Recent findings on pitting and crevice corrosion: comparing SAF 2707 HD™

a cura di: **Alessandra Spaghetti** alessandra.spaghetti@sandvik.com **- Sandvik Materials Technology**

INTRODUCTION

Hyper-duplex is a grade in the austenitic-ferritic family that recently has seen use in refinery application and some special acidic condition both showing very good performance while at the same time being a cost-effective solution. Very often, harsh conditions for the heat exchanger tubes cause people to consider very expensive grade such as titanium or UNS N10276, while hyper-duplex could perform just as well.

To better understand the properties of UNS S32707 and its advantages in this paper SAF 2707 HD™ compared has been compared with some of the most commonly used high alloyed materials:

- UNS S32750 (super-duplex) and UNS S31254 (6Mo)
- UNS N06625 (Alloy 625)

Hyper-duplex vs super-duplex

The first generation of duplex grades were developed during the 50's (as showed in figure 1) and after several studies finally a new generation came in the market: the hyper-duplex. One of the way to classify the grade resistance is the Pitting Resistance Equivalent Number (the formula is showed in figure 1). SAF2707HD™, with a PRE higher than 49, shows outstanding corrosion resistance properties towards localized corrosion.

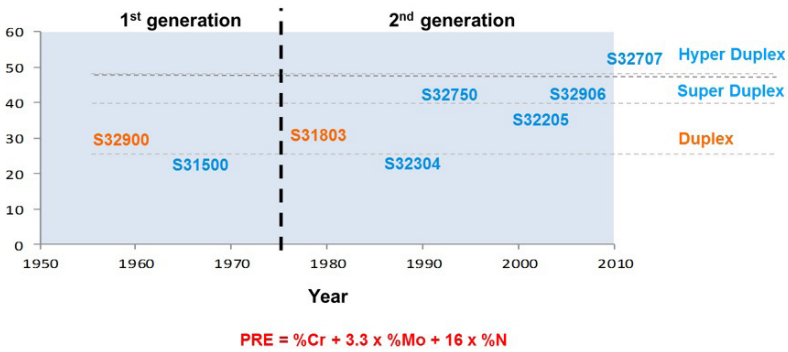

Fig. 1 - Development of duplex stainless steels.

Tab. 1 - is shows the calculated pitting resistance equivalent (PRE) numbers for the super-duplex, UNS S31254 and hyper-duplex alloys

UNS	%C max	%Cr	%Ni	%Mo	%N	PRE* Nominal
S32750	0.03	25	7	4	0.3	42
S32707	0.03	27	6.5	5	0.4	49
S31254	0.02	20	18	6.1	0.2	43

(*) PRE = %Cr + 3.3 x %Mo + 16 x %N

Yield strength and strength for the hyper-duplex alloy are also improved compared to other austenitic-ferritic alloys as shown in Table 2.

Tab. 2 - Mechanical properties comparison of some duplex grades and 6Mo.

Grade	Yield strength 0.2% offset MPa min	Tensile strength MPa	Elongation A% min	Hardness Vickers average
UNS S32707	700	920-1100	25	335
UNS S32750	550	800-1000	25	290
UNS S32205	450	680-880	25	260
UNS S32304	400	600-820	25	230

Duplex grades are well known for their pitting and crevice corrosion resistance. The hyper-duplex grade has an increased critical pitting and crevice temperature (respectively CPT and CCT) of about 20 °C more compared to superduplex (this can be also seen in figure 2), which can really make a difference for heat exchanger tubes, allowing the user a wider operation window and harsher process conditions. Laboratory tests have been performed according to ASTM G48 and the results are shown in Figure 2. In ASTM G48 a solution containing approximately 4% w/w of chlorides is used, more or less twice than the content in seawater. To further challenge the hyper-duplex grade and check its resistance to very low pH a test with the so called "Green Death" solution was performed. This is an aqueous mixture with a pH lower than 1. Composition and results are showed in Figure 3. It's clear that UNS S32707 maintains its good performance demonstrated in ASTM G48, while UNS S32705 and UNS 31254 have a drop in CPT due to very low pH.

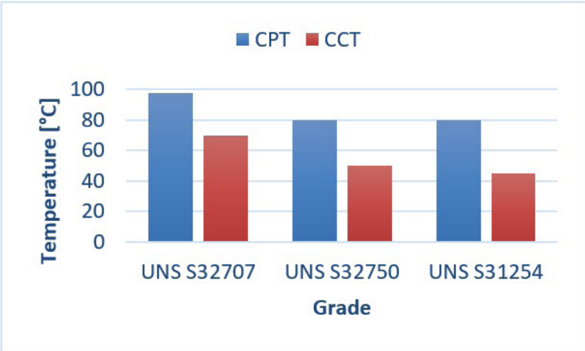

Fig. 2 - Results from pitting and crevice corrosion tests according to ASTM G48.

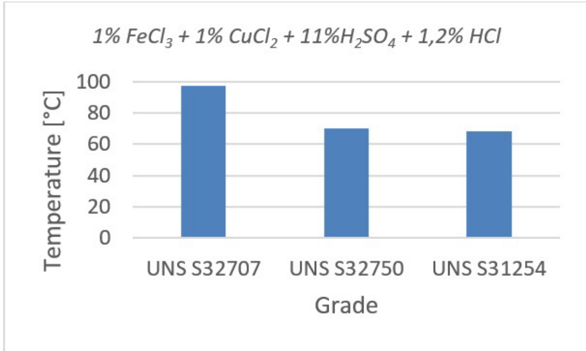

Fig. 3 - CPT tests performed in Green Death solution.

The laboratory tests can be used as a guide, but when it comes to material selection it is necessary to consider the actual chlorides content in the process media. The presence of impurities other than chlorides can also strongly affect the behavior of the materials, reducing their performances despite being present in small quantities. It can be concluded that the hyper-duplex grade has a clear advantage compared to the super-duplex one, allowing a higher temperature in the process and/or improving the mechanical properties of the equipment with positive sides in relation to heat exchange and cost reduction due to the possibility to reduce the wall thickness.

Hyper-duplex vs Alloy 625

As mentioned earlier, material selections tend to be too conservative. This is for example often the case when Alloy 625 is selected for environments with high chloride contents. That is sometimes an overestimation and we're going to make some analysis to go more in depth in this topic. Below follows a comparison of the corrosion properties found in the literature for UNS S32707 and UNS N06625. Mechanical properties for the grades are shown in Table 3.

Tab. 3 - Mechanical properties comparison

Grade	Proof strength $Rp_{0.2}$ [MPa]	Tensile strength R_m [MPa]	Elongation %	Density [g/cm³]	Hardness HRC
UNS S32707	≥ 700	920-1100	≥ 25	7.8	≤ 34
UNS N06625	414-517	827-965	30-55	8.44	≤ 40

According to test performed using ASTM G48 practice C and D, Alloy 625 has lower CPT and CCT compared to UNS S32707 (Table 4).

Tab. 4 - Pitting and crevice corrosion comparison according to data found in literature

Grade	Test method	CPT [°C]	CCT [°C]
UNS S32707	ASTM G48 Prac. C	> 95	70
	ASTM G48 Prac. D		
UNS N06625	ASTM G48 Prac. C	> 85	35
	ASTM G48 Prac. D		

Based on the experience, it is common to choose Alloy 625 for different kind of seawater services. In Table 5 the performance of creviced samples of Alloy 625 and UNS S32707 in natural seawater have been compared. From these results is evident that Alloy 625 has worst crevice corrosion properties in seawater compared to hyper-duplex.

Tab. 5 - Natural seawater crevice corrosion tests

Grade	T [°C]	Exposure time [days]	Corrosion depth [mm]	Crevice former
UNS S32707	RT	120	0	PVDF
UNS N06625	RT	180	0.11	PTFE

Laboratory tests using modified ASTM G150 methods have also been performed in order to evaluate CPT and CCT for the two grades and to find the right standard to do so, being aware that duplex and Ni-based alloys have very different corrosion mechanisms. To challenge the materials we have needed to test it with a chlorides content of 13% by weight (25% NaCl). The tests were performed as follows:

- CPT and CCT were determined by, from room temperature, successively increasing the temperature by 1°C/min while maintaining a fixed potential
- CPT and CCT values were determined when corrosion current >100 µA/cm2 were recorded for more than 60 s.

Both UNS S32707 and Alloy 625 were first tested with an applied potential of 700 mV vs. SCE, which is the common applied potential for stainless steels such as UNS S32707.

However, due to a different surface reaction for Alloy 625 this alloy was also tested at 500 mV and 300mV vs. SCE. The results from the experiments are shown in Table 5.

Tab. 6 - Tests results with 13% w/w chloride solution, using modified ASTM G150 methods

Grade	300 mV	500 mV	700 mV	CPT [°C]	CCT [°C]
UNS S32707	[-]	[-]	[-]	93 @700 mV	71 @700 mV
Alloy 625	Pitting	Uniform corrosion	Uniform corrosion	102 @300 mV	40 @300 mV

The result in table 6 are confirming the data found in literature, but we need to consider that the results showed are obtained at different potential and applied to materials that are part of different families and thus different surface chemistry, repassivation velocity and corrosion mechanisms.

Conclusions

Based on the obtained results the following conclusions can be made:

- Alloy 625 is not a stainless steel and will not react the same as UNS S32707.
- 300 mVSCE is a much lower potential and thus milder environment compared to 700 mVSCE.
- According to AST G48,
- According to ASTM G48, the CPT of hyper-duplex is about 97.5 °C and the CCT is about 79°C. Both values are about 20°C higher than those of super-duplex. UNS S32707 shows better resistance towards chloride induced localized corrosion compared to UNS N06625.
- Duplex grades are less prone to alloying element price variation considering that they have a low nickel content.
- Hyper-duplex has higher mechanical properties which allow wall thickness reduction of the tubes with improved efficiency of the heat exchanger.
- Hyper-duplex is harder than super-duplex and austenitic grades and this gives better resistance towards erosion-corrosion

Hyper-duplex UNS S32707 shows an important improvement compared to super-duplex grades with both CPT and CCT being considerably higher. These properties makes it possible to select this grade instead of more expensive ones, especially when it comes to hot seawater. The result from the study on Alloy 625 indicates that the performance of UNS S32707 and Alloy 625 are similar in terms of pitting corrosion resistance but that UNS S32707 has better crevice corrosion resistance.