ROLLED ALLOYS

REPORT

THE USE OF ZERON 100 SUPER DUPLEX STAINLESS STEEL FOR SWRO DESALINATION APPLICATIONS.

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SUMMARY

This report describes the mechanical properties and corrosion resistance of Zeron 100 super duplex stainless steel and its use in seawater reverse osmosis (SWRO) desalination plants. The design stresses and cost savings benefits of utilising Zeron 100 are discussed. Some of the applications and service experiences are presented.

1.0 INTRODUCTION

With rising populations and industrial expansion there has been a steadily increasing demand for fresh water. In areas where natural supplies are limited and there is easy access to the sea or saline boreholes, then desalination offers a solution. There are three main desalination processes, multi-stage flash (MSF), reverse osmosis (RO) and multiple effect distillation (MED). With the improvements in membrane efficiency and the lowering of membrane costs, RO is becoming increasingly the first choice method of desalination. It has the advantage that it can be equally efficient as small units for hotels etc as well as in large, modular municipal units. This report describes the mechanical and corrosion properties of Zeron 100 superduplex stainless steel and the areas in SWRO desalination plant where it is finding increasing use.

2.0 ALLOY PROPERTIES

2.1 Development

During the late 1970's there was a demand from the offshore oil and gas industry for a more corrosion resistant, high strength stainless steel for seawater, firewater and injection pumps. RA Materials modified existing 25%Cr duplex alloys to produce Zeron 100, the first of the superduplex stainless steels. This casting alloy quickly proved its worth during the 1980's and led to a demand for a wrought equivalent. RA Materials developed a wrought version of Zeron 100 in 1987/8 and took major orders for piping systems in the alloy in 1989. Since that time Zeron 100 has seen worldwide use in difficult marine environments with great success in both cast and wrought forms.

2.2 Properties

Zeron 100 is a superduplex stainless steel i.e. it is 50% austenite and 50% ferrite. This gives the alloy the benefits of the austenitic microstructure, such as ductility, and also those of the ferritic microstructure, such as strength.

The composition of Zeron 100 in both cast and wrought forms is shown in Table 1, with some common stainless steels for comparison. The pitting resistance equivalent number or PREN is a guide to the corrosion resistance in chloride-containing fluids, where
PREN =%Cr + 3.3 x %Mo + 16 x %N.

Zeron 100 is the only superduplex alloy to guarantee a minimum PREN value greater than 40.

Zeron 100 is a high strength alloy with good ductility and formability. The minimum mechanical properties at 20°C are shown in Table 2. This shows that the minimum 0.2% proof stress for wrought Zeron 100 is over twice that of 316L stainless steel and 1.8 times that of 6%Mo austenitic alloys. This means that in the design of vessels and piping systems, particularly at high pressure, it is possible to use a reduced thickness of Zeron 100. This is not only reduces costs by using less metal, but also lowers fabrication times and costs. This is discussed in more detail in Section 5.

Vessels are usually designed to ASME VIII div 1 or PD 5500 while piping is usually designed to ASME B31.3. Zeron 100 (UNS S32760) has been submitted and accepted into all three codes with the design stresses shown in Table 3. Zeron 100 is listed in the current edition of ASME B31.3 and can be found under code case 2245-1 in ASME VIII div 1 and enquiry case 5500/87 in PD5500.

Zeron 100 is readily welded by all the common arc welding processes. If the weld is to be heat treated after fabrication, it is welded with matching composition filler metal, Zeron 100M. If the weld is to be used in the as-welded condition, it is fabricated with over-alloyed filler metal, Z100X. This contains 2 to 2.5 wt% more nickel than the parent alloy to ensure the correct phase balance in the weld metal. Like all high alloy stainless steels it is important to exercise strict control over joint design and to keep heat inputs and interpass temperatures low. Welds in Zeron 100 have been successfully qualified with a wide range of processes with metal thicknesses from 1mm to 63mm. The selection of the best welding parameters is described in a separate publication[1]. Some of the experiences with welding Zeron 100 for a range of projects have been described by Warburton et al[2].

Zeron 100 is available in a wide variety of product forms, including pipes, fittings, flanges, bar, plate, fasteners and billet for fast-track forging, as well as castings for pumps and valves. In excess of £4m-worth of wrought products is held in stock in our Manchester warehouse.

3.0 REVERSE OSMOSIS

Figure 1 shows a schematic diagram of a typical SWRO plant. In the low pressure section, seawater is taken in and filtered, typically down to 1µm. Chlorine is frequently injected at the inlet to control fouling, added either continuously or intermittently. Chlorine will damage the RO membranes and so it is removed at the inlet to the high pressure pumps by injecting bisulphite to control the redox potential. The redox potential is usually in the range +250 to 350 mV $Ag/AgCl_{sat}$. In the high pressure section, typically 65 to 100 bar, the seawater enters the membrane cells. To make drinking water it is often necessary to take the first stage permeate and pass it through a second set of membrane cells to further reduce the chloride content of the water. The water entering the second stage typically has a chloride content of 2,000 to 4,000 mg/l. The concentrated brine from both stages is still at high pressure and so energy is recovered from the waste stream prior to discharge. Early plants used the reject brine to power a pelton wheel turbine to make electricity. However, modern plants use the more efficient method of hydraulic energy recovery. This reduces the size of the high pressure pumps, which reduces costs because of reduced electricity consumption.

The permeate, or drinking water, can then be put into the water distribution system, often with a small addition of chlorine/hypochlorite to disinfect the water.

4.0 CORROSION

4.1 Low Pressure Feed

The low pressure section is just like any other piping handling natural or chlorinated seawater. It is very common to use stainless steels in this section and they must resist crevice corrosion. Kovachs and Redmond[3] reviewed a large quantity of crevice corrosion data from exposure tests in warm seawater. They showed that only alloys that could pass an ASTM G48B (crevice) test in ferric chloride at 35℃ would resist crevice corrosion in warm seawater (Figure 2). They then plotted the ASTM G48B threshold temperature for crevice corrosion against the PREN of the various alloys, as shown in Figure 3. The results show three separate lines for ferritic, duplex and austenitic stainless steels. To get a pass in the G48B test at 35℃ it is necessary for a duplex stainless steel to have a PREN>40 and an austenitic alloy to have a PREN >43. Only the superduplex and 6%Mo austenitic alloys meet these criteria.

These results have been confirmed by numerous workers who have carried out crevice corrosion tests on stainless steels in both natural and chlorinated seawater. Figure 4 shows the results of tests from both the UK[4, 6] and the USA[5] in natural seawater, while Figure 5 shows data for chlorinated seawater[6]. Figure 6 shows data for chlorinated seawater at 40°C[7]. All of these results show that lower alloy stainless steels such as 316L, 904L and 22%Cr duplex are susceptible to crevice corrosion, even at relatively low seawater temperatures. Figure 6 shows that at 40°C even 6%Mo austenitic stainless steel can suffer corrosion, but Zeron 100 superduplex suffered no attack.

The limiting factor for corrosion of superduplex stainless steel in warm seawater is the weld metal, and the performance of this can be improved by pickling, either by immersion in a bath or by use of a pickling paste formulated for superduplex alloys for 2 hours [8].

Where pickling is not practical, it has been found[8] that a gentle start up can increase the CPT of Zeron 100 welds. A typical start up regime would be:-

Cold seawater – 2 days min
Cold chlorinated seawater – 5 days min
Hot chlorinated seawater – thereafter

Experiences in the North Sea[9] have demonstrated the benefit of a gentle start up for Zeron 100.

4.2 High Pressure Feed

In the high pressure section, the fact that the seawater is filtered and treated and has a relatively low redox potential, means that conditions are somewhat less aggressive than in the low pressure section. Figure 7 shows the potentials that a high alloy stainless steel can achieve in seawater. In natural seawater a biofilm forms within a few days or weeks and this gives a potential around +300mV SCE. When the seawater is chlorinated the potential increases to ~600mV SCE because chlorine is a powerful oxidising agent. If the seawater temperature is increased 25° to 30°C above normal ambient temperature, the biofilm cannot form and the potential is much lower. If the oxygen content of the water is reduced, the potential decreases even further.

A redox potential in the range +250 to +350mV Ag/AgClsat is equivalent to a stainless steel potential of +100 to +200 mV SCE, as shown in Figure 7. RA Materials have carried out laboratory crevice corrosion tests at different potentials to determine the relative threshold or critical crevice corrosion temperature (CCT) for various alloys. The results, in Figure 8, show that even at the reduced potentials in the high pressure feed section, lower alloy materials are susceptible to crevice corrosion and only Zeron 100 and 6%Mo alloys will be resistant.

This has been confirmed by service experience and several authors [10,11] have reported failures of 316L, 904L and 22%Cr in SWRO applications and its replacement by Zeron 100 or 6%Mo austenitic alloys.

4.3 Brine Reject

The redox potential in the brine reject section is the same as in the high pressure feed. However, the chloride concentration can now be up to double that in the seawater feed (i.e. ~40,000 mg/l). The critical crevice temperature of Zeron 100 is not very sensitive to chloride concentration, as shown in Figure 9, this means that the reduction in CCT in going from 20,000 to 40,000 mg/l chloride is very small. Other stainless steels tend to follow the same trend as Zeron 100 and this means that the same alloy should be used in the reject brine section as is used in the high pressure feed. This means Zeron 100 or 6%Mo austenitic alloys.

5.0 COST COMPARISONS

The high strength of Zeron 100, compared with many other stainless steels, means that it can be used to reduce wall thickness and lower costs, both of metal and in fabrication. Piping is normally designed to ASME B31.3 and the results of calculations for a pipework system operating at 70 bar and 25℃ are shown in Table 4. This shows that up to NPS 8 pipe size, schedule 10S wall thickness can be used with Zeron 100.

In order to evaluate the potential savings, comparisons have been made with UNS S31254, a common 6%Mo austenitic alloy. Size for size, piping in Zeron 100 is 5 – 15% less costly than 6%Mo austenitic, depending on pipe size and the method of manufacture, because of its lower nickel and molybdenum content. For the purposes of this evaluation a mean differential of 10% has been used.

The results in Table 5 show that where a schedule size reduction in pipe can be utilised, the savings range from 25% with NPS 1 pipe to 60% with NPS 8 pipe. With larger pipe sizes both alloys are normally in a schedule 40S wall thickness resulting in 10% cost savings. However, for a sufficiently large pipe order, NPS 10 size and larger could be produced as seam welded pipe to schedule 20. This will result in cost savings of 38% for NPS 10 and 39% for NPS 12 compared with schedule 40S in 6%Mo austenitic.

Hence there are large potential cost savings to be made by utilising the high strength of Zeron 100. The parts of an RO plant requiring high strength are the high pressure feed pipes and the brine reject piping, which can both take advantage of these cost savings.

6.0 SERVICE EXPERIENCE

Zeron 100 has been in service in seawater around the world since 1986 as a cast product and since 1990 as a wrought product.

Table 6 shows some of the seawater and firewater systems supplied in Zeron 100 around the world. Zeron 100 piping has been used for seawater and firewater piping in the North Sea with excellent results. On the Scott platform some of the sea water discharges are at 40℃ and there have been no corrosion problems after 10 years[9]. On the piper Bravo platform the discharge temperature from three heat exchangers was raised from 20° to 55℃, with no corrosion problems after 2 years[9]. The temperature has been increased again to 65℃ and there have still been no corrosion problems after a further 8 years. These experiences show the good resistance of Zeron 100 to crevice corrosion at elevated temperatures.

Table 7 shows some of the RO desalination projects that have utilised Zeron 100. These can vary from small, skid mounted units for hotels and similar small users (Figure 10) to large, modularised units for municipal use (Figure 11). A variation of reverse osmosis is used by the oil and gas industry for removing sulphate from seawater for injecting into wells to increase production. Zeron 100 has been used for a number of sulphate removal modules (Table 7) and a modular unit for an FPSO is shown in Figure 12. Zeron 100 has also been used for constructing the filter vessels on the low pressure seawater feed lines as shown in Figure 13. Zeron 100 has now been used all over the world for both SWRO plants and in sulphate removal plants with great success.

7.0 CONCLUSIONS

Zeron 100 has exceptionally good resistance to corrosion in seawater, which combined with its fabricability and availability in all product forms, makes it eminently suitable for a wide range of applications in SWRO desalination plant. The high strength of Zeron 100 enables it to be used very cost effectively by reducing wall thicknesses. This saves money not only on the initial material costs, but also on subsequent fabrication time and costs. The service experience with Zeron 100 confirm its selection as a corrosion resistant, high reliability alloy that is also readily available.

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TABLE 1. The composition of Zeron 100 compared with some common stainless steels.

ALLOY	NOMINAL COMPOSITION (WT%)							PREN*
	Fe	Cr	Ni	Mo	Cu	W	N	
316L	bal +	17	10	2	-	-	-	24
904L	bal	20	25	4.5	1	-	-	35
22%Cr Duplex	bal	22	5	3	-	-	0.15	35
6%Mo Aust.	bal	20	18	6	0.7	-	0.2	43
Zeron 100 (Wrought)	**bal**	**25**	**7**	**3.5**	**0.7**	**0.7**	**0.25**	**>40**
Zeron 100 (Cast)	**bal**	**25**	**8**	**3.5**	**0.7**	**0.7**	**0.25**	**>40**

+ bal = Balance

* PREN = % Cr + 3.3 x % Mo + 16 x % N

TABLE 2. Minimum mechanical properties at room temperature of Zeron 100 compared with some common stainless steels.

ALLOY	0.2% PROOF STRESS (MPa)	UTS (MPa)	ELONGATION (%)	(MAX) HARDNESS (HRC)
316L	170	485	35	22
904L	215	490	35	22
6%Mo Aust	300	650	35	22
Zeron 100 (Wrought)	**550**	**750**	**25**	**28**
Zeron 100 (Cast)	**450**	**700**	**25**	**24**

TABLE 3. Design stresses for wrought Zeron 100 to British and American vessel and pipe codes.

TEMPERATURE (℃)	DESIGN STRESS (MPa)		
	PD5500*	ASME VIII div 1+	ASME B31.3
20	319	214	250
50	319	214	250
100	300	212	246
150	281	203	237
200	269	200	235
250	250	200	234
300		200	234

* Enquiry case 5500/87
+ Code case 2245-1

TABLE 4. Pipe wall thickness and schedule sizes to ASME B31.3 for Zeron 100 at 25°C.

PIPE SIZE (NPS)	PRESSURE (bar)	REQUIRED NOMINAL WALL THICKNESS (mm)	NEAREST STANDARD SCHEDULE SIZE
1	70	0.53	10S
2	70	0.95	10S
4	70	1.81	10S
6	70	2.66	10S
8	70	3.46	10S
10	70	4.32	20
12	70	5.12	20

TABLE 5. Relative costs of Zeron 100 piping compared with 6Mo austenitic.

PIPE SIZE (NPS)	6%Mo AUSTENTIC		ZERON 100	
	SCHEDULE	REL. COST*	SCHEDULE	REL. COST*
1	40S	100	10S	75
2	40S	100	10S	65
4	40S	100	10S	47
6	40S	100	10S	44
8	40S	100	10S	40
10	40S	100	40S	90
12	40S	100	40S	90

* 6%Mo = 100

TABLE 6. Major seawater and firewater systems in Zeron 100.

CLIENT	CONTRACTOR	PROJECT
Amerada Hess	Brown & Root	Ivanhoe/Rob Roy (Seawater system)
Mobil	Davy McKee	Beryl A (Firewater/Deluge system)
British Gas	Global	Morecambe Bay (Seawater discharge)
BP	Brown & Root Vickers	BP Bruce (Firewater/seawater)
Amerada Hess	Foster Wheeler	Scott (Seawater system)
QGPC	Global Eng.	Diyab (Hook up system)
Hamilton Oil	Brown & Root	Liverpool Bay (Seawater/firewater)
EE Caledonia	Brown & Root	Piper Bravo (Seawater/firewater)
ONGC	Hyundai	Neelam (Column pipes)
Johnston Hunt	-	BP Forth (Heat Exchanger)
Maersk		Harald West (Heat Exchanger)
AGIP	Weir Westgarth	Tiffany (Sulphate RO removal)
Ministry of Environment (Spain)	FCC/SPA	Adege-Aronas (RO plant)
Degremont	-	Vado-Ligure (RO Plant)
Sual Power Station	Weir Westgarth	Sual (RO Plant)

TABLE 7. Some of the desalination projects supplied in Zeron 100 superduplex stainless steel.

CLIENT	PROJECT	CONTRACTOR	SYSTEM TYPE
Agip	Tiffany	Weir Westgarth Ltd.	Sulphate Removal Module ($15,000m^3$/day)
Ministry of Environment Dept. for Water Installations & Quality	Adeje-Aronas Tenerife	Formento De Construcciones Y Contratas SA (FCC) & Servicious Y Procesos Ambientalessa (SPA)	R.O. Plant ($27,000m^3$/day)
ENEL	Vado Ligure Italy	Degremont	R.O. Plant
Consejo Insular de Aguas de Tenerife (Tenerife Island Water Council)	Playa De Las Americas Phase 2A	FCC/SPA	R.O. Plant ($27,000m^3$/day)
Consejo Insular de Aguas de Tenerife (Tenerife Island Water Council)	Roque Prieto-Guia Seawater Plant	SPA	R.O. Plant ($7,000m^3$/day)
Consejo Insular de Aguas de Tenerife (Tenerife Island Water Council)	Playa De Las Americas Phase 2B	FCC/SPA	R.O. Plant ($7,000m^3$/day)
Sual Power Station	Sual Pangasinan Philippines	Weir Westgarth Ltd.	R.O. Plant ($8,000m^3$/day)
Tampa Bay Desal	Tampa Bay	Covanta	H.P. Seawater Feed (SWRO $106,000M^3$/d)
KBR	Greater Plutonio	Weir Westgarth	SRP ($66,450m^3$/d)
Palm Water	Palm (Phase 1+2)	Hyflux	SWRO plant ($2x32,000m^3$/d)
UTE Idom Torrevieja	Torrevieja	Acconia	SWRO plant ($20,000m^3$/d)

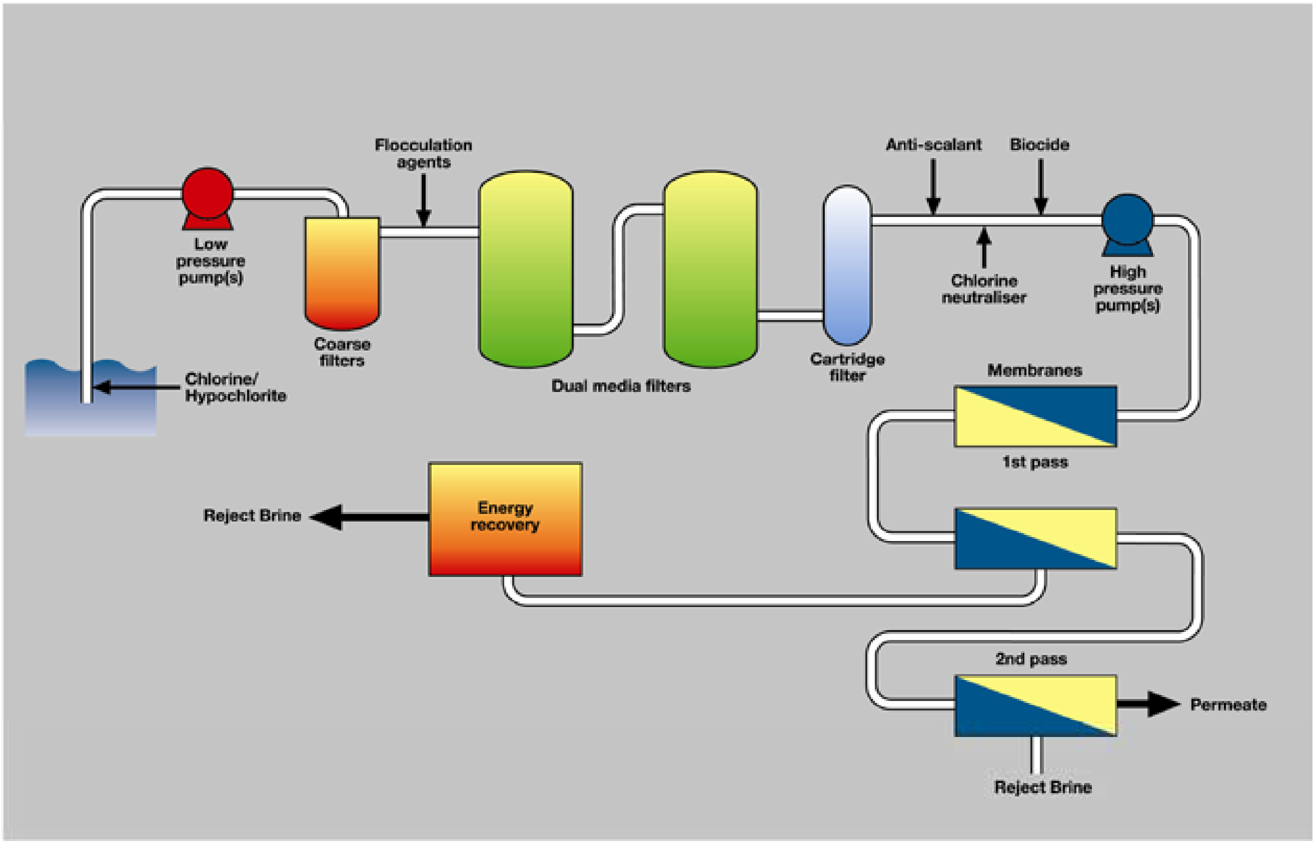

FIGURE 1 Schematic diagram of a typical seawater reverse osmosis plant.

FIGURE 2 Percentage of sites attacked vs critical crevice temperature in ASTM G48 (Ref 3)

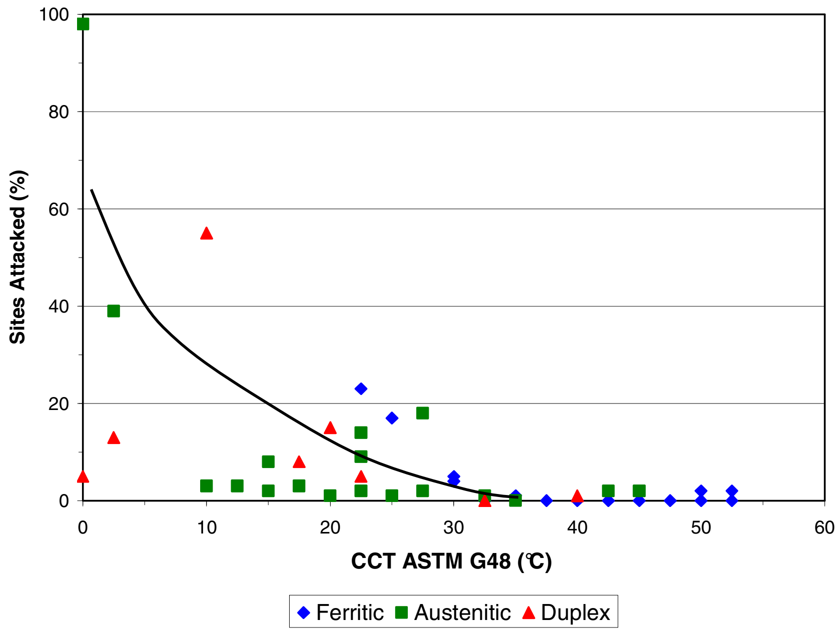

FIGURE 3 Relationship between PREN and critical crevice temperature (ASTM G48) [Ref 3]

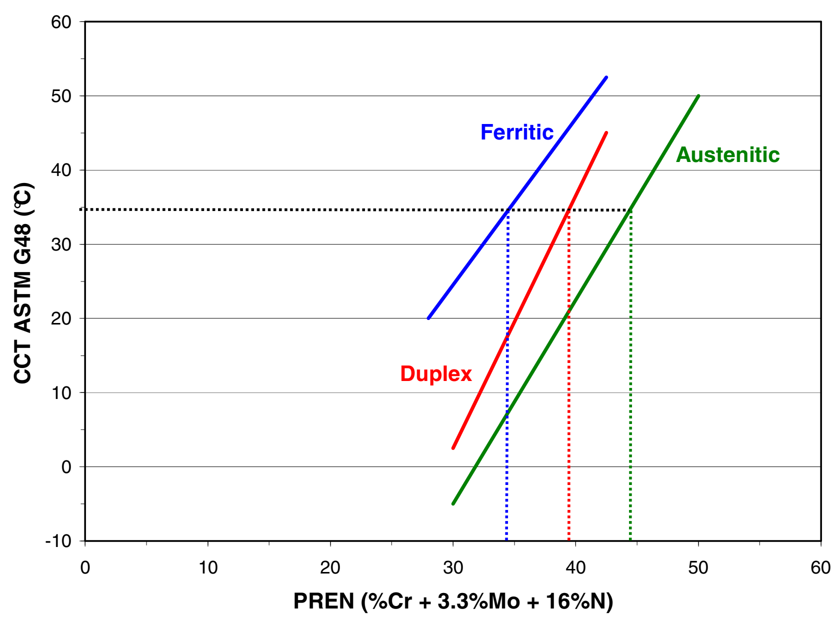

FIGURE 4 Depth of crevice attack in natural seawater at various temperatures (Refs 4, 5, 6)

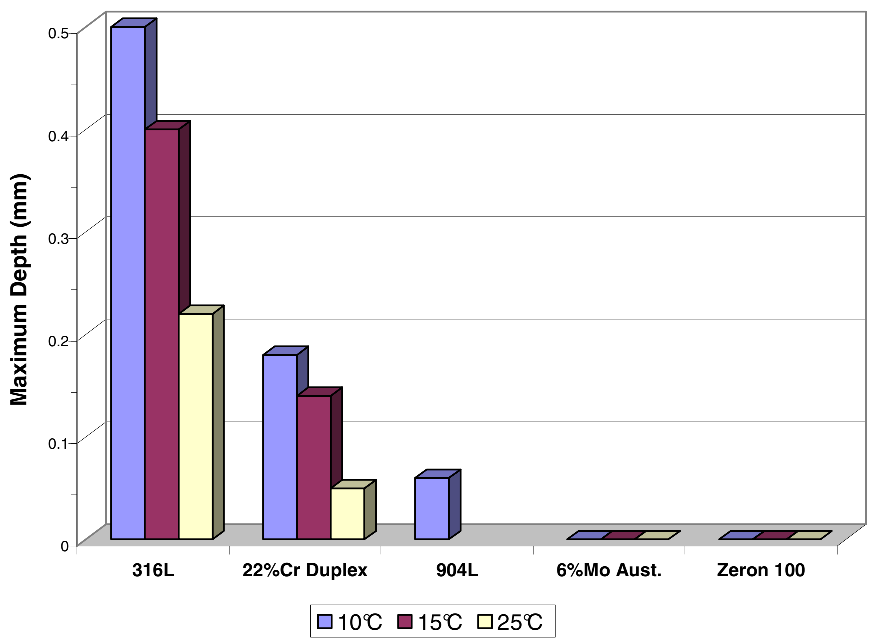

FIGURE 5 Depth of crevice attack in seawater with 1mg/L chlorine at 16℃ [Ref 6]

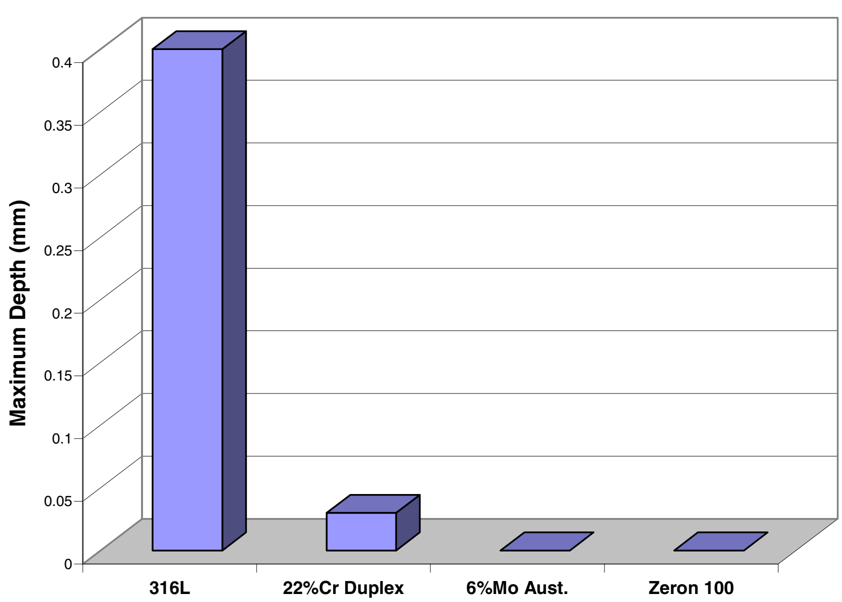

FIGURE 6 Depth of crevice attack in seawater with 1mg/L chlorine at 40°C [Ref 7]

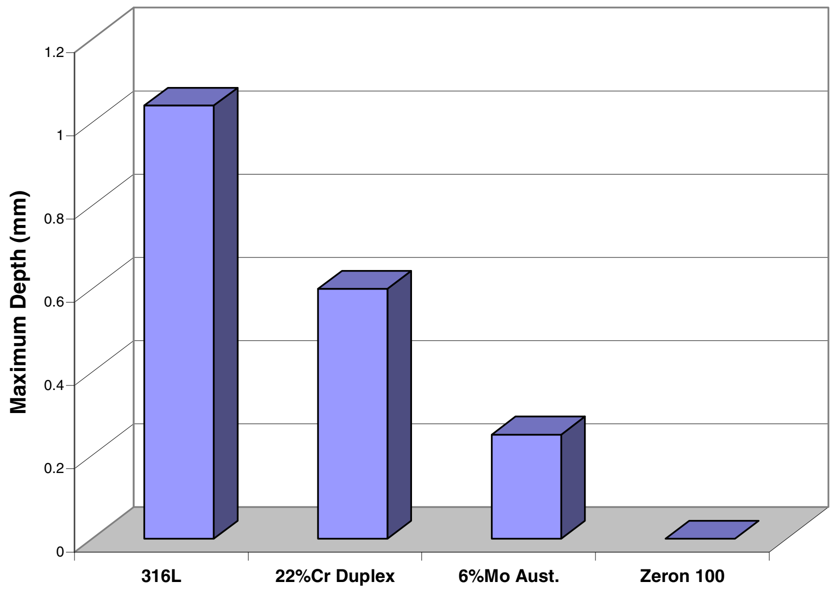

FIGURE 7 Typical potentials of stainless steel in seawater

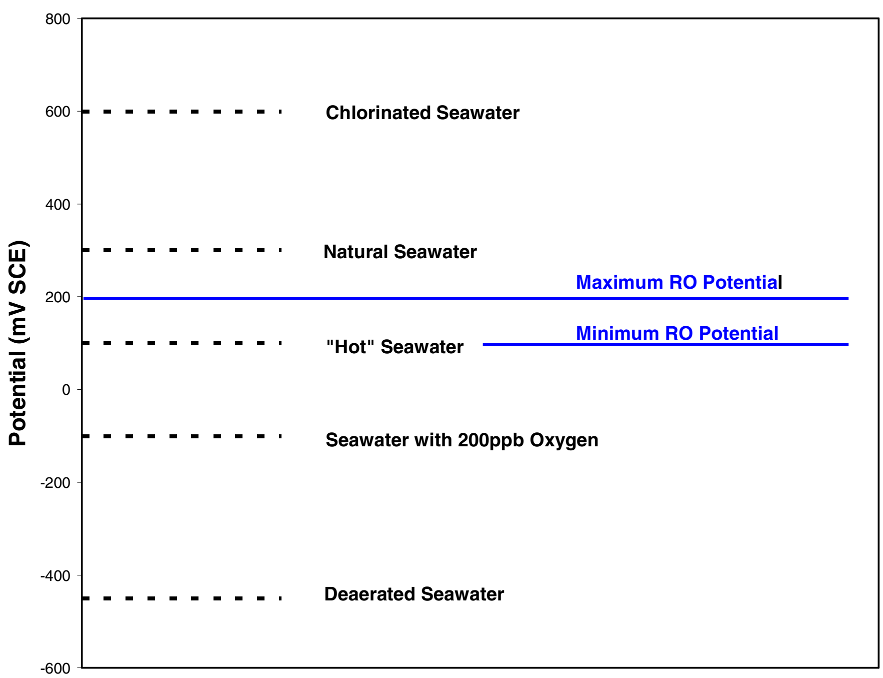

FIGURE 8 Relative CCT in seawater as a function of potential

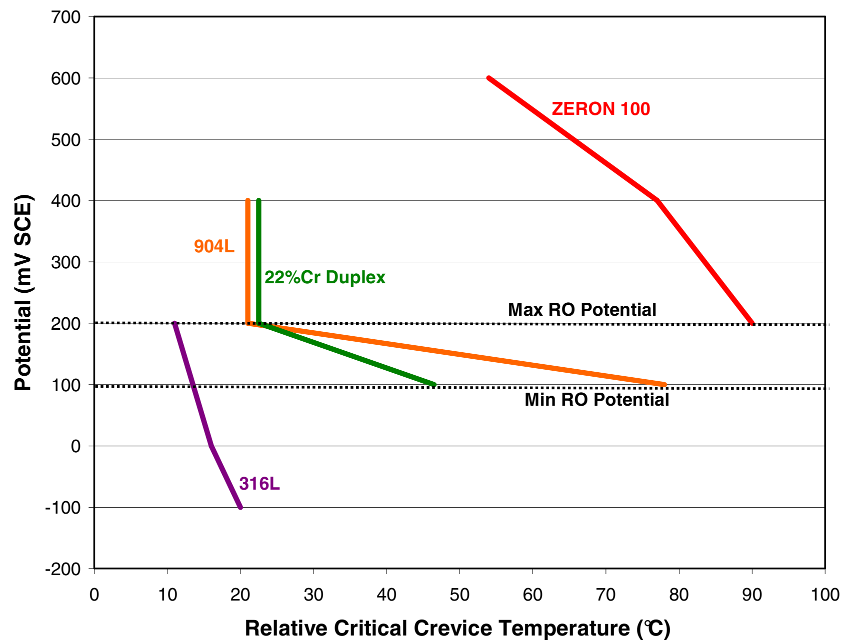

FIGURE 9 Relative CCT as a function of chloride content at various potentials

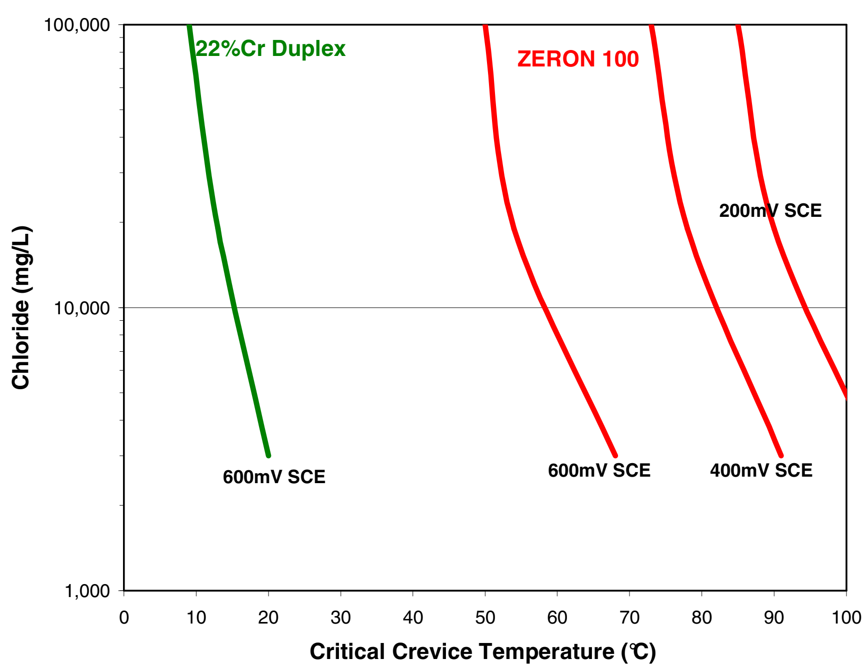

FIGURE 10 Small RO module for a Spanish hotel.

FIGURE 11 Large desalination plant at Tampa Bay, USA.

FIGURE 12 Modular sulphate removal unit for an FPSO.

FIGURE 13 Zeron 100 filter vessel for a seawater RO plant.