Sandvik SAF 2707 HD® (UNS S32707) – a hyper-duplex stainless steel for severe chloride containing environments

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Abstract

This paper introduces the new hyper-duplex stainless steel Sandvik SAF 2707 HD.

The general material properties of Sandvik SAF 2707 HD are presented, including chemical composition, corrosion and mechanical properties. Results are given also for weld metals, welded with GTAW (TIG) and a matching (Sandvik 27.9.5.L) filler material.

With a nominal PRE (%Cr + 3.3%Mo+16%N) of 49, the new grade has significantly improved corrosion resistance in chloride solutions compared with currently available super duplex stainless steels (e.g. UNS S32750) and the 6Mo austenitic stainless steels (e.g. UNS S31254).

This makes Sandvik SAF 2707 HD particularly interesting for use in applications involving hot seawater. Compared with the current super-duplex grades, Sandvik SAF 2707 HD also extends safe operating conditions in a number of other chloride containing acidic environments, e.g. in critical heat exchangers in oil refineries. Some references for Sandvik SAF 2707 HD in industrial heat exchanger applications are highlighted.

Introduction

Since their introduction more than 15 years ago, super-duplex stainless steels, such as UNS S32750, S32760 and S32520, have found widespread use in industries such as oil and gas, petrochemical and chemical processing. Their popularity is attributed to an attractive combination of high corrosion resistance, excellent mechanical properties and also a relatively low cost compared to other higher performance materials, such as super austenitic stainless steels and Ni-based alloys.

Despite a very broad range of applications for super-duplex stainless steels, there are areas where the corrosion resistance of these grades is insufficient for a long service life, and where more expensive materials, with even higher corrosion resistance, are needed.

As an example, the corrosion resistance for different duplex stainless steels in seawater applications has been much discussed during the last decade, and even though the existing super-duplex stainless steels do not corrode in seawater at lower temperatures, they have some limits in higher temperature service. There was a clear desire, therefore, for new grades with a higher corrosion resistance than was available from existing super-duplex stainless steels.

To that end, Sandvik SAF 2707 HD was developed. In addition to a high chloride corrosion resistance, it also offers increased mechanical properties over e.g. Sandvik SAF 2507® (UNS S32750). The improved corrosion resistance extends the use of duplex stainless steels in aggressive chloride environments, such as in hot tropical seawater.

With the high costs often associated with maintenance, and the desire to prolong the periods between planned inspections, increased reliability is a key factor in lowering overall life cycle costs. The selected materials of construction need to withstand the often variable service conditions experienced, and to perform also in cases of shorter periods of non-stable operating conditions. With this background, a further development of the super-duplex stainless steels has been a natural step in order to meet the current and future industry demands for economical, high performance materials.

Chemical composition and PRE value

Sandvik SAF 2707 HD (UNS S32707) has a well-balanced composition, with approximately 50% ferrite and 50% austenite and is designed for use in acidic chloride containing environments. The combination of chromium, nitrogen and molybdenum increases resistance to localized corrosion, i.e. pitting and crevice corrosion. In duplex materials, it is important that the individual PRE numbers of the two phases, austenite and ferrite, are similar, in order to prevent the initiation of corrosion attack in the weaker phase. In Sandvik SAF 2707 HD, the nominal PRE number is 49, where PRE=%Cr + 3.3%Mo + 16%N (% by weight). The individual PRE numbers of the two phases are typically balanced to within 1 PRE unit of the average. The elemental content is also balanced to give high impact toughness and a reduced risk of the formation of embrittling phases during annealing.

The nominal chemical compositions of Sandvik SAF 2707 HD and Sandvik SAF 2507 are given in table 1.

Table 1. Nominal chemical composition of two highly alloyed duplex stainless steels, wt-%

Grade Sandvik	UNS	C max	Cr	Ni	Mo	N	PRE* nominal
SAF 2507	S32750	0.03	25	7	4	0.3	42
SAF 2707 HD	S32707	0.03	27	6.5	5	0.4	49

*PRE = Pitting Resistance Equivalent (=%Cr + 3.3%Mo + 16%N)

Localized corrosion

In chloride containing waters under oxidizing conditions, pitting or crevice corrosion are perhaps the most common failure modes for stainless steels. Modern duplex stainless steels, such as Sandvik SAF 2507, were developed explicitly to have high resistance to pitting and crevice corrosion. All the experience gained from this grade has been utilized when developing Sandvik SAF 2707 HD.

In a modified version of ASTM G48A, test samples are exposed for periods of 24 hours in 6% $FeCl_3$. When pits are detected together with a substantial weight loss (> 5 mg), the test is interrupted. Otherwise, the temperature is increased 5°C (9°F) and the test continued. The critical pitting temperature (CPT) of Sandvik SAF 2707 HD defined in this way was 97.5°C, compared to approximately 80°C for Sandvik SAF 2507.

Crevice corrosion tests were performed in 6% $FeCl_3$, with a crevice specified in the MTI-2 procedure, where an artificial crevice is mounted on the sample with a torque of 0.28 Nm. Also, in this case, the increase in critical crevice corrosion temperature (CCT) is significant. Results obtained, compared with Sandvik SAF 2507 (UNS S32750), are given in Figure 1.

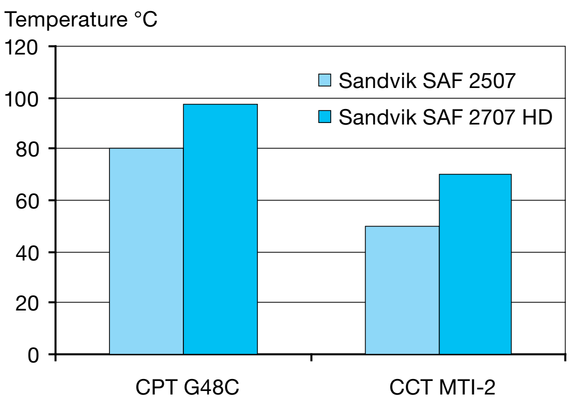

Figure 1. Critical pitting temperature in modified G-48A and critical crevice corrosion temperature obtained in MTI-2 testing.

Critical pitting temperatures (CPT) can also be measured in potentiostatic tests. Figure 2 shows CPT as a function of the concentrations of sodium chloride, from 3 to 25% and of pH. The applied potential during the test was 600 mV vs. SCE, which is approximately the same redox potential as that used in the ASTM G48 tests. This high potential is normally not encountered in chloride containing media. The possible application temperatures in chloride containing media of lower redox potentials, e.g. process streams in refineries or natural unchlorinated seawater is, therefore, typically much higher.

In particular, at low pH and high chloride concentrations, Sandvik SAF 2707 HD shows a much higher resistance than Sandvik SAF 2507 and austenitic 6Mo+N alloys.

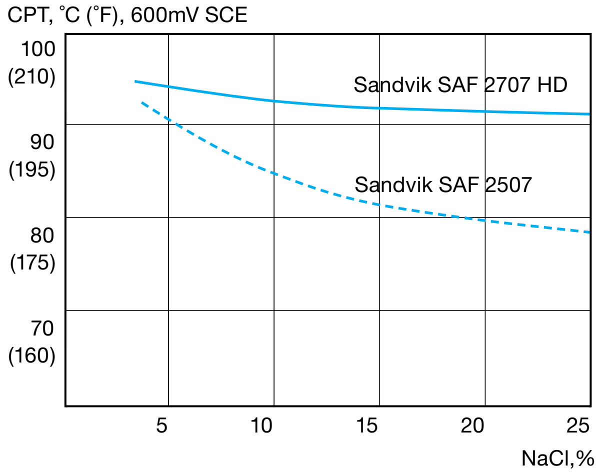

Figure 2. Critical pitting temperatures (CPT) at varying concentrations of sodium chloride, from 3 to 25% (potentiostatic determination at +600mV SCE with surface ground with 220 grit paper).

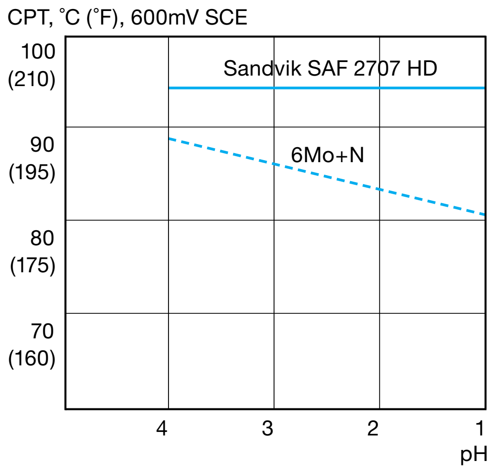

Figure 3. Critical pitting temperatures (CPT) in 3% NaCl with varying pH (potentiostatic determination at +600mV SCE with surface ground with 220 grit paper).

The high corrosion resistance in acidic, lower pH, chloride solutions is also demonstrated by results obtained in a Green Death (1%$FeCl_3$ + 1%$CuCl_2$ + 11%H_2SO_4 + 1.2%HCl) test solution. Table 2 shows that in this environment, the critical pitting temperature (CPT) is increased by 25 ˚C compared with Sandvik SAF 2507.

Table 2. Critical pitting temperature determined in "Green death"

Alloy	CPT (˚C)
Sandvik SAF 2707 HD	97.5
Sandvik SAF 2507	72.5
6Mo+N	70

General corrosion

General corrosion can limit the service life of a stainless steel component in contact with a process solution. Sandvik SAF 2707 HD is highly resistant to corrosion by organic acids, e.g. formic acid and acetic acid, as shown in the isocorrosion diagrams in figures 4 and 5. It also remains resistant in contaminated acid. The alloy is, therefore, a competitive alternative to high alloyed austenitic stainless steels and Ni-base alloys in applications where standard austenitic stainless steels corrode at a high rate.

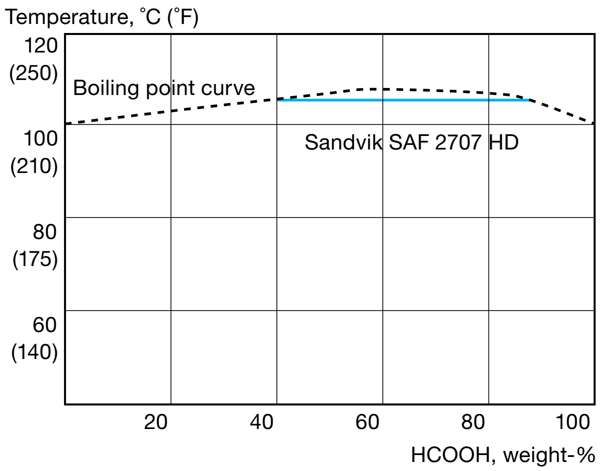

Figure 4. Isocorrosion diagram in naturally aerated formic acid. The curve represents a corrosion rate of 0.1mm/year (4mpy) in a stagnant test solution.

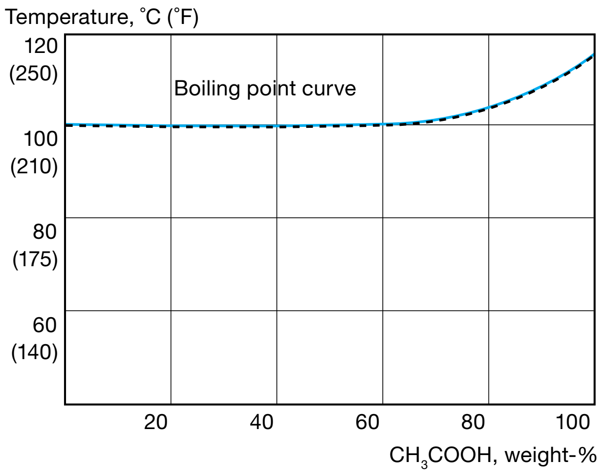

Figure 5. Isocorrosion diagram in naturally aerated acetic acid. The curve represents a corrosion rate of 0.1mm/year (4mpy) in a stagnant test solution.

The corrosion rate of Sandvik SAF 2707 HD in formic acid at 105°C and in boiling conditions was compared with the Ni-based material C-276 (UNS N10276) over the full range of concentrations. The results showed that at 105°C, Sandvik SAF 2707 HD had a significantly lower corrosion rate than C-276 for all concentrations. Also at boiling conditions, the corrosion rate for Sandvik SAF 2707 HD was lower in concentrations up to approx. 50% formic acid, while C-276 performed better in boiling conditions at the highest concentrations.

Stress corrosion cracking

Stress corrosion cracking (SCC) is perhaps the most serious form of corrosion encountered in industrial processes as it can lead to rapid material failure. Standard austenitic grades can crack even at very low chloride levels. The risk of SCC can be eliminated with the use of more resistant materials, such as high nickel alloys or duplex stainless steels. While the austenitic steels in many cases become resistant at Ni levels above 25%, the duplex alloys will have the same or higher resistance at much lower alloying levels, due to the dual phase structure [2]. The SCC resistance of Sandvik SAF 2707 HD in chloride solutions at high temperatures is illustrated in figure 6. An autoclave SCC test, where the samples are loaded to the yield strength $R_{p0.2}$ level, was conducted. The pressure was approximately 100 bar and the oxygen content 8 ppm. Fresh NaCl solution was pumped constantly into the chamber and duration of the test was 1000h (6 weeks). There were no signs of SCC up to 1000 ppm Cl^- /300°C and 10000 ppm Cl^- /250°C.

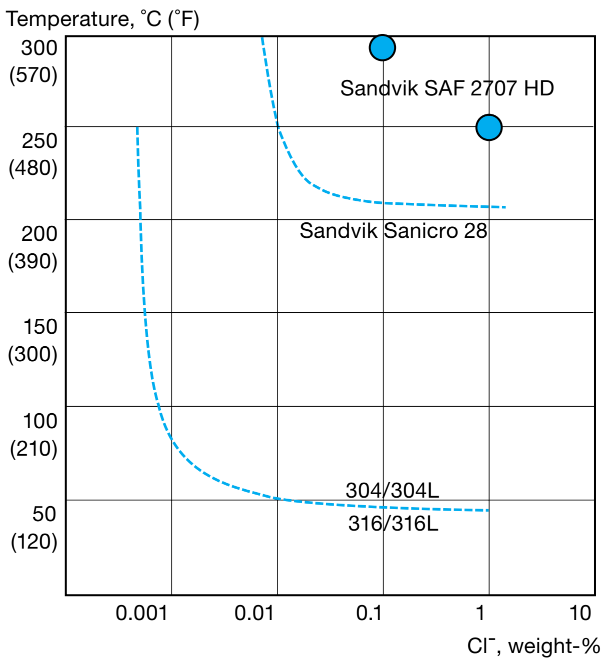

Figure 6. SCC resistance in oxygen bearing (abt. 8 ppm) neutral chloride solutions. Testing time 1000 hours. Applied stress equal to proof strength at testing temperature. Sandvik Sanicro 28 = UNS N08028.

Mechanical properties

Sandvik SAF 2707 HD was designed to have high mechanical strength. The duplex structure accounts for a yield strength about twice that of austenitic stainless steels with corresponding pitting corrosion resistance. The higher strength of the duplex material will in many cases allow substantial reductions in material thickness, lowering the weight and total cost of the installation. In spite of the high strength, ductility remains at a high level and fabrication procedures, such as bending and expansion, can be performed in the same way as for austenitic steels [2].

Typical values for heat exchanger tubes are yield strength $R_{p0.2}$ 800 MPa and tensile strength 1000 MPa. The elongation value is above 25% in the quenched annealed condition. When a metal is exposed to high temperatures, the effect of solution strengthening and deformation hardening decreases, since the diffusion rate of both substitution and interstitial atoms increase and the density of dislocation decreases, due to the high velocities of dislocation movements. This leads to a decrease in both yield and tensile strength [2]. Figure 7 shows the mean yield strength $R_{p0.2}$ and figure 8 shows the mean tensile strength R_m, measured on heat exchanger tubes with wall thicknesses up to 4 mm in the temperature range 20-300˚C (68-572˚F). The yield strength $R_{p0.2}$ and the tensile strength R_m are high over the whole temperature range up to 300˚C.

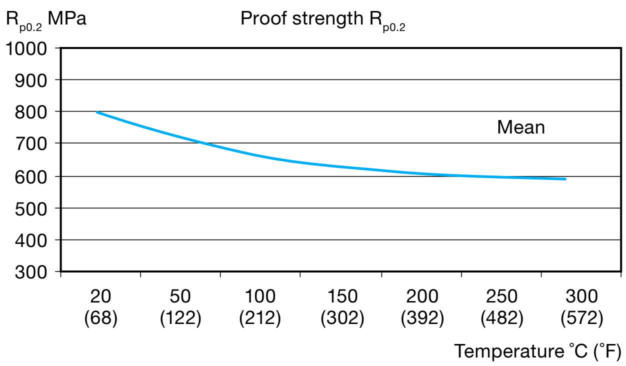

Figure 7. Proof strength $R_{p0.2}$ of Sandvik SAF 2707 HD.

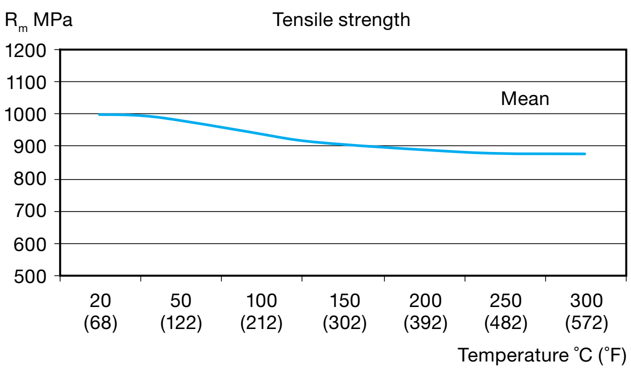

Figure 8. Tensile strength R_m of Sandvik SAF 2707 HD.

Impact strength

The temperature range for using duplex stainless steels is approximately -50°C to 300°C, with some variations on the design limits within different grades and standards. The reason for the lower limit is the fact that duplex, similar to other materials with a ferritic matrix, are embrittled at lower temperatures. The upper limit is also due to embrittlement, where the ferrite phase undergoes a transformation over time. The phenomenon is referred to as 475°C (885°F)-embrittlement, because the ferrite decomposition rate is typically highest around that temperature. Sandvik SAF 2707 HD possesses very good impact strength. The ductile to brittle transition temperature is below -50°C (-58°F). Figure 10 shows impact energy (KCV) in the temperature range -200˚C-100˚C (-328-212˚F). The samples are taken in the longitudinal and transversal direction from 200x13mm hot extruded and solution annealed pipe.

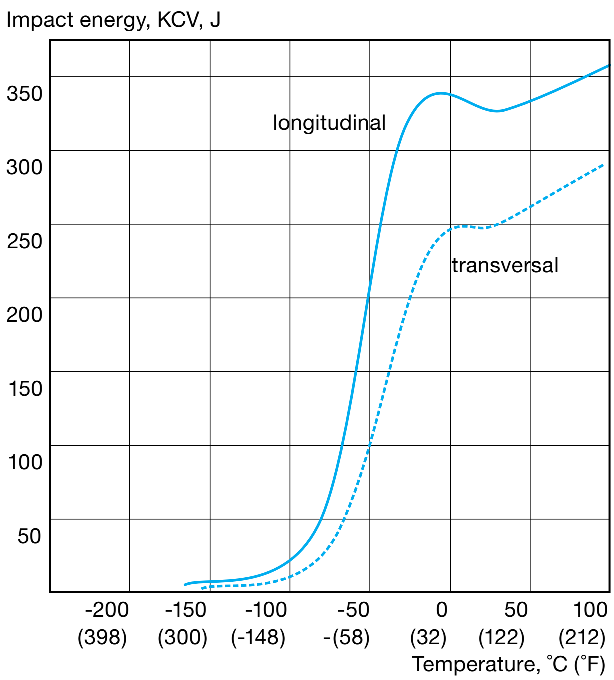

Figure 9. Impact energy curve for Sandvik SAF 2707 HD using standard Charpy V specimens 10x10mm.

Welding

A welding consumable designated Sandvik 27.9.5.L has been developed for welding Sandvik SAF 2707 HD. Sandvik 27.9.5.L weld metal and HAZ have a ferritic-austenitic microstructure with ferrite content in the range of 30-70%. High nitrogen content in the material gives a rapid austenite formation during welding. In order to compensate for nitrogen losses during gas shielded welding, a shielding gas of Ar + 2-3% N_2 should be used.

Sandvik 27.9.5.L filler material contains an increased nickel level to promote austenite reformation and hence improved pitting resistance.

It is important to control the ferrite content in order to obtain a microstructure free from intermetallic precipitates, and it should generally be in the range 30-70%. Precipitates such as Cr2N and σ-phase can influence corrosion and mechanical properties negatively if a sufficiently large amount is present in the microstructure. Due to the structural stability of Sandvik SAF 2707 HD, the thermal cycle during welding must be kept under close control for optimum properties in the weld. Too high a heat input should be avoided to minimize the risk of precipitating σ-phase and other intermetallic phases. Too low a heat input should also be avoided to minimize the risk of precipitating too high ferrite content and the precipitation of nitrides. For this reason, the lower end of the heat input interval in table 3 should not be used for heavy gauges.

Table 3. Heat control

Factor	Limit
Preheat[a)]	Not applicable[a)]
Interpass temperature	<100°C
Heat input	0.2 kJ/mm<Q<1.5 kJ/mm

[a)] A preheat of 50-70°C can be carried out when there is a risk of condensed moisture on joint surfaces, tubesheets etc. Preheating with an open flame should be avoided.

Post weld cleaning can be done mechanically by stainless steel brush, Scotch Brite grinding wheel (or similar), pickling with Sandvik pickling paste or by combining mechanical cleaning and pickling. A combination of mechanical cleaning and pickling generally gives the best result from a corrosion point of view.

TIG/GTAW (Tungsten-Inert-Gas /Gas-Tungsten-Arc-Welding) is recommended for tube-to-tubesheet welding. Both manual and mechanized TIG welding can be used. Due to the rapid cooling in tube-to-tubesheet welding, it is important to use nitrogen mixed shielding gas, Ar + 2-3% N_2, in order to promote austenite reformation. Tube-to-tubesheet welding can be performed with all the common joint preparations used for other super-duplex grades. Sandvik SAF 2707 HD can be successfully welded to tube sheets of various materials, e.g. Sandvik SAF 2205, Sandvik SAF 2507, and carbon steels.

The critical pitting temperature (CPT) in the earlier described, modified version of ASTM G48A testing was measured at 77.5°C, which is significantly higher than the corresponding values for a super duplex TIG/GTAW weld metal. Typical tensile properties for TIG/GTAW all weld metal are summarised in table 4.

Table 4. Typical tensile properties for Sandvik 27.9.5.L TIG/GTAW all weld metal (Shielding gas: Ar+2%N_2)

$R_{p0.2}$ MPa	R_m MPa	A %
800	950	30

Impact values for the weld metal in the temperature interval -60°C to +20°C can be seen in figure 10.

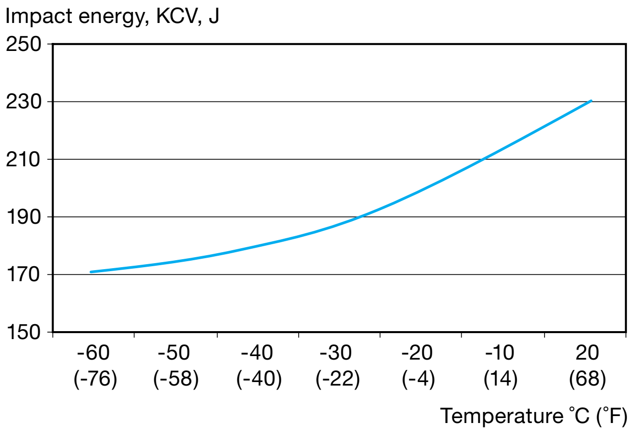

Figure 10. Impact energy values for weld metal Sandvik 27.9.5L in the temperature interval -60°C to 20°C.

Application examples – heat exchanger service

In order to verify the material and gain industrial reference information, Sandvik SAF 2707 HD has been evaluated during the last couple of years in a variety of industrial heat exchanger applications operating under severe corrosive conditions. Some examples are given below to describe the experiences gained.

At the end of 2003, a US oil refinery decided to retube a complete tube bundle with Sandvik SAF 2707 HD in a top pump-around exchanger in an atmospheric distillation unit. In the same application, carbon steel had a lifetime expectancy of only around 9 months. The problems were caused by chloride attacks under deposits of amine-chloride salts and iron sulphide deposits. The increased corrosivity seen in this unit came from a higher use of lower quality crude oils. An upgrading of the metallurgy to Sandvik SAF 2507 super-duplex stainless steel had been done already for most of these exchangers, but the grade was considered to be operating very close to its limits, as some pitting had been observed in the bundles having the most severe conditions. One bundle also experienced some cracking, which was traced back to faults during the fabrication (retubing) process. The Sandvik SAF 2707 HD tubes were installed as replacement material in this particular bundle, and, to date, have performed excellently [3].

A European refinery had similar problems with a short lifetime on carbon steels in air coolers in an atmospheric crude distillation overhead system. The lifetime of a maximum of 2 years was not sufficient in view of this plant's aim to prolong the intervals between turnarounds. Sandvik SAF 2707 HD test tubes, with external Al-fins, were installed in the most critical part of the air cooler, and were in excellent condition when inspected after more than one year in service.

Another European refinery also saw the benefits of using Sandvik SAF 2707 HD for service in an overhead condenser unit to replace carbon steel giving only a short life time, with bundles being replaced typically after only 5-7 months in service. Installation was carried out in January 2006, and performance to date has been good.

A refinery in the Middle East selected Sandvik SAF 2707 HD for a full condenser cooled with seawater on the tube side. The shell side service was condensing hydrocarbons, also giving concerns relating to HCl dewpoint deposit formation. The main issue, however, was the seawater tube side, where metal temperatures were estimated to reach as high as approx. 70°C.

Seawater corrosion was a concern also for a chemical plant located on the Mediterranean Sea. This plant selected Sandvik SAF 2707 HD as a more reliable option compared with Sandvik SAF 2507 for a seawater cooled exchanger. The unit has been in service since the end of year 2005.

A chemical plant in South America, producing boric acid and boron salts, had corrosion problems on 6Mo super austenitic stainless steel, due to high chloride contents and temperatures. Sandvik SAF 2707 HD tubes were installed as replacements during mid 2005.

Conclusions

- Sandvik SAF 2707 HD has excellent resistance to pitting and crevice corrosion in chloride containing environments, as well as to chloride induced stress corrosion cracking. Sandvik SAF 2707 HD also shows very good results against general corrosion in organic acids.

- The mechanical properties of Sandvik SAF 2707 HD are high. The high yield strength may give design and cost advantages compared to other high performance materials.

- The weldability of Sandvik SAF 2707 HD is good.

- The excellent corrosion performance of Sandvik SAF 2707 HD has been verified in a number of process plant heat exchanger installations.

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