Paper No.
11351

NACE INTERNATIONAL CORROSION 2011 CONFERENCE & EXPO

THE CORROSION OF SUPERDUPLEX STAINLESS STEEL IN DIFFERENT TYPES OF SEAWATER

R Francis, G Byrne and G Warburton
Rolled Alloys Technology Group
Unit 16, Walker Industrial Park
Walker Road
Blackburn BB1 2QE
UK

ABSTRACT

Superduplex stainless steels have been used in seawater systems since 1986 as castings and since 1990 as wrought product. The performance has generally been excellent with few problems. However, seawater is a complex medium and, depending on the redox potential, stainless steels can adopt a wide range of potentials, spanning over a volt. Different methods of operation can lead to service potentials right across this range and the limits of use of superduplex stainless steel vary according to the potential. They cover the range from stagnant deaerated conditions, where the risk of microbially influenced corrosion is high, to chlorinated, flowing seawater, where the risk of crevice corrosion is high. The present paper describes some of the service environments commonly in use and the conditions that give rise to specific operating potentials. The limits of use under these conditions are described utilizing both laboratory and service experience. The results show the ability of superduplex stainless steel to tolerate a wide range of marine service environments without suffering localised corrosion.

Keywords: seawater, crevice corrosion, stainless steels, desalination, MIC

INTRODUCTION

Superduplex stainless steels have been used in seawater service since 1986 as castings and since 1990 as wrought product. They have been very successful in both cooling and firewater systems[1], and they have also been used for a wide variety of other applications in the marine environment. The nature of these environments can differ widely from normal, aerated seawater, and can introduce additional factors that may increase the aggressivity. This paper reviews the performance limits of superduplex stainless steel in a wide range of marine environments.

THE ALLOY

The data in this paper is all concerned with the authors' company's alloy, ZERON® 100, the first of the superduplex stainless steels. It is covered by UNS J93380, for castings, and UNS S32760, for wrought products, and is known by the generic name of alloy Z100.

® Registered trademark of Rolled Alloys

The alloy has a nominal composition of Fe/25Cr/7Ni/3.5Mo/0.25N/0.7Cu/0.7W, with a PREN>40, where PREN = % Cr + 3.3 x % Mo + 16 x % N. This is recognized as the minimum level of alloying required to resist crevice corrosion in seawater by standards, such as the Norwegian oil and gas NORSOK standard[2].

Alloy Z100 is roughly 50/50 austenite/ferrite and combines high strength with good corrosion resistance in a wide range of environments. The alloy is readily weldable by all the common arc welding techniques and welds of thickness from 1 to 90mm are in service. The alloy is readily available in a wide variety of product forms, enabling most components to be manufactured simply.

POTENTIALS

High alloy stainless steels have a wide passive range and, depending on the cathodic reaction, they can adopt a wide range of electrochemical potentials. This is shown in Figure 1[3].

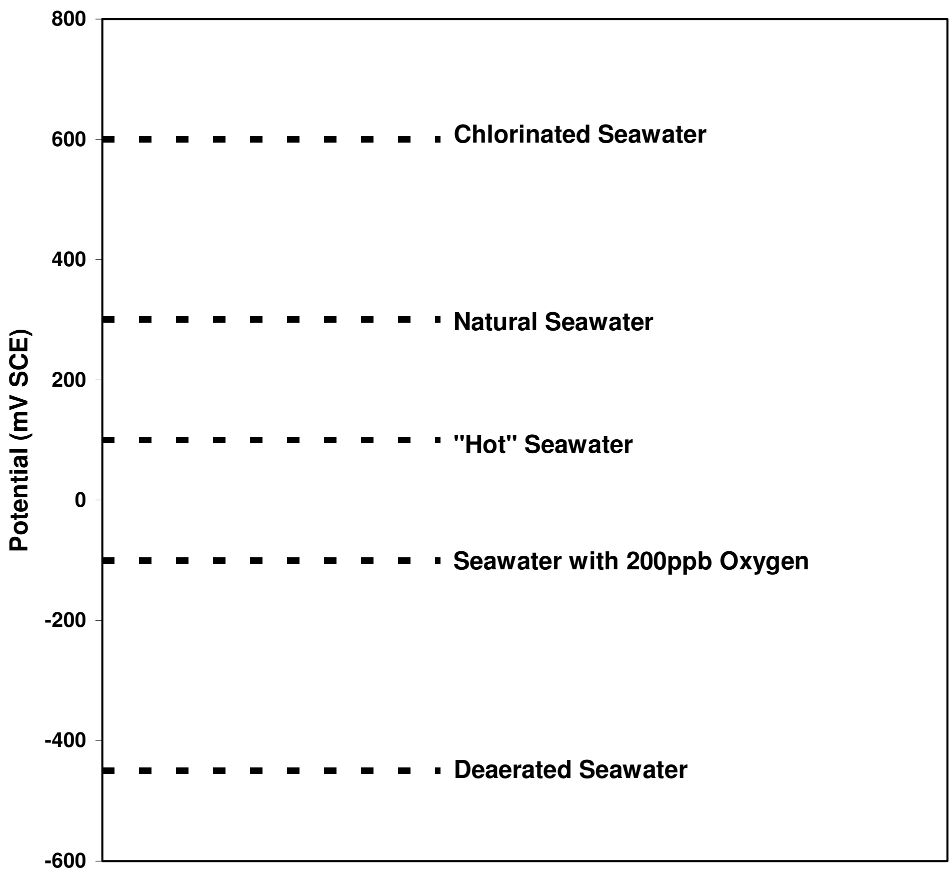

Figure 1 Typical potentials of stainless steels in seawater[3].

In natural, aerated seawater a biofilm forms on the stainless steel in a time that can vary from 2 days to 2 weeks. The biofilm depolarises the cathodic reaction (the reduction of dissolved oxygen) and gives an open circuit potential of around +300mV SCE. If the seawater is chlorinated, to control fouling (typically 0.5 to 1.0mg/L chlorine), the cathodic reaction is the reduction of hypochlorite to chloride[4] and the potential increases to around +600mV SCE.

If the seawater is heated to 25 to 30°C above normal, local ambient, then the biofilm cannot form and the potential is more negative, around +100mV SCE. Normal, local ambient temperature would be 0°C in the Antarctic and around 20°C in the Mediterranean Sea and it is the increase above this that prevents the biofilm development[5].

If the oxygen content of the seawater is reduced, the potential further decreases and can be around -100mV SCE with 200ppb dissolved oxygen. Further reduction of the dissolved oxygen content lowers the potential even further, reaching -450mV SCE in fully deaerated seawater.

The corrosion resistance and limits of use of superduplex stainless steels vary greatly over this potential range, as described below.

NATURAL SEAWATER

Alloy Z100 has excellent resistance to crevice corrosion and has been widely used in natural seawater all over the world. It has been used extensively for pumps and column pipes for seawater lift, and also for the bolts on the column pipes and pumps. This service includes the Middle East, Europe and the Far East, at seawater temperatures from 4 to 40°C.

Some other applications include the use of Z100 bolting to fasten rubber fenders to a dockside in Bahrain (Figure 2) and the alloy's use for the tracks on the Thames Barrier in London (Figure 3).

Figure 2 Z100 bolting on fenders on a dock in Bahrain

Figure 3 Z100 tracks on the Thames Barrier

The barrier is raised when exceptionally high tides are expected, to prevent London from flooding. The five gates are operated by arms running on a rail that can be fully or partially immersed. Z100 was chosen for its strength and corrosion resistance to replace the original low alloy steel that had worn and corroded. The Z100 rails are designed to last a minimum of 40 years.

CHLORINATED SEAWATER

Most seawater cooling systems are chlorinated to prevent fouling and alloy Z100 has excellent resistance to crevice corrosion under these conditions. Figure 4 shows the maximum depth of crevice corrosion after 60 days exposure at 16°C with 1mg/L chlorine[6]. The 25%Cr duplex was UNS S32550 with a PREN of ~37. The results show that only Z100 and 6%Mo austenitic alloys resisted crevice corrosion. Figure 5 shows similar data at 40°C and crevice corrosion then occurred on the 6%Mo alloy, while alloy Z100 resisted attack. Francis and Byrne reviewed the service experience with superduplex stainless steel in seawater and showed successful applications up to 40°C[1].

In addition to piping applications, superduplex stainless steel has also been used in chlorinated seawater for filter vessels and heat exchangers, with excellent results.

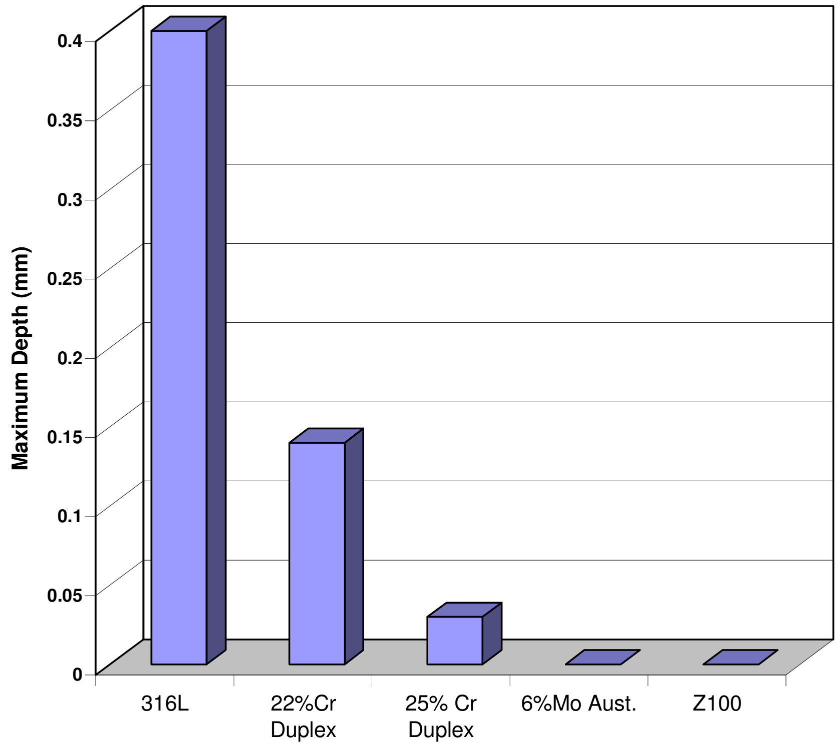

Figure 4 Depth of crevice corrosion in seawater at 16℃ with 1mg/L chlorine[6].

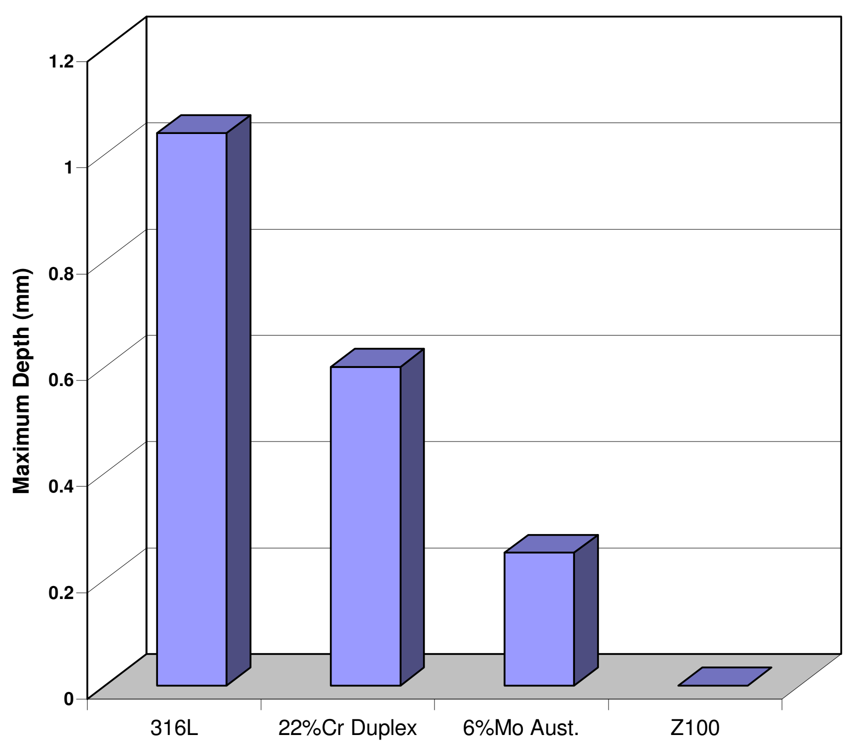

Figure 5 Depth of crevice corrosion in seawater at 40℃ with 1mg/L chlorine[6].

Extending the Limits

The limit of use with superduplex stainless steel in chlorinated seawater is normally 40℃, and the performance is limited by the welds[1, 7]. These are made with a matching filler containing 2 to 2.5% extra nickel to ensure a 50/50 phase balance in the weld metal. Mostly the alloy is used in the as-welded condition, but the limits of use can be extended[1, 7], as follows.

Pickling of the welds has been shown to increase the pitting temperature of welds by 10 to 15℃[7]. This technique has been applied to piping spools on a number of projects where seawater temperatures exceeded 40℃[1].

Where pickling is not an option, a soft start up is an alternative. This offers increased corrosion resistance, for example to piping downstream of heat exchangers. The recommendation is:

- Cold natural seawater for 48 hours
- Cold chlorinated seawater for 5 days minimum
- Warm chlorinated seawater thereafter

This treatment allows a passive film to form with fewer defects that is more resistant to local breakdown. Francis and Byrne[1] describe the successful use of a soft start up on a North Sea platform, where the piping downstream of three gas coolers ran at ~20℃ for several months. Then more wells were brought on stream and the heat exchanger discharge temperature rose to ~55℃. After two years there were no leaks and the discharge temperature was further increased to ~65℃. After 10 years no leaks have been reported. This experience demonstrates the ability of a soft start up to extend the safe operating temperature range.

SEAWATER REVERSE OSMOSIS DESALINATION

With the increasing shortage of fresh water for drinking and agriculture, desalination is being increasingly used to make up the shortfall. Reverse osmosis is a very widely used technology for desalination and this uses stainless steels for pumps, valves, piping and vessels.

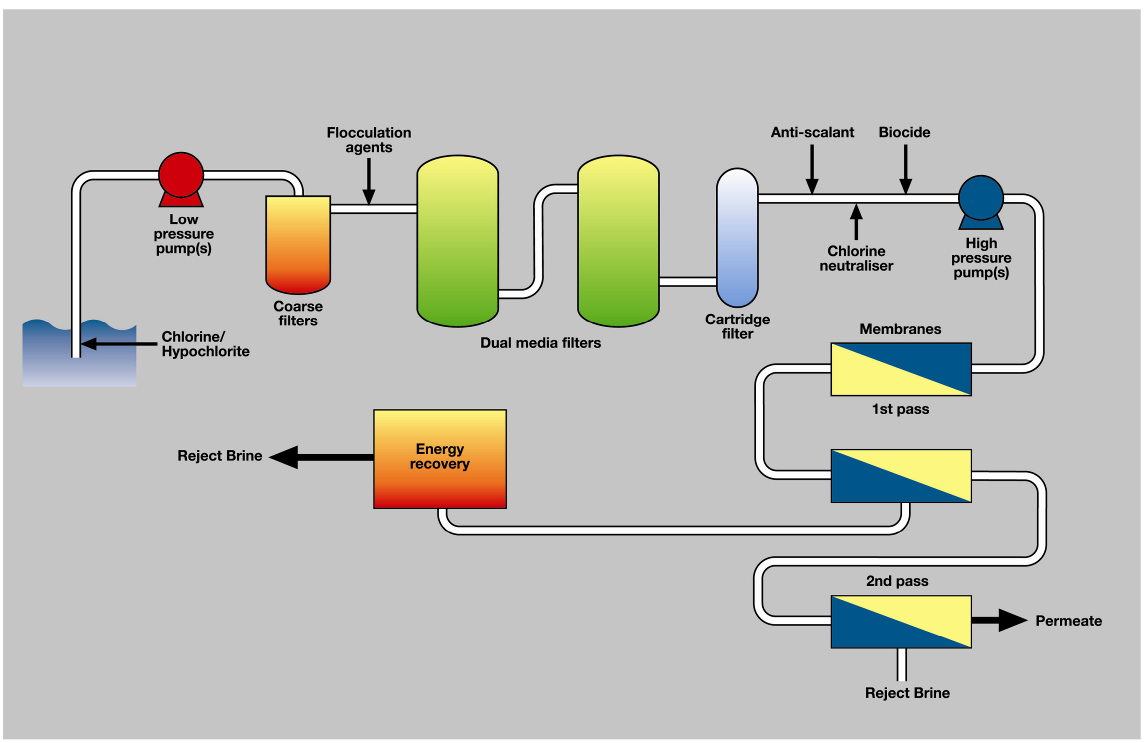

Figure 6 Schematic drawing of a typical SWRO plant.

The Technique

A simplified schematic drawing of a typical SWRO plant is shown in Figure 6. The economics of an RO plant depend, greatly, on the life of the membranes and so water treatment to help preserve them is mandatory. The seawater may be chlorinated to prevent fouling in the inlet (low pressure) section, but it must be removed prior to the high pressure pumps, as chlorine will damage the membranes. This is usually done with a chemical, such as sodium metabisulphite, the additions of which are monitored and controlled by a redox probe. A non-oxidizing biocide is usually added prior to the high pressure pumps to prevent fouling of the membranes, while an anti-scalant is also added, as scaling will reduce the membrane efficiency. The feed water is also finely filtered (5µm or less) to prevent blocking of the membranes. Chemicals are often added before the low pressure filters to aid the coagulation of colloidal matter.

The pressure in the low pressure system is typically ~1MPa, but this is increased by the high pressure pumps to anywhere from 6 to 8MPa for normal systems, with high recovery systems operating at feed pressures up to 10MPa. A typical system operates at 7MPa. The permeate (produced fresh water) exits around 0.1MPa, so that the reject brine is at ~6.9MPa and contains most of the energy. To minimize costs, most of the energy is recovered from the reject brine prior to discharge.

In the offshore oil and gas industry there is a variant of RO desalination, known as sulphate removal. This uses a different membrane to greatly reduce the sulphate content of seawater being injected to enhance oil recovery. If the strata in which injection occurs contain barium or strontium salts, the formation of insoluble sulphates will plug the pores in the formation and hinder oil recovery. Not all oilfields require this technology, but as development moves to deeper and hotter wells, more fields are using sulphate removal. Apart from the membranes, it is virtually identical to conventional RO, and uses the same materials.

Corrosion in SWRO Plants

In the low pressure feed section (Figure 6), the seawater is similar to a cooling water system and may operate with natural seawater or chlorinated seawater. The chlorine may be low level continuous or intermittently at a higher level. After all the water treatment, the high pressure section operates at a redox potential of +250 to +350mV $Ag/AgCl_{sat}$. If the redox potential is higher, the membranes will be damaged and to achieve lower redox potentials, uneconomically large quantities of chemicals are required. This redox potential range corresponds to an open circuit potential of +100mV to +200mV SCE for stainless steels[8]. Most SWRO plants operate close to the maximum redox potential.

Tests were conducted by Byrne et al[8] to determine the critical crevice corrosion temperature (CCT) for a range of stainless steels as a function of potential. The results, in Figure 7, show that 316L stainless steel (UNS S31603) would be totally unsuitable for SWRO plants because of the low temperature at which crevice corrosion initiates. Alloys such as 22%Cr duplex (UNS S31803) and 904L (UNS N08904) showed good crevice corrosion resistance at +100mV SCE, but much reduced resistance (CCT = 20 to 25℃) at +200mV SCE. As most SWRO plants operate close to the maximum redox potential, stainless steels will have a potential close to +200mV SCE. This explains the failures in service of both 904L and 22%Cr duplex[8, 9]. Figure 7 clearly shows that the better crevice corrosion resistance of alloy Z100 is needed to give reliable performance under SWRO conditions. Alloy Z100 has given good service in both the high pressure and reject brine sections of SWRO plants all over the world.

LOW OXYGEN SEAWATER

In the offshore oil and gas industry it is common to inject deaerated seawater to maintain the well pressure and sustain production. On some platforms, where there are large quantities of produced water, this is injected into the oil bearing strata instead. Where there are only small quantities of produced water, it is necessary to mix the deaerated produced water with deaerated seawater.

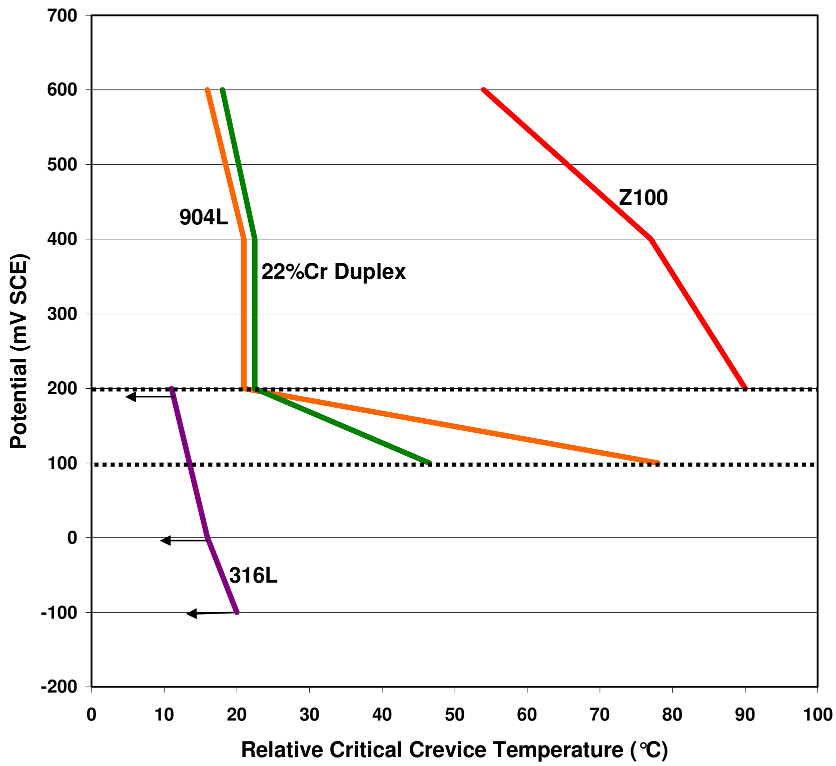

Figure 7 Relative CCT of some stainless steels in seawater as a function of potential[8].

Deaeration plants offshore are often not very efficient and deaerated seawater for injection may contain anything from 50ppb to 500ppb dissolved oxygen. Because the produced water is hot, often with a high chloride content, there is concern about the corrosion of stainless steels used in mixed water injection systems.

The authors have tested samples of Z100 in seawater with extra sodium chloride to increase the chloride content to 100,000mg/L with oxygen contents of 50, 200 and 410ppb dissolved oxygen and 0.1MPa CO_2. The samples were creviced wrought and cast Z100 and plain welded wrought Z100. The results after 30days exposure are shown in Table 1.

OXYGEN (ppb)	TEMPERATURE (°C)	RESULT(Pass/Fail)		
		Wrought	Weld*	Cast
50	120	P	P	P
	140	P	P	P/F
200	100	P	P	P
	120	P	P	F
410	80	P	P	P/F
	100	P	P	P

*pitting test

Table 1 Results of crevice and pitting corrosion tests of Z100 in a simulated mixed injection water.

It can be seen that wrought material resisted crevice corrosion and pitting at welds under all the test conditions, while the cast alloy suffered some crevice corrosion. Where the letters P/F appear in Table 1, this means that one sample passed and one suffered corrosion. The results show that the cast alloy was susceptible to crevice corrosion in some tests, but it still resisted attack up to high temperatures. No tests were conducted in sour brines. Under similar test conditions, 22%Cr duplex suffered attack in the temperature range 40 to 60°C[10].

DEAERATED SEAWATER

When metals are exposed to seawater in a restricted space, where fresh water cannot enter easily, the aerobic bacteria will consume the dissolved oxygen in a relatively short time. Once the oxygen has gone, anaerobic bacteria, such as sulphate reducers (SRB), can become active. These bacteria convert the sulphate in seawater to sulphide as part of their metabolic process. This can cause corrosion of carbon and low alloy steels, and failures of equipment in service by microbially influenced corrosion (MIC) are well documented in the literature.

To assess the resistance of a range of materials to MIC, Francis et al[11] exposed pipes in an aggressive marine mud off the south coast of the UK. Some of the pipes were fully buried in the mud and others were part immersed, with the upper half being continuously exposed to seawater. The exposure rig is shown at low tide in Figure 8. At high tide the frame was fully under water. The alloys exposed were carbon steel, 316L stainless steel and Z100.

Figure 8 The appearance of the MIC test frame at low tide.

After 5 years exposure, there was general corrosion of the carbon steel below the mudline at about the same rate as in aerated seawater (0.1mm/y). Both the carbon steel and the 316L were pitted, as shown in Table 2.

ALLOY	**DEPTH (mm) [10 Deepest]**	**MEAN DEPTH (mm)**
Carbon steel	0.50; 0.60; 0.23; 0.14; 0.27; 0.46; 0.36; 0.46; **0.64**; 0.50	0.42
316L	0.23; 0.10; 0.24; 0.23; 0.32 0.31; 0.36; **0.37**; 0.25; 0.29	0.27
Z100	0	0

Table 2 Depths of the pits on fully buried pipe sections.

No corrosion was seen on the Z100, either above or below the mud line or at the welds. This excellent resistance of Z100 to MIC has been confirmed by service experience. The alloy has been used for a subsea heat exchanger off the coast of Australia, to replace carbon steel that was corroding by MIC on the inside. This has been in service for over ten years without problems. Alloy Z100 has also been used as fasteners and clamps in a number of docks, which include exposure below the mudline. No failures or corrosion have been reported.

CONCLUSIONS

1. Stainless steels can adopt a wide range of potentials in seawater depending upon the redox potential and local conditions.
2. Alloy Z100 has good corrosion resistance over the complete range of conditions and over a useful, practical temperature range.
3. This has been demonstrated by many years of successful service experience all over the world.

REFERENCES

1. R Francis and G Byrne, *Stainless Steel World*, Volume 16, June 2004, page 53, KCI.

2. NORSOK M-001 Rev 4, Materials Selection, August 2004.

3. R Francis, *Brit. Corr. J.* 29, 1 (1994) 53

4. P D Goodman, *Brit. Corr. J.* 22, 1 (1987) 56

5. G Alabiso, V Scotto, A Mollica, U Montini, G Marcenaro and R Dellepiane, “Stainless Steel Corrosion in Antarctic Seawater: A Contribution from the Italian PNRA Project”, Seawater Corrosion of Stainless Steels: Mechanisms and Experiences, European Federation of Corrosion Publication No. 19, IOM, 1996, page 95.

6. R Francis, Stainless Steel ’87, York, UK. Sept 1987. IOM, p192.

7. R Francis and G Warburton, Paper 630, Corrosion 2000, “The Effect of Post Weld Surface Treatments on the Corrosion Resistance of Superduplex Stainless Steel Welds in Seawater”, NACE International, Houston Texas, March 2000.

8. G Byrne, R Francis, G Warburton and J Wilson, “Electrochemical Potential and the Corrosion Resistance of Stainless Steels in SWRO applications”, presented at IDA International Desalination Conference, Dubai, UAE, October 2009.

9. J O Olsson and M M Snis, “Don’t Repeat Mistakes! An SWRO Plant Case Study”, presented at IDA International Desalination Conference, Singapore, September 2005.

10. T Rogne and R Johnsen, Paper 295, Corrosion ’96, “The Effects of CO_2 and Oxygen on the corrosion of S31254 and S31803 in Brine Solutions”, NACE International, Houston, Texas, March 1996.

11. R. Francis, G Byrne and H S Campbell, Paper 313, “The Corrosion of some Stainless Steels in a Marine Mud”, Corrosion ’99, NACE International, Houston, Texas, April 1999.