Overhead condensers (OHC) are critical to oil refineries. The OHC is essentially a large heat exchanger used for cooling and condensing the crude oil distillation tower (CDU), the first processing unit in virtually all petroleum refineries, by exchanging heat with the incoming crude oil via either an air cooled or water cooled condenser.

Selecting the best performing available materials for OHCs has become ever more critical and complicated due to issues of under-deposit corrosion which is caused by the presence of hydrochloric acid (HCl) and ammonium chloride (NH4Cl). In particular, oil refineries are seeking new materials that can provide higher levels of safety and reliability for more cost effective long term operations.

Today, many different materials are used on OHCs and their effective performance depends greatly on the local service conditions and each refinery’s operational requirements. The combined effects of these causes must be taken into consideration when selecting materials for longer term and more cost effective performance.

Corrosion media in OHCs
Stainless steel components within OHCs are subjected to several corrosion mechanisms during operations. Documented causes of corrosion include HCl dew point, chloride pitting, hydrogen sulphide (H2S) and, in particular, NH4Cl deposits.

HCl is also often present in the OHC in crude oil refineries and is well known for being very corrosive because it lowers the levels of pH at the same time as chlorides are present. In order to control the pH in the OHC, it has become common practice to inject ammonia (NH3) or neutralising amines into the system. This method increases the pH of the media but will also lead to the formation of dissolved NH4Cl, also known as salmiac, which has very high solubility in water. Since the water content at the inlet of the OHC is usually low, and the amounts of HCl and NH3 can be high in units which do not utilise water wash, there is a risk of salmiac precipitation in the OHC.

Precipitation of salmiac can form deposits in the OHC and, in really bad cases, causes complete blockage of the equipment.

Salmiac deposits are not harmful in themselves, but can create a crevice-like situation on the heat exchanger tubes which may in turn cause harmful under-deposit corrosion. Consequently, the situation can become very bad because part of the salmiac deposit may dissolve and lead to very high local chloride concentrations. It is because of these factors that under-deposit corrosion is a common problem within oil refineries’ OHCs.

Case study
A number of refineries around the world have reported severe corrosion problems in their OHCs. These include one Canadian heavy oil operator that had experienced premature failure with the duplex overhead condenser tubes in its crude unit. The material was supposed to last for about 10 years, yet had only been in...
80 ppm chlorides. \( \text{NH}_3 \) had been injected into the overhead system as a pH neutraliser, while the shell side fluids entered at approximately 44 kPag at 130°C and exited at approximately 78°C.

\( \text{NH}_4 \text{Cl} \) deposits had not been expected during operations, as these should have been avoided by proper washing; wash water was also injected just prior to the shell side of each heat exchanger inlet to wash away any salt that might have formed as the vapour condensed. Nevertheless, it was clear from the significant amount of loose deposits present on the tubes that the 22% Cr grade had been unable to withstand the severe conditions.

**Failure analysis**

For analysis, the two failed tubes were named Tube A and Tube B. Each had been located a few feet from the tube sheet and at the bottom of the heat exchanger while in service. Figure 1 shows the tubes in as-received condition alongside a pail of the deposit material.

A leak was observed in Tube A (see Figure 2) and the area immediately surrounding the leak was roughened due to external corrosion damage. This corrosion scale was submitted to an X-ray diffraction (XRD) analysis that did not identify any significant corrosion products located immediately around the leak. This result, or lack thereof, can be explained by the rapid release of higher pressure tube side fluids which had probably rushed through the perforation and caused erosive removal of the corrosion scale in this region.
No leaks were readily visible in Tube B, but similar external corrosion damage was visible on portions of the tube (see Figure 3). Due to the apparent similarity of the corrosion damage, further examination was limited to Tube A.

In order to detect any acid soluble sulphides or carbonates, chemical spot testing was performed on both the interior and exterior of the heat exchanger tubes. A similar test was also performed in order to detect possible chlorides. The interior and exterior surfaces of the tube were then sandblasted to remove all scale and debris, and to reveal the extent of the corrosion attack. It was discovered that the most severe corrosion damage, including the leak, tended to be concentrated on one side of the tube exterior (see Figure 4). This was likely the top side of the tube where deposit formation may have occurred due to sedimentation.

**Chemical analysis**

Chemical spot testing of the failed tube gave no positive indications for either acid soluble sulphides or carbonates. However, it should be mentioned that such a test is not totally conclusive because all sulphides are not acid soluble. Tests to detect the presence of chlorides yielded mildly positive indications on both the interior and exterior of the tubes. The cross section of the tube (see Figure 5) illustrates the external nature of the corrosion attack. It can be clearly seen that the inside surface is relatively smooth and has not been subject to corrosion except very close to the leak.

The microstructure of the investigated tube was considered typical for a duplex stainless steel, and no unusual phases or defects could be observed (see Figure 6).

Energy-dispersive X-ray spectroscopy (EDS) analysis of Tube A (see Figure 7) indicated that the material composition was consistent with a 22% Cr duplex stainless steel such as UNS S31803 and UNS S32205. This is indicated by relatively strong iron and chromium peaks (the major alloying elements), with lesser peaks for nickel, molybdenum, manganese and silicon. An average measured microhardness of 268 HV 500 gf was also considered typical for this type of material.

X-ray differentiation (XRD) measurements of the deposit found in the heat exchanger (see Table 1) revealed that the most abundant compound present was salmiac formed by

<table>
<thead>
<tr>
<th>Species</th>
<th>Approximate amount/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salmiac (NH₄Cl)</td>
<td>71</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>22</td>
</tr>
<tr>
<td>Quartz (SiO₂)</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 1
reaction between HCl present in the water and NH\textsubscript{3} injected in order to maintain the pH neutrality of the water phase. A significant amount of elemental sulphur and a small amount of quartz (sand) were also detected in the loose deposit material. There is no data about the amount of sulphur in the incoming media on the shell side of the heat exchanger.

A summary of the results from XRD analysis performed on the corrosion scale found on the exterior of tube is shown in Table 2. More than half of the sample was made up of austenite/ferrite duplex material metal scrapings collected along with the corrosion scale. The most abundant corrosion product detected was greigite (Fe\textsubscript{3}S\textsubscript{4}) which, together with FeS and Fe\textsubscript{2}S, is a corrosion product of iron based metals in the presence of H\textsubscript{2}S and/or sulphur corrosion.

Another conventional explanation for the participation of sulphur species in accelerating corrosion in this case is its participation in an autocatalytic reaction which regenerates HCl:

\[
\text{FeCl}_2 + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{HCl}
\]

Synthetic hazelwoodite (Ni\textsubscript{3}S\textsubscript{2}) was also detected; this is a nickel sulphide corrosion product that can form during corrosion of duplex stainless steels associated with exposure to H\textsubscript{2}S and chlorides.

### Corrosion of the 22% Cr tube

Results from the investigation of the 22% Cr tube show that the material was good from a metallurgical point of view. The failure can instead be attributed to the fact that the operational environment was too severe for the duplex grade, which resulted in under-deposit corrosion. The deposit found in the heat exchanger comprised mainly salmiac, but a significant amount of sulphur was also present. Elemental sulphur in water can act as an oxidising agent comparable in certain respects to oxygen, according to the Materials Technology Institute (MTI), and the presence of sulphur would then assist in promoting chloride-induced under deposit corrosion due to its oxidising nature. Such phenomena would explain the presence of sulphur containing iron and nickel salts in the corrosion products. The presence of Iron(II) oxide FeO (OH,Cl), a corrosion product associated with acidic, chloride containing environments, corroborated the idea of a chloride induced corrosion mechanism. Since sulphur containing salts do not passivate the stainless steel surface, the steel would be prone to further corrosion attacks. Repassivation could be slow or even being completely inhibited.

### Hyper-duplex stainless steel

Based on failure analysis of the 22% Cr tube, hyper-duplex grade Sandvik SAF 2707 HD (UNS S32707) was recommended as the best material for the application. Designed for highly corrosive conditions, the material was initially developed as an advanced replacement for super-duplex grades. However, the grade’s high strength, corrosion resistance and cost efficiency properties were better than expected, especially in chlorinated seawater, with resistance...
to pitting corrosion and stress corrosion cracking (SCC) that are demonstrably superior to standard duplex stainless steels.

Successful applications of the hyper-duplex material have resulted in longer service life-cycles and reduced plant shutdowns; in one instance, a reduction from eight shutdowns to just one over an eight-year period. Sandvik SAF 2707 HD has enabled large cost savings for refineries by reducing needs for material replacement, manpower and lost production.

Tests also found that it can be a superior alternative to Ni alloys. Table 3 illustrates the chemical composition of Sandvik SAF 2707 HD, and compares it alongside the established super-duplex stainless steel grade UNS 32750. By contrast with unstable high Ni alloys, the Ni content of the hyper-duplex can be kept as low as 6.5% due to the grade’s nominal 0.4% nitrogen (N) content which also stabilises the austenitic structure.

Also important are the material levels of chromium (Cr), molybdenum (Mo) and nitrogen (N) which, in combination, reinforce the material’s superior pitting and crevice corrosion resistance in chloride contaminated media. The chemical balance imbues the steel with a duplex, austenitic-ferritic, microstructure that is 50% ferrite and 50% austenite. The austenitic-ferritic properties of the material imbue the grade improved mechanical strength, an ability to withstand greater external loads and pressures from all directions, and better fabricability.

Chromium is the most common element for enhancing a stainless steel’s resistance to general and localised corrosion; compared with the 22% Cr tube, Sandvik SAF 2707 HD is 27% Cr. This instils the material with superior corrosion resistance.

The material has a nominal PRE value of 49 which, compared to 22% Cr grades that usually have a PRE number of 30 to 35, provides the grade with superior pitting and crevice corrosion resistance in chloride containing environments. The higher the PRE number of a stainless steel, the lower the risk of chloride induced SCC. This is among the reasons why hyper-duplex grades are used successfully in atmospheric overhead condensers as a demonstrably cost effective solution for such applications.

Material qualifications of hyper-duplex
After the twisting procedure, the corrosion resistance and the mechanical properties of the tubes were tested. All tests were performed at WH Laboratories in Houston, Texas. All qualifications were performed on tubes corresponding to UNS S32707 in ASME SA 789-04. The tube dimensions were OD 25.4 mm × wall thickness 2.11 mm and were produced from heat number 501695.

All tests performed intended to show that the twisted material can maintain the same corrosion properties as the base material. Specific testing for SCC was not considered during this evaluation as the hardness results achieved after twisting were under the maximum level for the base metal specification. SCC tests will be considered for further evaluation.

Corrosion testing was performed in accordance with ASTM G48 A (2) on two samples cut from two different twisted tubes. The test solution was prepared in accordance with ASTM G48 A and each test specimen was tested in a one litre beaker maintained at 80ºC +/-2ºC for a period of 24 hours. After the 24-hour test period, the samples were rinsed and cleaned in an ultrasonic bath in order to remove deposits. They were then dried, weighed and examined at 20x magnification by stereomicroscope. A visual examination and photographic reproduction of specimen surfaces, along with specimen mass losses, are often sufficient to characterise the pitting and crevice resistance of duplex grades. According to the standard if the material loss is above 0.0001 g/cm² or 10 mdd, indication of pitting corrosion is considered.

The microstructure of two twisted tubes was analysed according to ASTM A923 A. The samples were polished to 0.3 micron surface and then electrolytically etched for 20 seconds at 2 volts using a sodium hydroxide electrolyte. The ferrite content of each sample was determined using manual point counting according to ASTM E562. Magnification used for the point counting was 1000x, the grid used was 5×5 squares and a total of 32 fields were counted for each sample.

Also measured was the
The failed 22% Cr heat exchanger tubes were subjected to external chloride pitting corrosion attack. Cause of the attack was most likely due to an under-deposit corrosion mechanism triggered by precipitation of salmiac on the shell side of the heat exchanger. This was formed as a result of the addition of NH₃ in order to neutralise the HCl present. Deposits found in the heat exchanger contained, apart from salmiac, a significant amount of elemental sulphur. It is believed that the sulphur has probably taken an active part in the chloride pitting corrosion mechanism since both iron and nickel containing sulphur species were found in the corrosion products.

Hyper-duplex UNS S32707 has been chosen as the replacement material for the 22% Cr duplex grade. It has been shown that it can successfully be twisted by cold-working without altering the mechanical properties and corrosion resistance. The same heat exchanger design can thus be used with the new tubes and the fabrication procedure does not need to be altered.

Marcelo Senatore is Global Technical Marketing Manager, Sandvik Materials Technology, São Paulo, Brazil. He is the Sandvik representative with MTI, Vice Chairman of NACE TEG 114-X (Applications of Duplex and Ferritic Stainless Steels in the Process Industry) and Vice Chairman of the API-938C Committee (Use of Duplex SS in Oil Refineries). He holds a BA in metallurgical engineering from FEI in Sao Paulo, Brazil, and is an MBA candidate from FGV.

**Conclusion**

Vickers hardness of the twisted tubes using a 10 kg weight. Two samples were analysed at the as-twisted section and at the straight section. Results of the Vickers hardness was converted to Rockwell C hardness using the standard API 938 C(3) curve for duplex stainless steel. During the hardness testing, the temperature was 24°C and the humidity 40%.

Corrosion rates achieved after the G 48A test were 3.1 mdd for sample A and 2.6 mdd for sample B, which is well below the allowed 10 mdd corrosion rate at 80°C for passing the test. Thus the samples passed the corrosion testing without remarks. Mechanical deformation of the tubes from the twisting procedure apparently does not affect the corrosion properties of the material. These were expected results as the corrosion resistance of stainless steel towards pitting and crevice corrosion are rarely affected by mechanical deformation.

**Figure 8** shows the microstructures of samples A and B, respectively. Both tube samples display normal microstructures for a duplex stainless steel. The average percent of ferrite achieved for sample A was 40.3 ±1.2% and for sample B 42.3 ±1.8%. Both samples thus had ferrite content within the 35-65% range limit and were approved. The twisted section presented average hardness of HRC 28.4 measured at the tube’s ID and HRC 28.9 measured at the tube’s OD, while the straight section presented average hardness of HRC 27.2 measured at the tube’s ID and HRC 26.3 measured at the tube’s OD. All the results were approved as they were under the base metal specification limit of 34 HRC.

The material qualification has shown that the hyper-duplex grade UNS S32707 can indeed be twisted in the same way as the 22% Cr tubes. Results from corrosion and mechanical testing performed on the twisted hyper-duplex tubes show that the material properties are unaffected by the twisting operation. It is thus not necessary to perform any additional heat treatment of the tubes. This makes it possible to replace the original 22% Cr tubes with hyper-duplex ones without changing the design of the heat exchanger and with no extra costs due to additional fabrication steps. The heat transfer area of the heat exchanger will be the same.

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