

Materials Selection for Membrane Plants Handling Brackish Waters, Seawater and Brines

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[Rolled Alloys]**

ABSTRACT

Membranes are traditionally used for producing low chloride waters, for potable and agricultural needs, from high chloride waters using reverse osmosis. With increasing demand for fresh water, there is also a drive to clean up waste waters and recycle them. Membrane technology is proving a useful technology for cleaning up waste waters rather than just removing chloride. Reliable plant operation requires the selection of corrosion resistant materials for piping, vessels, pumps and valves and stainless steels have long been the preferred choice. The use of the family of austenitic stainless steels (304L, 316L, 904L and 6% Mo) is compared and contrasted with the corresponding well established family of duplex stainless steels (2101, 2003, 2205 and ZERON 100). The duplex stainless steels are attractive because of their low use of strategic metals, such as nickel and molybdenum, compared with austenitic alloys and also because of their higher strength. This enables the use of thinner walls in high pressure applications when compared to austenitic grades. These two factors combine to reduced material costs and provide more price stability. There are also newer "lean duplex" grades available and the paper considers where they may be successfully deployed in membrane systems. The paper outlines the fabrication requirements and compares the corrosion resistance of duplex and austenitic stainless steels in a range of waters and suggests practical limits of use in membrane systems. In addition the effect of microbial induced corrosion (MIC) is also discussed.

1. INTRODUCTION

Membrane technology is becoming increasingly the preferred method for producing drinking water from seawater and brackish waters. Because of the general shortage of water in many regions of the world and the desire to reduce the discharge of a wide range of chemicals, bacteria and salts, membrane technology is also being used to treat waste waters. Figure 1 shows the size range of some of the many constituents in waste waters and the ability of various processes to remove them.

Not all of these will be used at once and the combination of methods for a particular site will depend on the contaminants in the water and the desired final quality. Reverse osmosis (RO) often features as the final stage because of its ability to remove chlorides and other ions, as well as reduce hardness.

Whichever of these removal methods are chosen for a particular treatment plant, it is important to select the correct materials of construction to avoid corrosion and unwanted shutdowns due to leaks. As with seawater reverse osmosis (SWRO), stainless steels are a common choice for piping, vessels, pumps and valves and this paper reviews the limits of use of some of the commonly available grades.

2. ALLOYS

2.1 COMPOSITION

Stainless steels for RO systems are usually austenitic or duplex. The duplex stainless steels are roughly 50/50 austenite/ferrite and combine the ductility of the austenite with the strength of the ferrite. Table 1 shows the composition of some common grades. The presence of chromium, molybdenum, tungsten and nitrogen all combine to give resistance to localised attack by chlorides. The pitting resistance equivalent number, or PREN, is an empirical number that gives an indication of an alloy's resistance to attack by chlorides.

$$\text{PREN} = \%Cr + 3.3(\%Mo + 0.5x\%W) + 16x\%N$$

The higher the PREN, the greater is the resistance to localised attack.

It can be seen from Table 1 that for every austenitic alloy there is a duplex stainless steel with a similar PREN. The advantage of duplex stainless steels is that they contain less of the strategic element nickel than their austenitic equivalents and so are less expensive. Some current examples are the price of 2205, which is about the same as that of 316L, and that of Z100, which is about 70% of the cost of 6%Mo alloys.

2.2 Mechanical Properties

Table 2 shows the minimum mechanical properties at room temperature for some common austenitic and duplex stainless steels. It can be seen that the duplex stainless steels are much stronger than their austenitic equivalents, which offers scope for wall thickness reductions and further cost savings.

Table 3 shows the design stresses to ASME for both pipes and vessels. The higher design stresses for duplex alloys not only means that there is scope for savings due to

wall thickness reductions, but also due to reduced welding time and cost. This is particularly noticeable in RO plants for larger diameter piping operating at higher pressures¹.

3.3 WELDING

316L and 317L are readily welded, usually using matching composition consumables. The higher molybdenum content of 904L and the 6%Mo alloys means that an alloy 625 type nickel-based filler is usually required to produce a weld with adequate corrosion resistance. This means that these alloys require more care when welding, with tighter control on heat input and interpass temperature.

The lean duplex alloys, 2101 and 2003, are usually welded with 2209 filler, as is used for 2205. This ensures that the weld metal is at least as corrosion resistant as the parent metal and this filler is readily available. Z100 is welded with Z100X filler, which contains an extra 2 to 2.5% nickel to ensure the correct phase balance in the weld metal. All duplex alloys require the same level of care when welding as 904L and 6%Mo alloys, i.e. fully qualified welders working to approved procedures. The duplex alloys have been welded successfully for many years and there are a large number of fabricators familiar with welding them.

3. CORROSION

Stainless steels do not suffer from general corrosion, but can suffer from a variety of forms of localised attack in the presence of chlorides. The resistance of various alloys to the types of corrosion likely to be found in membrane waste water plants is discussed below.

3.1 PITTING CORROSION

The resistance to pitting is commonly assessed using the ASTM G48 method E corrosion test in ferric chloride. Whilst not predicting the performance in service, the test does enable the relative resistance to pitting to be compared for a number of alloys.

Table 4 shows the critical pitting temperature for a range of alloys and it can be seen that the duplex alloys are as good as, or better, than their equivalent austenitic grade. The ASTM G150 test determines the critical pitting temperature (CPT) under less oxidising conditions than ferric chloride. Figure 2 shows the CPT for various alloys and, again, the CPT of the duplex alloys is equivalent to, or greater than that of their equivalent austenitic grade.

3.2 CREVICE CORROSION

Crevice corrosion is found in RO plants at victaulic-type couplings and flanged joints. It is important that alloys resist corrosion at such locations. Figure 3 shows the crevice corrosion temperature (CCT) limit at various chloride concentrations for some of the lower alloyed stainless steels, using crevice washers on flat plate (ASTM G78). No data were available for 317L and 904L. It can be seen that the crevice corrosion resistance increases as the PREN increases. The curves for 316L, 2003 and 2205 are more or less parallel, but that for 2101 is much steeper. This is believed to be due to 2101

containing little molybdenum compared with the other alloys in Figure 3, and instead relies on chromium and nitrogen for its corrosion resistance.

Figure 4 shows the effect of chloride on the CCT for 2205, 904L, Z100 and 6% Mo alloys over a range of potentials. The potential of +600mV SCE is very oxidising, while the less oxidising potential of +200mV SCE is typical of that seen in SWRO high pressure systems. One important feature is that the alloys are not very sensitive to variations in chloride concentration from 10,000 to 100,000mg/L.

In seawater, stainless steels can adopt a wide range of potentials, as shown in Figure 5². In natural seawater a biofilm forms on the surface in 2 to 20 days and this depolarises the cathodic reaction (the reduction of dissolved oxygen) resulting in a potential of ~+300mV SCE. If small amounts of chlorine/hypochlorite are added to control fouling, the cathodic reaction becomes the reduction of hypochlorite to chloride, and the potential increases to ~+600mV SCE. If the seawater is heated to 25 to 30°C above its normal local ambient temperature, no biofilm forms and the potential is ~+150mV SCE. As the dissolved oxygen content is reduced, the potential decreases further, to ~-100mV SCE with 200ppb oxygen, and to ~-450mV SCE when fully deaerated. The water treatment in RO plants means that the potential in the high pressure section is usually about +200mV SCE.

Figure 6 shows the critical crevice temperature (CCT) in seawater as a function of potential. 316L corroded at the commencement of every test at all potentials and does not resist corrosion at room temperature at all. The CCT for 904L and 2205 was only a little above 20°C at +200mV SCE, although it increased at lower potentials. This explains why some plants using these alloys have had crevice corrosion failures^{1, 3}. As most SWRO plants operate at temperatures greater than 25°C, these alloys cannot be considered suitable and the greater corrosion resistance of Z100 or the 6%Mo alloys is required⁴.

Figure 7 summarises the chloride limits for each of the alloys in Table 1 at 20°C. These chloride limits decrease for the lower alloys as the water temperature increases. The results show that the chloride limits in RO systems are the same for duplex and their equivalent austenitic alloys, except for 2101. However, at 35°C and higher, 2101 and 316L can be regarded as having the same resistance, although the chloride limit is lower for both alloys, as shown in Figure 3.

3.3 MICROBIALY INFLUENCED CORROSION

In waste waters there will inevitably be bacteria and some of these can have an influence on corrosion in a number of ways.

1. Production of aggressive metabolic products, such as sulphuric acid, or chelating agents.
2. Cathodic depolarisation associated with anaerobic growth.
3. Changes in oxygen potential, salt concentration, pH etc, which establish local electrochemical cells.
4. Removal of corrosion inhibitors or protective coatings.
5. The biomass itself stimulates attack, for example by creating an occluded cell.

Where the water is not chlorinated, or otherwise treated to inhibit biological activity, biological colonisation occurs rapidly. There are bacteria that thrive under oxidising conditions i.e. aerated seawater. One type is the iron oxidising bacterium. This works by creating a differential aeration cell and it is usually a problem with cast iron and carbon steel. Stainless steels are more resistant to this type of attack because of their high chromium content. Another type of bacterium that thrives under aerated conditions is the sulphur-oxidising species, which creates sulphuric acid as a by-product. This will cause severe attack of carbon steel and may cause corrosion of lower alloy stainless steels. Hence, alloys that are resistant to sulphuric acid at all concentrations, such as stainless steels with high chromium and copper contents should be selected when these bacteria are active.

When the water is stagnant, the aerobic bacteria will consume the available oxygen and then the anaerobic bacteria will become active. The most well known are the sulphate reducing bacteria (SRB), which produce H_2S as a by-product.

Remember that once a biomass forms on a metal surface, the conditions beneath it can be very different to those in the bulk fluid, so that SRB can be flourishing under a deposit because it is anaerobic, while the main water stream is aerobic.

It is well documented that SRB can cause microbially influenced corrosion (MIC) of 300 series stainless steels, such as 316L^{5,6}. They thrive in shielded areas, such as under deposits, or downstream of girth welds under slow flow conditions⁷. Figure 8 shows MIC of the welds on a 316L vessel that carried a low chloride water.

Data on MIC of higher alloys is scarce but Tuthill⁸ describes numerous reported service failures and concludes that the higher the PREN, the less is the risk of MIC. He reports no cases of MIC of 6% Mo alloys and Z100 has also been shown to be resistant to MIC⁹.

Data on 904L and 2205 is mixed. Tuthill reports one case of an MIC failure of 904L⁸. Iversen describes the successful use of 2205 in waste water plants in Sweden¹⁰, but the temperature was low and the water was not very aggressive to lower alloys with respect to MIC. Heselmans reported a failure of a 2205 pipe by MIC in a waste water in less than three months¹¹. Hence, it appears that 904L and 2205 are more resistant to MIC than 316L, but may suffer attack in aggressive conditions. Only 6%Mo and Z100 appear to be resistant to MIC under these conditions.

4. DISCUSSION

The data presented above show that duplex stainless steels are cost-effective materials to resist corrosion in waste water treatment plants using membrane technology. The selection of a particular grade will depend on the chloride concentration in the water and the temperature. The presence of bacteria will also affect performance and where these are present and active, more resistant, high alloy grades may be required.

In addition to their low relative cost, duplex stainless steels offer the possibility of further savings in higher pressure systems, due to their higher design stresses than equivalent austenitic alloys. Duplex stainless steels are widely used in many industries and so they are readily available in a wide range of product forms, often ex-stock.

5. CONCLUSIONS

1. There is a range of austenitic and duplex stainless steels that can be considered for membrane waste water treatment systems.
2. For every austenitic stainless steel there is an equivalent duplex alloy that offers equivalent corrosion resistance, lower cost and higher strength.
3. The selection of the correct grade depends upon the chloride concentration, the water temperature and the microbial activity within the water.

REFERENCES

1. G Byrne, R Francis, G Warburton, R.J Bullock and C Kuzler, "The Selection, Design, Fabrication and Performance of Zeron 100® in SWRO Applications." Presented at IDA Conference, Bahamas, October 2003.
2. R Francis, Galvanic Corrosion – A Practical Guide for Engineers, NACE International, 2001.
3. J Olsson and M Snis, "Don't Repeat Mistakes! An SWRO Plant Case Study" International Desalination Association World Congress, Singapore, September 2005.
4. R Francis, G Warburton, G Byrne and J Wilson, "Electrochemical Potential and the Corrosion Resistance of Stainless Steels in SWRO Applications", IDA International Desalination Conference, Dubai, UAE, October, 2009
5. L Shreir, R A Jarman and G T Burstein, Corrosion, 3rd Edition, Butterworths, Croydon, UK, 1994.
6. G Kobrin, S Lamb, A Tuthill, R A Avery and K A Selby, Nickel Institute Publication No. 10 085, 1998.
7. H Amaya, H Miyuki, Y Takeishi M Ozawa and Y Kikuchi, Paper 556, Corrosion 2002, Denver, CO, USA, April 2002, NACE International.
8. A H Tuthill, " Base Metal Resistance of Alloys to Microbially Influenced Corrosion" Unpublished report to Nickel Institute, 1993.
9. R Francis, G Byrne & H S Campbell. "The Corrosion of Some Stainless Steels in a Marine Mud" Paper 313, Corrosion '99, San Antonio, USA. April 1999, NACE International.
10. A Iversen, Paper 451, Corrosion 2002, Denver, CO, USA, April 2002, NACE International.
11. J Heselmans, Stainless Steel World, December 2006, page 2.

TABLE 1 The nominal composition of some common stainless steels

TYPE	ALLOY	NOMINAL COMPOSITION (wt%)							PREN*
		Fe	Cr	Ni	Mo	N	Cu	W	
Austenitic	316L	Bal	17	10	2	-	-	-	24
	317L	Bal	18	10	3	-	-	-	28
	904L	Bal	20	25	4	-	1.5	-	34
	6% Mo	Bal	20	25	6	0.2	0.7	-	43
Duplex	2101	Bal	21.5	1.5	0.3	0.22	0.3	-	26
	2003	Bal	20.5	3	2	0.17	-	-	>30
	2205	Bal	22	5	3	0.17	-	-	35
	Z100	Bal	25	7	3.5	0.25	0.7	0.7	>41

Bal = Balance

$$*PREN = \%Cr + 3.3(\%Mo + 0.5x\%W) + 16x\%N$$

TABLE 2 The minimum mechanical properties of some stainless steels at room temperature.

TYPE	ALLOY	0.2% PROOF STRESS (MPa)	TENSILE STRENGTH (MPa)	ELONGn. (%)	MAX. HARDNESS (HRC)
Austenitic	316L	170	485	45	22
	317L	205	515	40	22
	904L	230	530	40	22
	6% Mo	300	650	35	22
Duplex	2101	450	650	30	28
	2003	450	620	25	28
	2205	450	620	25	28
	Z100	550	750	25	28

TABLE 3 Design stresses at room temperature to ASME for some common stainless steels.

TYPE	ALLOY	DESIGN STRESS (MPa)	
		ASME B31.3 (Pipes)	ASME VIII Div. 1 (Vessels)
Austenitic	316L	115	115
	317L	138	138
	904L	143	140
	6% Mo	161	158
Duplex	2101	216	185
	2003	207	181
	2205	207	177
	Z100	250	214

TABLE 4 Critical pitting temperatures for some common stainless steels in ASTM G48 method E corrosion test.

TYPE	ALLOY	PREN	CPT (°C)
Austenitic	316L	24	10
	317L	28	20
	904L	34	30
	6%Mo	43	≥70
Duplex	2101	26	15
	2003	>30	25
	2205	35	30
	Z100	>41	≥70

FIGURE 1 The filtration spectrum

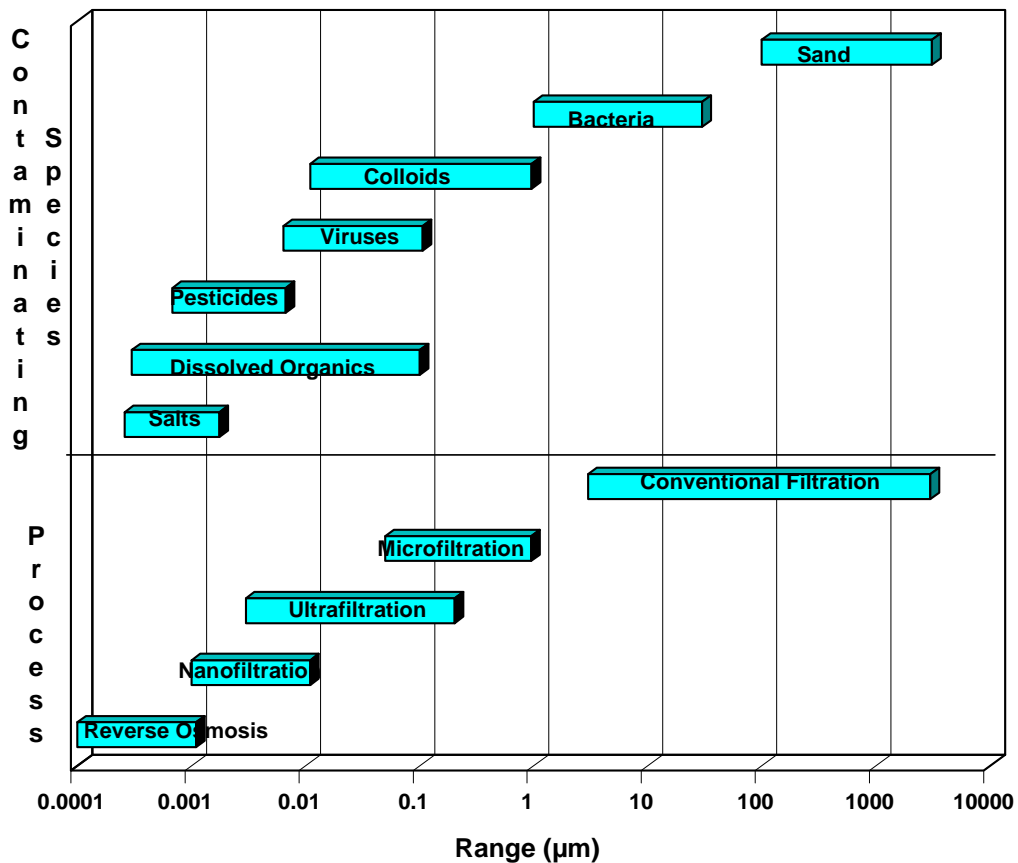


FIGURE 2 Critical pitting temperature in 1M sodium chloride to ASTM G150

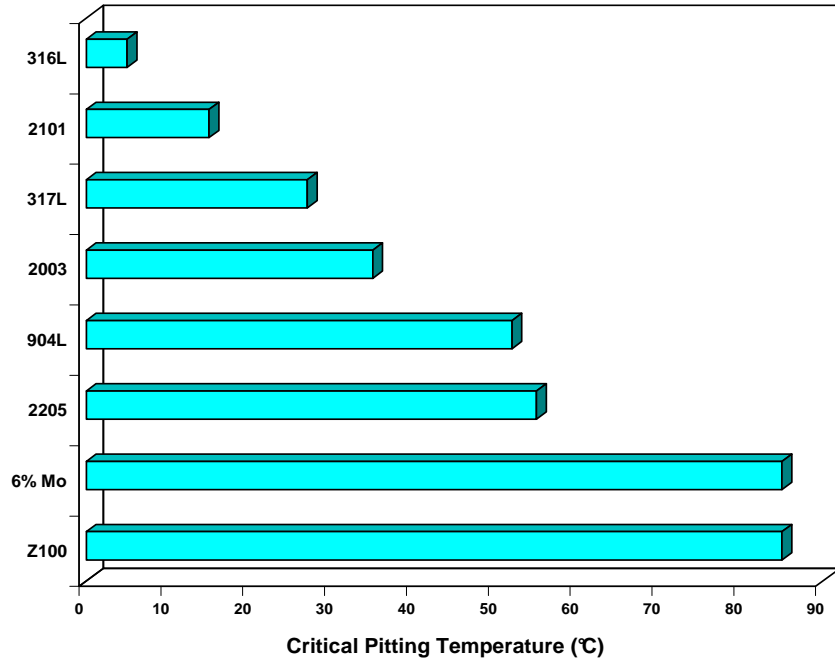


FIGURE 3 Effect of chloride concentration on crevice corrosion

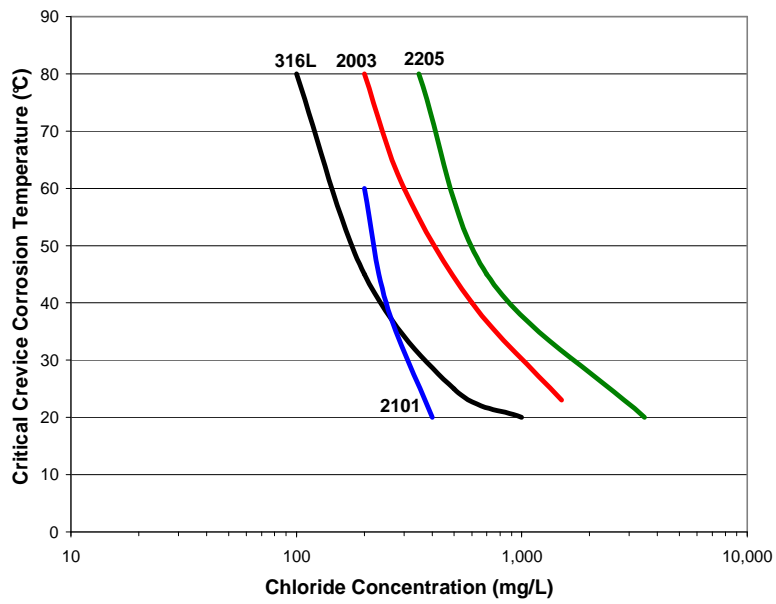


FIGURE 4 Effect of chloride on the CCT at various potentials

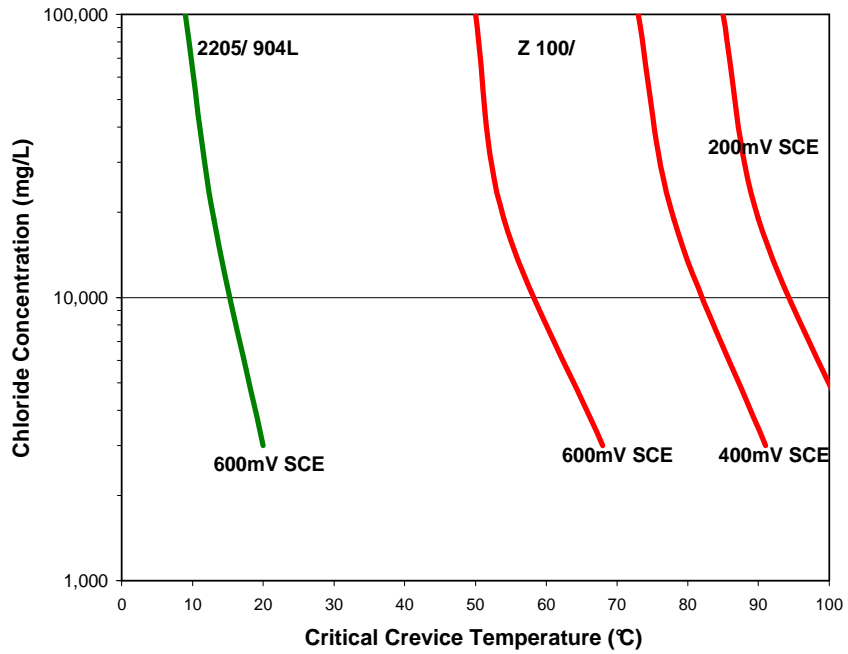


FIGURE 5 Some potentials adopted by stainless steels in seawater

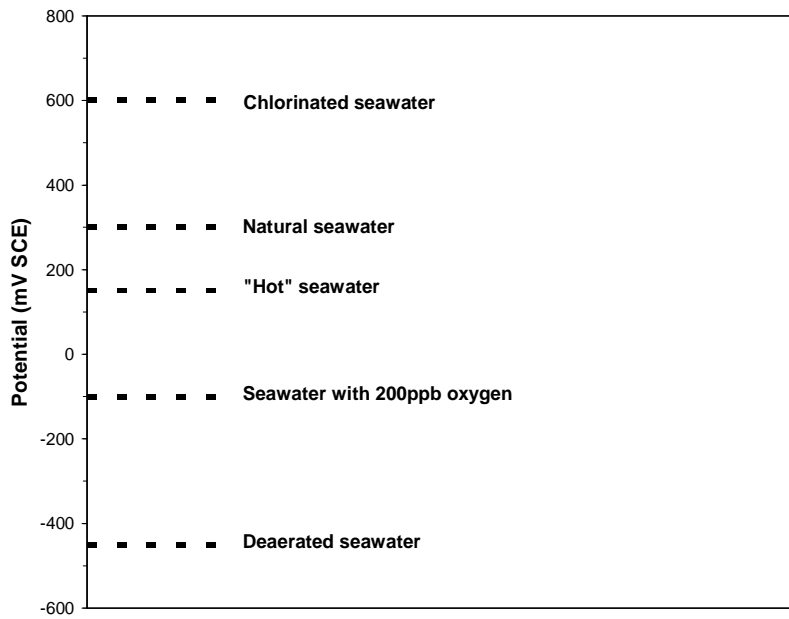


FIGURE 6 Relative CCT of some stainless steels in seawater as a function of temperature

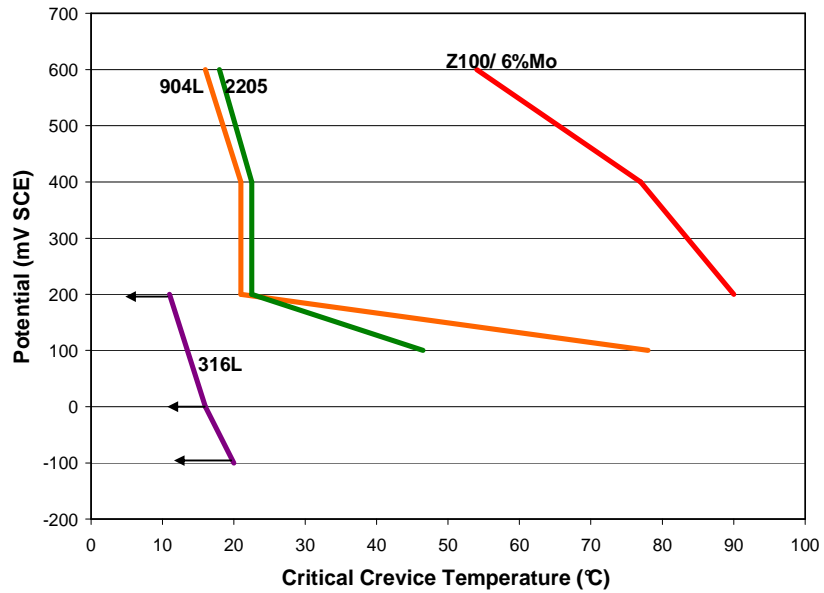
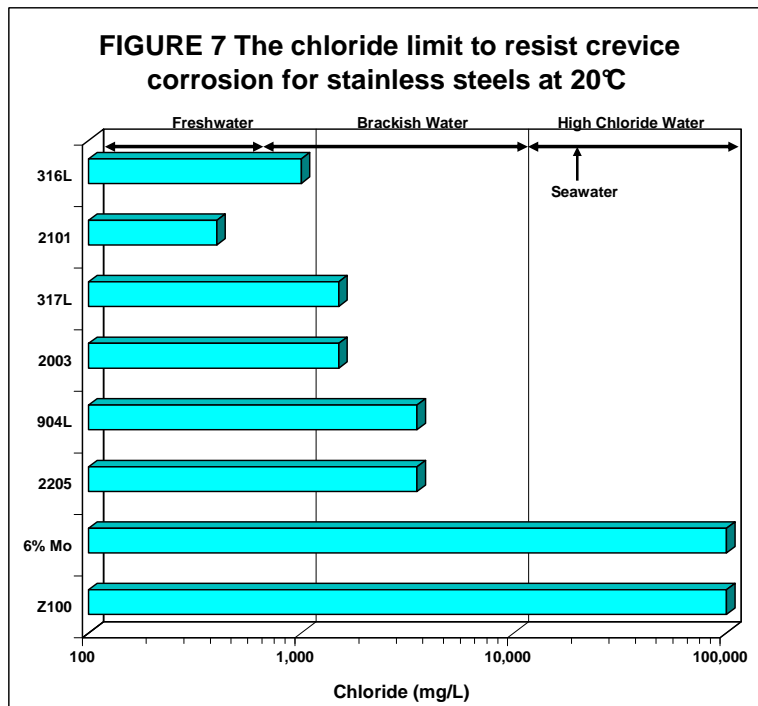
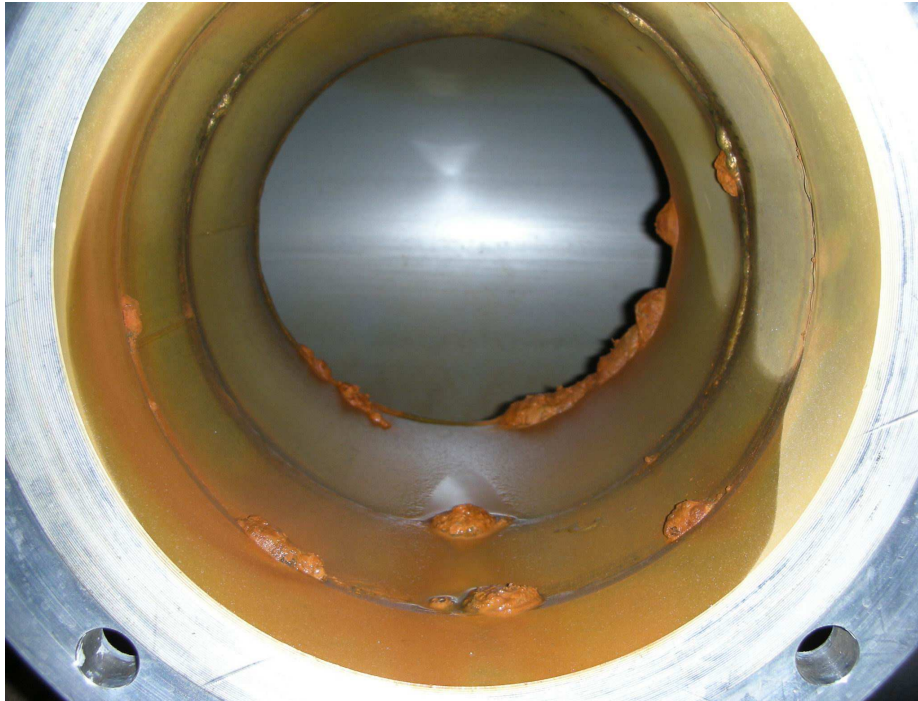


FIGURE 7 The chloride limit to resist crevice corrosion for stainless steels at 20°C





[Photo Courtesy Professor Ivan Juraga, University of Zagreb, Faculty of Mechanical Engineering and Naval Architecture]

FIGURE 8 MIC of 316L welds in a vessel handling waste water.