and acidic ammonium nitrate solutions the molybdenum-free type X2CrNiN 23 4 is used. The workhorse among the duplexes used in DSM and Stamicarbon-licensed plants is X2CrNiMoN 22 5 3. This gives good performance in, for example, a 12% NaCl solution with pH 14 at temperatures up to 200°C. In one instance it has lasted for nine years without any failure while a high nickel alloy failed after 2 years due to stress corrosion cracking.

Laboratory stress corrosion cracking examinations by means of drop evaporation tests (DET) showed that duplex stainless steels have a better stress corrosion cracking resistance in alkaline (chloride containing) solutions than high-nickel alloys.

Experience with duplex stainless steels in oxygen-free carbamate solutions was first reported at the 9th European Congress on Corrosion, 2–6 October 1989 in Utrecht, the Netherlands (Ref. 1). The first large-scale application of duplex stainless steel on this service was a condenser which gave 12 years of satisfactory service. The same unit in titanium and a high-nickel alloy had to be replaced after 5 and 8 years respectively. The duplex cost US $ 300,000 while at the time a high-nickel alloy unit would have cost US $ 1,000,000.

This paper discusses the application and benefits of duplexes used on urea service. It also reports on a new duplex stainless steel specially developed for carbamate service in urea plants.

2 Stamicarbon CO₂-stripping urea process

(Ref. 2) The production of urea is based on the following reaction mechanism:

2 NH₃ + CO₂ → NH₂COONH₄

NH₂COONH₄ → CO(NH₂)₂ + H₂O

The process flow diagram of the Stamicarbon stripping process is shown in figure 1. The synthesis section consists of a urea reactor (c), a stripper for unconverted reactants (d), a high-pressure carbamate condenser (e) and a high-pressure off-gas scrubber (f). In the carbamate condenser (e) CO₂ and NH₃ are converted into ammonium carbamate. In the reactor the ammonium carbamate is partly converted into urea and water.

The urea synthesis process takes place at a pressure of 140 bar and a temperature of 185°C. The bulk of the unconverted carbamate decomposes in the stripper, where ammonia and carbon dioxide are stripped off. This stripping is effected by countercurrent contact between the urea solution and oxygen-containing carbon dioxide at synthesis pressure. The oxygen is needed to maintain a passive (corrosion resistant) layer on the stainless steels in the synthesis section. On leaving the stripper, gaseous ammonia and carbon dioxide are condensed in the high-pressure carbamate condenser (e) at synthesis pressure. Before being purged from the synthesis section, the inert gases, mainly oxygen and nitrogen, are washed in the high-pressure scrubber (f)

Figure 1. Stamicarbon CO₂-stripping urea process.
with carbamate solution from the low-pressure recirculation section. The urea synthesis solution is highly corrosive, the most aggressive component being ammonium carbamate. Consequently, materials of construction to be used here must meet high standards in terms of composition and quality. Awareness of the important factors in materials selection, equipment design, manufacture and inspection, technological design and proper plant operations, together with periodic corrosion inspections, are the key factors for safe operation for many years.

3 Corrosion aspects

3.1 Condensation corrosion
Stainless steels in a corrosive environment like ammonium carbamate owe their corrosion resistance to the presence of a protective oxide layer on the surface. As long as this layer is intact, the metal corrodes only at a very low rate. Passive corrosion rates in liquid phases are generally between 0.01 and 0.1 mm/year. In gas phases where mixtures of ammonia, carbon dioxide and water vapour can condense to form carbamate solutions passive corrosion rates can increase to 0.2 mm/year. Active corrosion rates in carbamate solutions can be as high as 50 mm/year. Stainless steels exposed to carbamate-containing solutions in urea synthesis section can be kept in a passivated state by adding a given amount of oxygen. If the oxygen content drops below this limit, active corrosion starts after some time. Adding oxygen and maintaining a sufficiently high oxygen content in the various process streams are prerequisites to preventing corrosion of the equipment and pipelines.

From the point of view of corrosion prevention, condensation of NH₃-CO₂-H₂O gas mixtures to carbamate solutions warrants extra attention. Despite the presence of oxygen, a more corrosive condensate is initially formed on condensation. Passivation is believed to take place via a metal ion redox system, which is missing in freshly formed condensate. This accounts for the severe corrosion sometimes observed in cold spots in the channels of HP equipment and gas lines fabricated from urea grade 316L. Such corrosion can be prevented by adequate insulation and tracing. When condensation forms part of the process, as in the HP carbamate condenser, special technological measures must be taken. One such measure is adding an oxygen-rich liquid phase containing a metal ion redox system into the condenser, with liquid-gas distribution devices preventing dry spots on surfaces where condensation takes place.

The risk of condensation corrosion can also be diminished by choosing a more corrosion-resistant material of construction. The higher alloyed austenitic stainless steel type X2CrNiMoN 25 22 2 is less susceptible to condensation corrosion than urea grade 316L. Type X2CrNiMoN 22 5 3 duplex stainless steel has proved to be more corrosion-resistant in condensing environments too. Another benefit of duplex stainless steels is their higher strength. Duplex high-pressure piping can be much thinner than austenitic stainless steel piping. During a turnaround in October 1996, after being on-stream for about 28 years, the strip gas line from the HP stripper (d) to the HP carbamate condenser (e) had to be replaced due to condensation corrosion. The urea grade 316L line, measuring 219 X 22.2mm and 70 m long had a corrosion allowance of about 6mm. For duplex stainless steel a corrosion allowance of 4mm will do, so leading to 219 X 14mm pipe. Replacement by type X2CrNiMoN 22 5 3 duplex (seamless hot extruded) pipe gave a cost saving of about 10%.

Another advantage of duplex is its high resistance to chloride stress corrosion cracking. This can be particularly relevant for plants in coastal areas. Such piping in austenitic stainless steel needs to be suitably painted to minimise the risk of SCC. Duplex stainless steel piping need not be painted.

3.2 Stress corrosion cracking in HP carbamate condenser
The ammonia and carbon dioxide leaving the stripper are condensed in the HP carbamate condenser (e) at synthesis pressure. The heat released in the formation of ammonium carbamate is used for the production of 4.5 bar steam. Any chlorides entering the shell side of the HP carbamate condenser are likely to initiate stress corrosion cracking of the austenitic stainless steel tubes, starting from the outside surface of the tubes. Numerous cases of stress corrosion cracking are on record. Cracking has been observed in both urea grade 316L and X2CrNiMoN 25 22 2 tubes. An example of stress corrosion cracking a urea grade AISI 316L HP carbamate condenser tube is...
shown in figure 2. The location of the cracks is indicated in figure 3 for expanded-and-welded tubes and for welded tubes. Stamicarbon does not allow the tubes to be expanded in the tubesheet because this would render the leak detection system inoperative.

Leakage may result from pinholes in the tube joints. In most cases cracking merely occurred in or near the top tubesheet. The

Figure 2. External stress corrosion cracking of urea grade AISI 316L HP carbamate condenser tube (ø 25 X 20mm). Magn. 30×; etchant oxalic acid; neg. nr. 7/83882-24.

Figure 3. The location of cracks in HP carbamate condenser tubes.

Figure 4. Steam and condensate system in the urea process.
locations have been found to depend on the origin of the chloride contamination. The following causes of SCC in HP carbamate condensers have been identified:

- Chloride contamination of water used for hydrostatic testing, cleaning or flushing.
- Transport and storage in a chloride-containing (maritime) atmosphere (infiltration as a result of ‘breathing’ due to cyclic temperature changes).
- Chloride contamination of boiler feed water (e.g. leakage of vent condenser in steam condensate tank). The steam and condensate system in the urea process is shown in figure 4.

SCC in HP carbamate condensers can be avoided by changing the corrosive environment (inhibition) or by using a material that is more resistant to chloride SCC:

- The chloride content of water used for hydrostatic testing, flushing or cleaning should be less than 1 ppm. As an additional precaution it is advised to inhibit the water with 2% TSP (trisodium phosphate).
- During transport and storage in a chloride-containing atmosphere the equipment should be inerted with nitrogen (0.3-0.5 bar gauge).
- The chloride content of the blow-down should be less than 0.2 ppm. The oxygen content should be zero; this will be the case when the blow-down contains excess oxygen scavenger (0.1–0.5 ppm). If chloride contamination cannot be avoided, continuous inhibition with TSP should be considered.
- Application of a more SCC-resistant material like type X2CrNiMoN 22 5 3 duplex stainless steel.

For existing carbamate condensers the remedies were focused on changing the environment but for new equipment the use of duplex stainless steel was considered. We had gained ample experience with such steels in terms of SCC resistance. In a naphtha cracking plant of DSM two process steam generators, with U-bundles in type X2CrNiMoN 22 5 3 duplex stainless steel, have been in service since 1988. Conditions on the shell side are even more severe than in carbamate condensers. Steam is generated from chloride-containing process condensate (average chloride content 10 ppm with pH varying from 4–12) at a temperature of 180°C. The carbon steel tubesheet is overlay welded with AISI 309L (X2CrNi 24 12). The duplex stainless steel tubes were automatically welded (GTAW) with 309S/309Mo welding consumable. The tubes were lightly expanded within the tubesheet over a length of 25mm. The thickness of the tubesheet is 193mm. A light hydraulic expansion cannot prevent crevices between the tubes and the tubesheet. The horizontal bundle is not fully immersed, accumulation of corrosive components like chlorides is likely to occur in the wet/dry zone. Until now, after about nine years on stream, no corrosion has been observed in these steam generators. In numerous other applications we found that duplex stainless steels offer good SCC-resistance at pH values above about 4. At lower pH values the advantage of duplex stainless steels over austenitic stainless steel diminishes. This has been confirmed in stress corrosion cracking experiments by means of Constant Extension Rate Testing (CERT) (ref. 1, 3). Duplex stainless steel test coupons have been exposed in the HP synthesis section of the DSM urea plant since the mid-seventies. The average corrosion rate of X2CrNiMoN 22 5 3 proved to be as follows:

- top of reactor: 0.04mm/year
- top of stripper: 0.08mm/year
- top of HP carbamate condenser: 0.03mm/year

The corrosion rates of duplex stainless steel in the urea reactor and in the HP carbamate condenser are comparable with those of X2CrNiMoN 25 22 2. The measured corrosion rate of duplex in the stripper is slightly higher than that of type X2CrNiMoN 25 22 2 steel. Based on these results and experience with chloride-containing environments, we wondered if the chloride stress corrosion cracking problems in the HP carbamate condenser could be resolved by using duplex stainless steel instead of urea grade 316L or X2CrNiMoN 25 22 2. In order to assess the corrosion resistance of duplex stainless steel, we installed three tubes of X2CrNiMoN 22 5 3 in the HP carbamate condenser of the DSM urea plant for a period of 1.5 years. After this period, a maximum decrease in wall thickness of 0.05mm was found. Corrosion was slightly intergranular and had propagated via the ferrite/austenite grain boundaries (figure 5). In October 1993, the first HP carbamate condenser and HP scrubber with
duplex stainless steel tubes and tubesheets overlay welded with duplex stainless steel were installed in a urea plant. In September 1996, after 3 years on stream, the HP heat exchangers were checked by visual inspection and eddy current measurements of the tubes.

This inspection revealed no signs of corrosion, neither of the overlay welding and tube-to-tubesheet joints, nor of the tubes. A HP carbamate condenser with duplex stainless steel tubes and overlay welded tubesheets is only slightly more expensive than the same unit in urea grade AISI 316L and about 5% cheaper than one in X2CrNiMoN 25 22 2.

Three other HP heat exchangers with duplex stainless steel tubes and overlay welded tubesheets are now under construction.

3.3 Corrosion of HP stripper tubes

In the stripper the unconverted carbamate is decomposed and the ammonia and carbon dioxide are stripped off. Stripping is effected by countercurrent contact between the urea solution and carbon dioxide at synthesis pressure. The stripper is the falling film type. Liquid dividers with gas tubes are positioned on the protruding tube ends with the joints being sealed with PTFE bushes.

Process conditions are severest in the stripper, especially at the top of the tubes, due to the relatively low oxygen partial pressure and high tubewall temperature. In the Stamicarbon urea stripping plants the stripper tubes are fabricated from X2CrNiMoN 25 22 2. The corrosion rate of this material in these conditions is 0.05mm/year, which is quite low. If a liquid divider with PTFE bush is not properly seated a higher corrosion rate may occur due to flooding in the tube. Figure 6 shows part of a seriously corroded stripper tube due to flooding.

Given the performance of duplex stainless steels in oxygen-containing and oxygen-free carbamate solutions we feel sure that a duplex high in chromium and nitrogen and low in nickel will give good performance even in these extreme conditions.

4 Material requirements for duplex stainless steels

Experience has shown that duplex stainless steels to be exposed to carbamate solutions must meet particular requirements. They must have a homogeneous ferrite-austenite structure consisting of a ferritic matrix with austenite islands fully enclosed by ferrite.
The ferrite content of the base material must be between 40 and 60% whilst the ferrite content of the weld and the heat-affected zones must be between 30 and 70%. A lot of effort has been put into the development of a suitable quality test. We found that the Streicher test (ASTM A 262, Practice B) fills the bill. Duplex stainless steel test coupons that showed intergranular attack on exposure to carbamate solutions showed also intergranular attack in the Streicher test (figure 7).

We therefore decided that duplex stainless steels on ammonium carbamate service should be Streicher-tested in accordance with ASTM A 262 Practice B. Such steels shall meet the following requirements:

The value of the overall attack in as-delivered and in the final heat-treated condition (e.g. welding) as determined by the gravimetric method shall not exceed:

- 1.6 g/m² h. (10 μm/48 hr) for 22% Cr duplex types;
- 0.9 g/m² h. (6 μm/48 hr) for 25% Cr duplex types.

The depth of selective or intergranular attack as determined by microscopic examination after the Streicher test shall not exceed 100 μm in any direction.

Heat exchanger tubes shall be tested for homogeneity (ferrite-austenite ratio) by eddy-current testing. Longitudinally welded heat exchanger tubes are not acceptable. These requirements are included in the Stamicarbon material specification.

5 Development of a new type of duplex stainless steel for ammonium carbamate service

Sandvik and Stamicarbon decided to jointly develop a new type of duplex stainless steel specifically for urea synthesis equipment and piping (ref. 4). This new type of duplex, named Safurex, was to have the following properties:

- At least the same corrosion resistance to carbamate solutions as X2CrNiMoN 25 22 2.
- High resistance to stress corrosion cracking.
- Superior mechanical properties to urea grade AISI 316L and X2CrNiMoN 25 22 2.
- Good microstructure stability.
- Good weldability.

For exploratory tests, Sandvik produced several heats with different chemical compositions in a 170 kg ingot HF laboratory furnace. From the test results, laboratory examinations as well as field tests of some twenty heats with different chemical compositions the optimum alloy composition with respect to corrosion resistance, structure stability and weldability was selected. This composition is used in Safurex™. It contains in % by weight:

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>max. 0.05</td>
</tr>
<tr>
<td>Si</td>
<td>max. 0.8</td>
</tr>
<tr>
<td>Mn</td>
<td>0.3–4</td>
</tr>
<tr>
<td>Cr</td>
<td>28–35</td>
</tr>
<tr>
<td>Ni</td>
<td>3–10</td>
</tr>
<tr>
<td>Mo</td>
<td>1.0–3.0</td>
</tr>
<tr>
<td>N</td>
<td>0.2–0.6</td>
</tr>
<tr>
<td>Cu</td>
<td>max. 1.0</td>
</tr>
<tr>
<td>W</td>
<td>max. 2.0</td>
</tr>
<tr>
<td>S</td>
<td>max. 0.010</td>
</tr>
<tr>
<td>Ce</td>
<td>0–0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>Balance</td>
</tr>
</tbody>
</table>

For a follow-up research programme a 70-tonne AOD (argon oxygen decarburisation) production heat of Safurex™ was made. The investigations in laboratory experiments and field tests gave the following results:

- Safurex meets the following requirements in the Streicher test to ASTM A 262, Practice B:
  - overall attack: < 0.7 g/m²/h (0.78mm/year)
  - selective attack: < 100 μm.
- Safurex’s corrosion resistance to carbamate solutions is equal to or better than that of type X2CrNiMoN 25 22 2 material.
- The stress corrosion cracking resistance of Safurex is much better than that of austenitic stainless steels and equal to or even better than that of type X2CrNiMoN 22 5 3.
- The tensile strength of Safurex is about twice as high as that of urea grade AISI 316L and about 70% higher than that of X2CrNiMoN 25 22 2.
- The elongation of Safurex is >25% (A5).
- Safurex has a homogeneous microstructure with a ferritic matrix which fully encloses the austenite islands.
- Annealing and welding tests have shown good microstructure stability.
- Welding tests by GTAW using a matching Safurex filler wire and a matching
X2CrNiMoN 25 22 2 filler wire have shown good weldability.
- Like all duplex stainless steels, Safurex is susceptible to 475°C embrittlement. However, a holding time of 10 hours at 510°C does not cause any loss of ductility.

6 Conclusions
- Given their excellent corrosion resistance, higher strength and lower cost duplex stainless steels are an attractive alternative to austenitic stainless steel HP piping in urea plants.
- For plants in coastal areas duplex stainless steel has the added advantage of high chloride stress corrosion cracking resistance.
- Duplex stainless steels offer a good solution to stress corrosion cracking problems in the HP carbamate condensers. Such cracking can be initiated by chloride contamination of the condensate.
- Safurex™, is a promising material that withstands the severest corrosive (-erosive) conditions in carbamate solutions combined with a high strength and good stress corrosion cracking resistance.

References