Electrochemical Potential and the Corrosion Resistance of Stainless Steels in SWRO applications

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Abstract

This paper considers the relationship between critical pitting temperature (CPT), critical crevice temperature (CCT) and electrochemical potential (EP) for several high alloy stainless steels commonly used in raw seawater (as per seawater intake), chemically treated seawater (as per the high pressure feed) and brine reject section of seawater reverse osmosis plants.

This novel approach shows how water treatment alters the EP of some common stainless steels and how this affects CPT and CCT in each of the environments. Results applicable to creviced assemblies (flanged and other mechanical joint types) and welded joints are presented.

The paper identifies and explains how and why some high alloy stainless steels can and do exhibit variable performance from one plant to another under nominally the same operating conditions. Also identified are factors in fabrication that can optimise and enhance the corrosion resistance of the system, this being of particular significance to facilities being built to operate using warm seawater feed.

I.   INTRODUCTION

1.1   Background

Modern production of stainless steels dates back to the introduction of argon oxygen decarburising (AOD) steelmaking around 50 years ago. In the 1970's stainless steels were beginning to be considered seriously for use in sea water applications as a substitute for copper nickel alloys. At this time it was claimed that most stainless grades, from grade 316L and above were suitable for seawater service. Users were also subjected to a proliferation of new grades of high alloy stainless steel and nickel alloys with conflicting claims of resistance to corrosion in seawater and a strong variation in cost.

Evaluations of the corrosion resistance of stainless steels at this time were mostly based upon tests carried out in chloride-containing environments rather than natural seawater. The situation was further complicated by variations in test method, variations in severity of crevice assembly and variations in corrosion resistance of different product forms of the same alloy and of course the influence of welding.

By the late 1970's stainless steels were being deployed as high pressure seawater feed pipe work in SWRO applications. It is reported that grade 316L was deployed in plants in Jeddah, Malta and Australia between 1979 and 1995 with corrosion attack initiating quickly in all cases [1,2,3]. Thereafter the selection and use of stainless steels in the desalination industry has continued more as a process of trial and error leading to elimination of alloys starting at the lowest cost grades and working upwards. However, in parallel to this, the understanding of the mechanisms of corrosion of stainless steels in seawater and application limits have progressed. It has become clear that the CPT and CCT of alloys in chloride-containing environments are not only functions of salinity and alloy chemistry but are also influenced by potential.

1.2   Natural Seawater

Tests carried out on stainless steels in natural seawater[4] (Holyhead, in Anglesey, North Wales and elsewhere) have shown that on immersion the initial potential was in the range -300 to -100mV SCE and that this increased over a period of 2 to 20 days to +250 to +350mV SCE. The saturated calomel electrode (SCE) is a reference electrode commonly used in corrosion studies.

This change in potential is associated with the development of a biofilm on the surface of the steel. These biofilms play an active part in the mechanism of corrosion. It is believed that the biofilms stimulate the cathodic reaction in the corrosion mechanism, by enhancing the oxygen reduction reaction. Without biofilm formation the surfaces of stainless steels prove to be very inefficient cathodes. This means that testing of stainless steels for natural seawater applications in environments that do not properly incorporate the influence of the biofilm on the corrosion mechanism will over estimate the corrosion resistance of the alloy being tested.

1.3   Chlorinated Seawater

It has been observed that the potential of stainless steels in chlorinated seawater is a function of the residual chlorine level [5] i.e. the level realised after consumption of chlorine due to the sterilisation process.

Chlorination up to 0.1ppm residual level (just enough to kill marine organisms) saw potentials remain low at about +100mV SCE. At higher residual chlorine levels, above 0.1ppm the potentials

rise quickly to +500 to +600 mV SCE. From a corrosion of stainless steels stand point, the detrimental effect of the increased oxidising power associated with chlorination is offset by the decreasing efficiency of the cathodic reaction as the chlorination destroys the biofilm. This seems to hold up to residual chlorine levels of about 0.8 mg/l, whereas above this level, oxygen reduction is displaced as the primary cathodic reaction and reduction of hypochlorite takes over. Under these conditions of over chlorination, stainless steels can become very susceptible to crevice corrosion.

1.4   Chemically Treated or Filtered Seawater

In SWRO plants intake seawater can be chlorinated to prevent biofouling and provide disinfection or can be filtered to provide much the same effect.

Once chlorinated, the seawater then has to be de-chlorinated before it reaches the membranes to avoid damaging them. (As well as these treatments the seawater feed may also be subjected to further chemical treatments that acidify and flocculate). De- chlorination is often carried out by adding bisulphite, which not only serves to de-chlorinate, but it also acts as an oxygen scavenger. This has some positive effect with respect to increased corrosion resistance in the environment. The bisulphite additions are controlled to hold the redox potential in the range +350 mV to +250mV Ag/AgCl$_{sat}$ as this is the optimum range for membrane performance, but this is not sufficient to reduce the oxygen content of the seawater feed to levels that eliminate oxygen reduction as the cathodic reaction (the redox potential is the equilibrium electrode potential for a reversible oxidation/reduction reaction in a given electrolyte, in this case Ag/AgCl$_2$).

So having established that potential varies throughout the SWRO process it now remains to establish the influence of this on localised corrosion resistance.

II.   EXPERIMENTAL

2.1   Alloys Examined

Table 1 details the composition and product form of each of the alloys being examined.

Also included is the composition of the welding consumables used to make welded joints. Only 22% Cr duplex and ZERON 100 were tested in the welded form.

2.2   Test Method

2.2.1   Redox Potential vs EP

Samples of both ZERON 100 and 6%Mo austenitic were immersed in synthetic seawater that was continuously aerated and the potential was continuously monitored against a saturated calomel electrode. At the same time the potential of a redox probe was also monitored against its internal saturated Ag/AgCl$_2$ electrode. The potential was monitored until it was stable with time, which generally took 1 to 4 hours. The tests were repeated where additions of either hydrogen peroxide or sodium hypochlorite were made to give a range of redox potentials and so provides a calibration curve between Redox Potential and EP.

ALLOY	FORM	COMPOSITION (wt%)							PREN*
		Fe	Cr	Ni	Mo	N	Cu	W	
316L	Bar	Bal	17.4	11.4	2.07	-	-	-	24.3
904L	Plate	Bal	19.3	24.8	4.07	-	1.48	-	32.7
22% Cr	Bar	Bal	22.8	5.29	3.05	0.20	0.12	0.15	36.1
Duplex	Pipe	Bal	22.5	4.76	2.80	0.14	-	-	34.0
2209	Weld Wire	Bal	23.2	8.1	3.2	0.14	-	-	36.0
6% Mo Aust	Bar	Bal	19.8	17.8	5.98	0.21	0.59	-	42.8
ZERON 100	Bar	Bal	25.4	7.02	3.60	0.22	0.59	0.60	40.8
	Plate	Bal	25.4	6.98	3.67	0.25	0.58	0.61	41.4
Z100X	Weld Wire	Bal	25.4	9.4	3.73	0.23	0.61	0.63	41.4

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

Table 1. Composition of alloys and welding wires used in the corrosion tests.

2.2.2 SAMPLE PREPARATION

The CPT of welded material was determined because welds are very rarely present in crevices. Small samples were cut from GTA welded pipes or plates, 65 x 13 x 4mm, with the weld between the long edges. A ZERON 100X welding wire was attached to a short edge for an electrical connection (Figure 1).

Creviced samples from unwelded, parent material took the form of 10mm diameter cylinders that were 30mm long and were screwed onto the end of a sample holder. The crevice was created by a silicon rubber ring of 5mm square cross section and 7mm id (Figure 2).
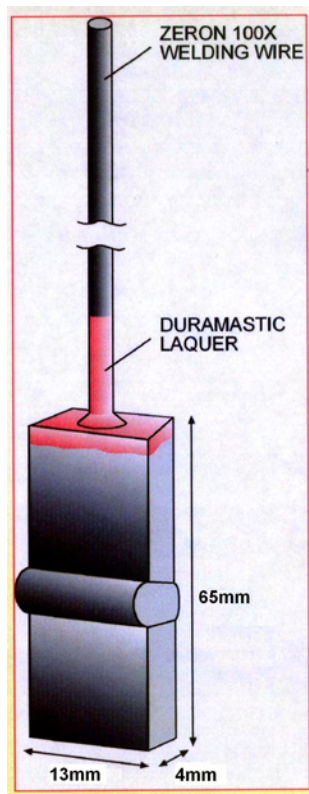
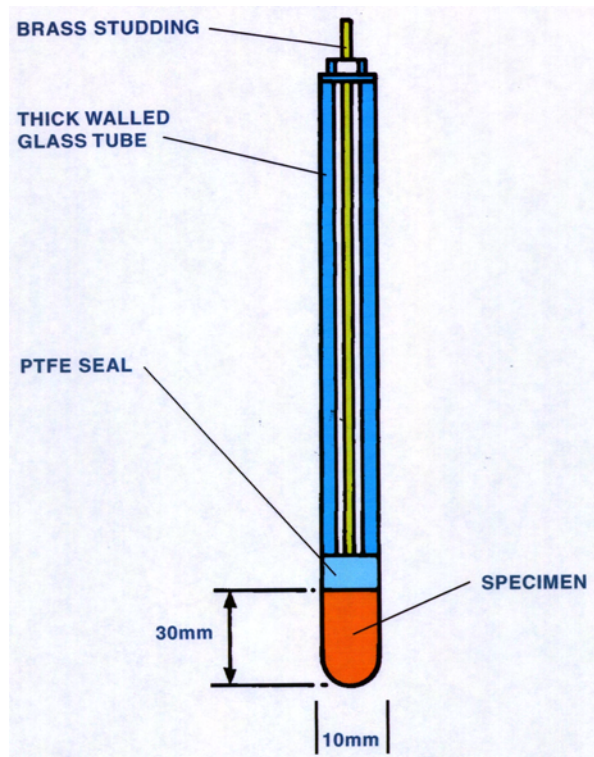Figure 1 Schematic diagram of welded test coupon.

Figure 2 Schematic diagram of creviced sample (Silicone ring omitted for clarity)

The test was conducted by polarising the sample to the test potential at a rate of 20mV/min at ambient temperature. The current density was allowed to stabilise for an hour or so and then the temperature was increased at 5mV/min until localised corrosion initiated as shown by a sudden

increase in the current density. Corrosion was said to initiate at a current density of $10\mu A/cm^2$ [6]. A typical current density versus time trace is shown in Figure 4, along with the temperature/ time trace. After the test the sample was examined for signs of corrosion.
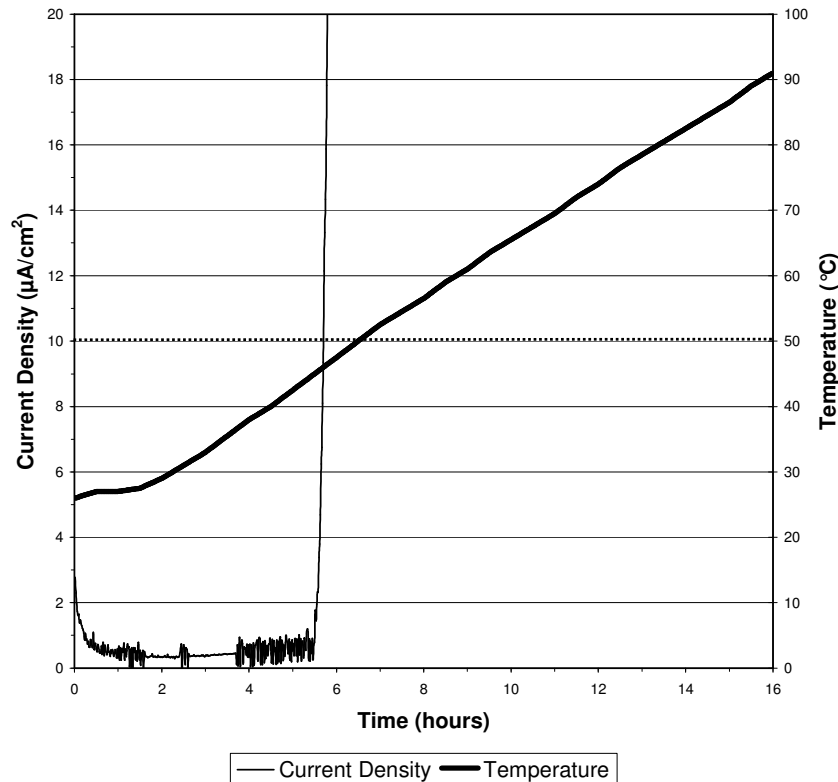

Figure 3 A typical current density and temperature versus time trace.

2.3 Test Solutions

Most of the tests were conducted in synthetic seawater as follows:-

Sodium bicarbonate	– 0.2g/l
Potassium chloride	– 0.7g/l
Calcium chloride	– 1.1g/l
Magnesium chloride	– 2.4g/l
Magnesium sulphate	– 3.3g/l
Sodium chloride	– 26.6g

The pH was adjusted in the range 8.0 ± 0.2 with 1M sodium hydroxide solution.

For the experiments on the effect of chloride, the same composition was used except for the sodium chloride, which was adjusted to give total chloride concentrations in the range 3,000 to 100,000 mg/l.

2.4 Pickling

In service it is the weld root that is exposed to seawater, so the weld caps were pickled with Avesta P107 pickling paste for 1½ hours to minimise the risk of pitting in the cap and to ensure testing of the weld root.

All samples were allowed to passivate in air for 24 hours after pickling and washing. In some tests the effect of pickling on the corrosion of the root was investigated and for these tests the roots were also pickled in the same way as for the cap.

2.5 Surface Roughness/Condition

Tests were carried out to determine the effect of the surface finish on the outside of pipes on crevice corrosion. Sections were cut from NPS 1.5 and NPS 2 pipes and a crevice was created with curved crevice washers fastened to a torque of 7Nm. Some samples were tested with an external machined finish for comparison (Figure 4). The internal surface of all samples was pickled to try and ensure that corrosion initiated on the external face.
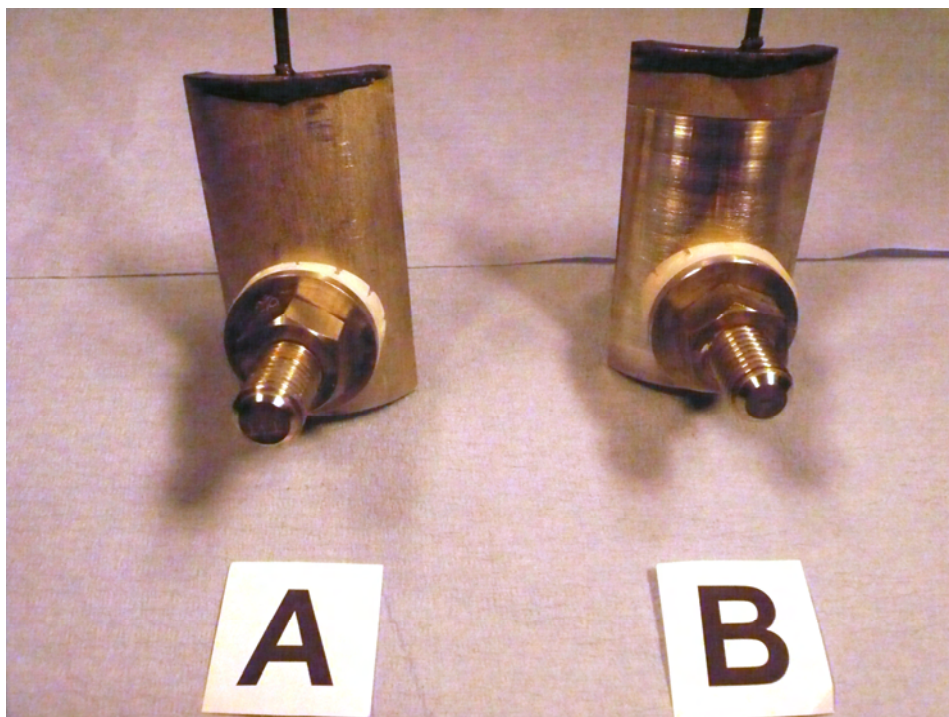

Figure 4 Appearance of creviced pipe sections, A) as received; B) machined.

III RESULTS

Figure 5 shows the results for the electrode potentials of high alloy stainless steels versus the redox potential in seawater with various additions, The results show that a redox potential of +250 to +350 mV Ag/AgCl$_{2sat}$ (the operating range for high pressure sea water feed pipe work) is equivalent to an electrode potential of +100 to +200mV SCE with a high alloy stainless steel.
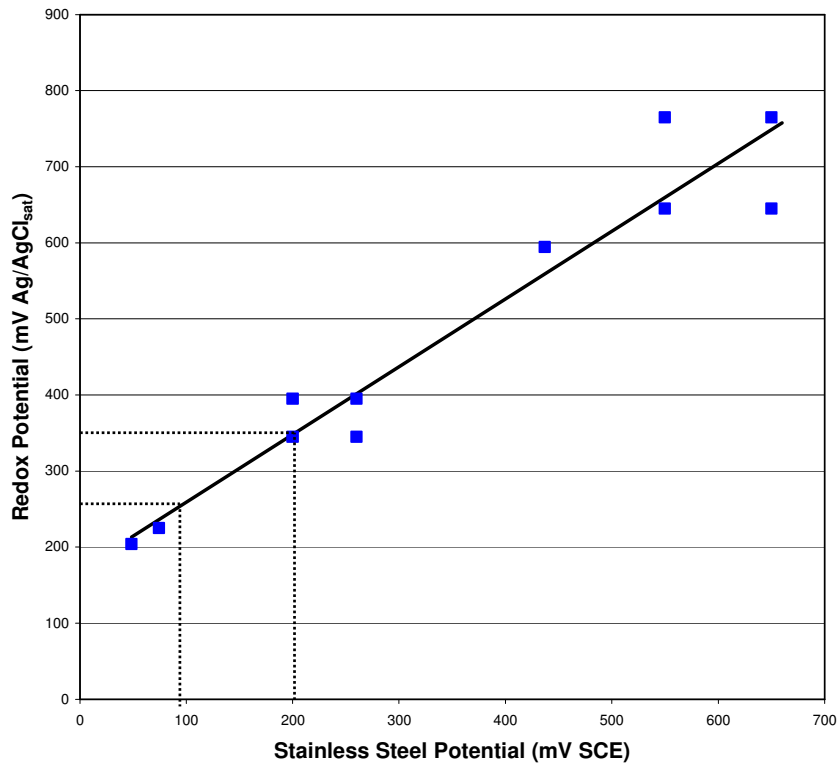
Figure 5 Effect of redox potential on stainless steel electrode potential in synthetic seawater.

Figure 6 shows the relative CCT of various stainless steels in seawater as a function of potential. The arrows indicate that corrosion occurred at ambient temperature and the true CCT was at a lower temperature.
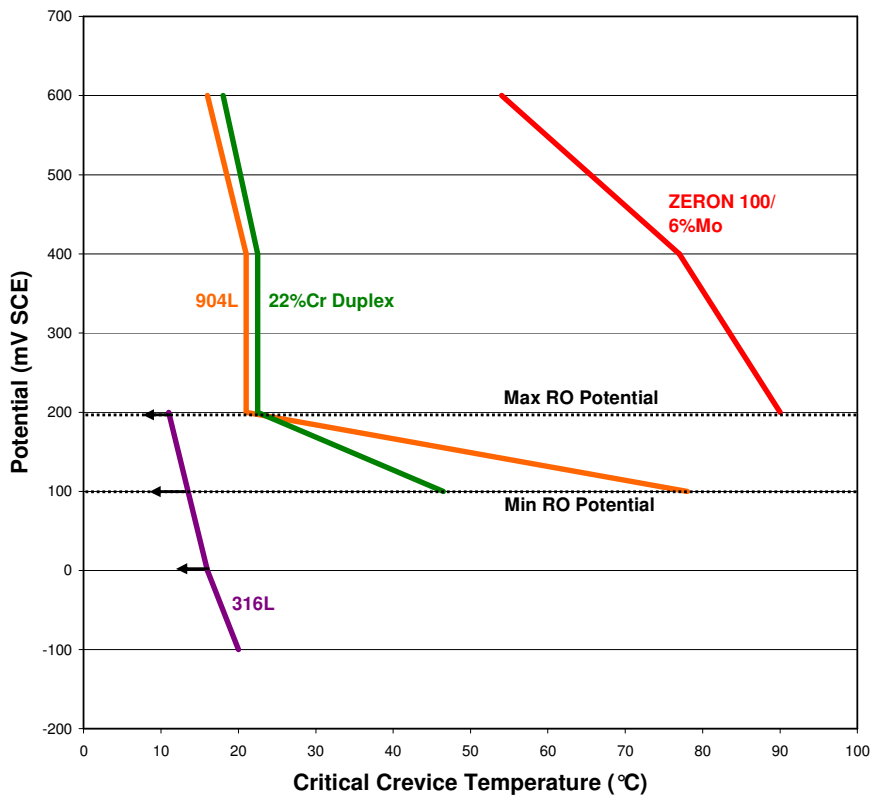

Figure 6 Effect of electrochemical potential in seawater on CCT of some stainless steels.

International Desalination Association World Congress REF:DB09-145

Figure 7 shows the relative CPT of welded samples and the relative CCT of parent metal for 22% Cr duplex and ZERON 100 superduplex stainless steel. The attack on the ZERON 100 welds all occurred in the weld root, while that on 22% Cr duplex occurred in the parent metal close to, or at the fusion line.
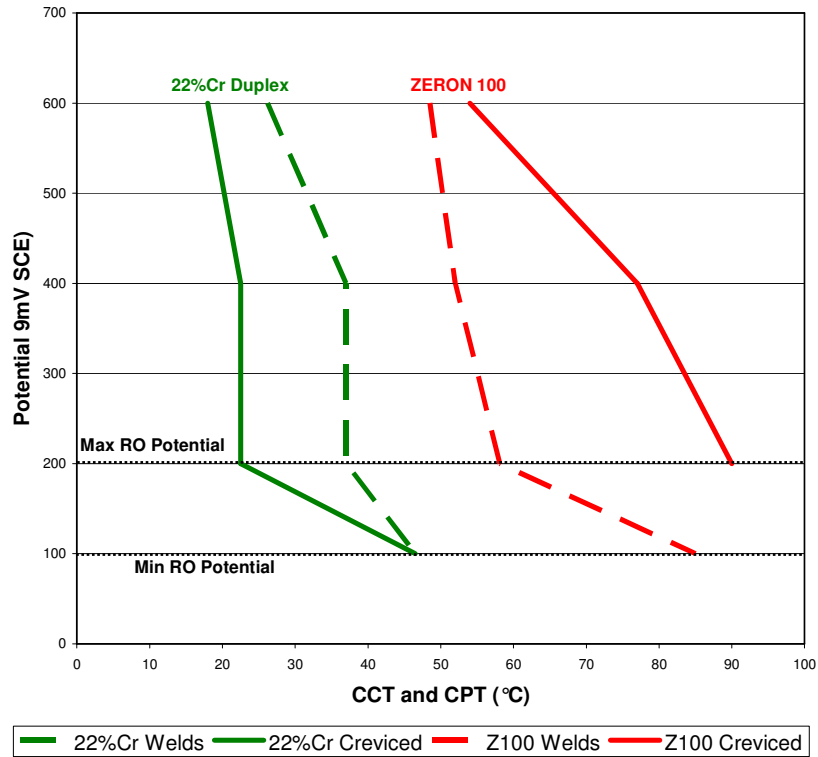

Figure 7 Comparison of CCT (parent) and CPT (welds) as a function of potential in seawater.
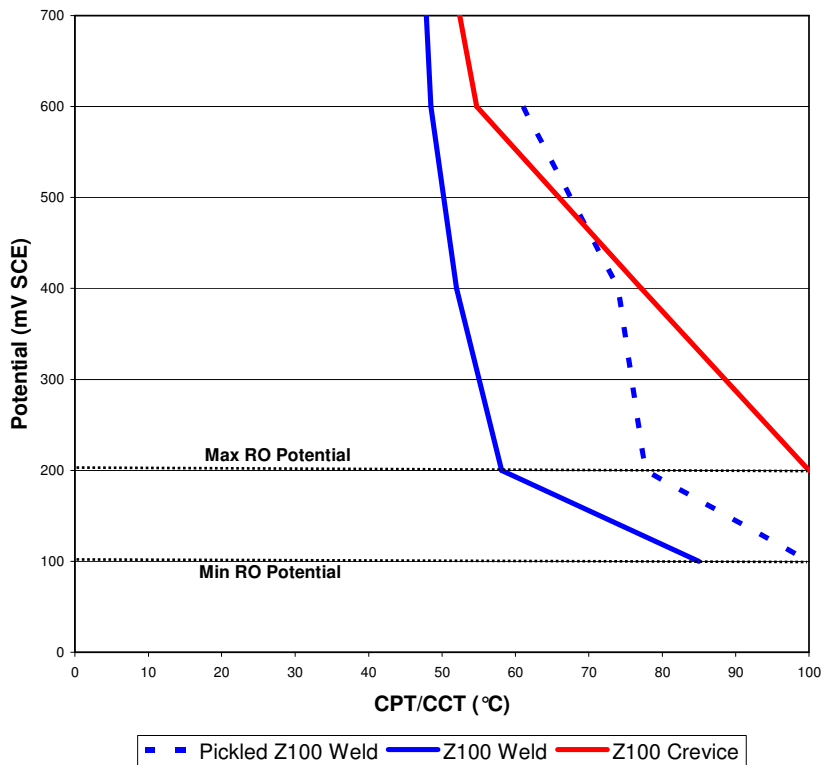

Figure 8 Effect of pickling on the CPT of Z100 welds in seawater.

Figure 8 shows the effect of acid pickling on the relative CPT of welds of Zeron 100, while Figure 9 shows the effect of chloride content on the relative CCT of the duplex stainless steels.
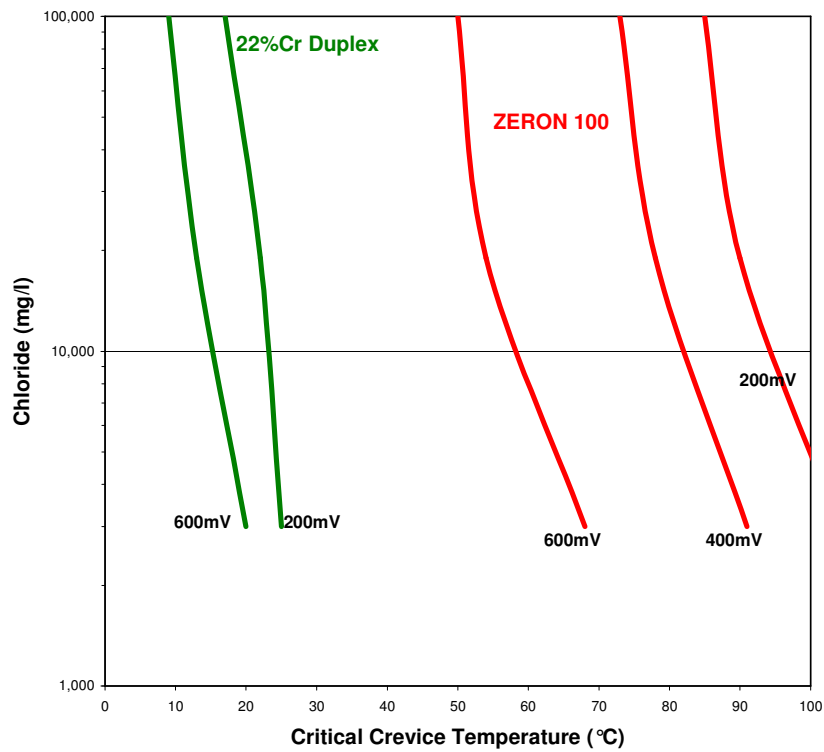

Figure 9 The effect of chloride on the CCT of duplex stainless steels in seawater.

. Figure 10 shows the effect of surface finish on the relative CCT of ZERON 100.
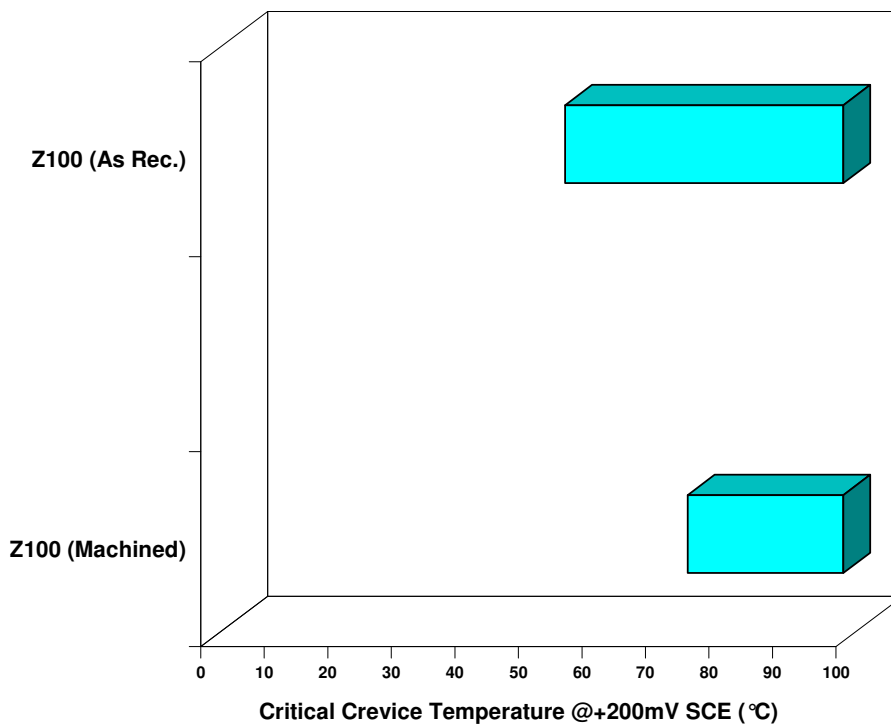

Figure 10 Effect of surface finish on the CCT of Z100 pipe at +200mV SCE in seawater.

IV. DISCUSSION

It is clear that the range of stainless steels tested gives rise to a wide range of relative CCT's as a function of potential. We use the term relative CCT because we believe that the crevice assembly used in these tests only approximates to the severity of the crevices that exist in SWRO plants. The test method utilized corresponds well to the performance observed in low pressure (15 to 20 bar, class 150lbs rated flanges) utility and fire water protection systems handling aerated, chlorinated seawater on offshore platforms and ships, but may overestimate CCT when trying to simulate victaulic type crevice assemblies in 70 bar, 600lbs flange rated systems. However, the method is considered sufficiently discerning to establish relative differences between alloys in this environment.

Figure 6 shows that the relative CCT of grade 316L at all potentials is below ambient for basically all countries currently utilizing SWRO technology and therefore should be avoided. The poor performance of 316L in these tests correlates well with service experience. For seawater intake where potentials of +300mV SCE (natural seawater) up to +600mV SCE (chlorinated seawater) can prevail, the use of 904L austenitic and 22% chromium duplex stainless steel steels should not be considered as the relative CCT is very low when compared with normal RO design temperatures. Indeed, service experience is that these alloys have suffered corrosion attack even in colder waters and at lower potentials in the range. These alloys appear to have little tolerance to more aggressive crevice assemblies and should be avoided. However, ZERON 100 and 6%Mo alloys exhibit quite high relative CCT's in this range of potentials. This correlates with excellent service performance demonstrated by these alloys when used for seawater service by the oil and gas industry, power generation industry and the desalination industry.

At lower potentials, in the range +100 to +200 mV SCE (the range applicable to the high pressure seawater feed part of the system because of the water treatments applied), the relative CCT of the lower alloy 904L austenitic and 22% chromium duplex stainless steels grades becomes very sensitive to potential. Moreover the CCT's measured at these potentials fall within the design temperature range for the majority of SWRO plants in operation or under construction in the world today. At low potentials the relative CCT can be high, and conversely at high potential's the CCT can be low. The rate of change of CCT with potential is quite high too. This means that small changes in potential can give big changes in relative CCT and therefore the performance of these grades can be critically dependent upon the water treatment applied. This phenomenon also explains the variable performance of these grades when deployed in SWRO applications [1, 7]. The position now is that these lower alloy grades should not be used in seawater applications. The higher grade stainless steels however, exhibit relative CCT's well above the design temperature range for SWRO plants at these potentials. As such, their crevice corrosion resistance is insensitive to water treatment and is sufficiently high to accommodate more aggressive crevice forms and Middle East conditions. These are widely accepted to be the most onerous in the world.

It is also important to consider weld performance, since large diameter pipes and butt weld fittings of welded construction are required and to build a plant all the pipes and fittings have to be joined by welding. Generally, seam welds in pipes and welds in fittings are subjected to post weld solution treatment and acid pickling. The heat treatment homogenizes the weld removing segregation and the pickling removes heat treatment scales and metal surfaces denuded in passivating elements as a consequence of the heat treatment process. Measurements of CPT and CCT on post weld solution treated joints in ZERON 100 again show CPT and CCT well above the design temperature of plants. Tests using crevice assemblies to simulate victaulic joints cut across long seam welds have been performed and the results show that the post weld heat treated and pickled weld seam also

exhibits a CCT above the design temperature of SWRO plants. However, it should be noted that if victaulic joints are to be used in large diameter pipes then special mechanical calibration of the pipe ends may be necessary as the commercial tolerance on pipe ovality is larger than the tolerance allowed for a victaulic joint.

Generally speaking, girth welds in pipe work systems are exposed to the environment in the "as welded" condition. Moreover, such joints do not form part of a crevice arrangement in the system. As such it is the critical pitting temperature (CPT) that is of interest. Figure 7 shows the CPT of welds and the CCT of parent material for ZERON 100 and 22% chromium duplex stainless steels. In the case of the 22% chromium steel joints, a 2209 duplex stainless steel welding consumable was used to make the joint. This had a PREN 2 points greater than that of parent metal, which ensures that the corrosion resistance of the weld is at least as good as that of the metal [8]. Metallurgical examination of these samples showed that the preferred sites of corrosion attack were the weld fusion line and the weld heat affected zone. This is because the PREN of the weld metal exceeds that of the parent and the weld thermal cycles induce grain growth, a change in the phase balance, austenite morphology and chemistry in the high temperature HAZ. At the fusion line we have the interface between the high temperature HAZ (PREN~34) and the weld metal (PREN~36) and, hence, this difference in corrosion resistance.

The CPT of the ZERON 100 welded samples was significantly higher. This data is consistent with previous publications advising temperature limits of 40°C with residual chlorine levels up to 0.8ppm (chlorinated seawater intake) [9].This limit can be further increased by pickling [10], as shown in Figure 8.

These results clearly show that the limiting factor with 22%Cr duplex is the crevice corrosion resistance of the parent metal at quite low temperatures (in the design range for plants), while that of ZERON 100 is in the pitting resistance of the welds at much higher temperatures (well above the design range for plants).

The results in Figure 9 show that chloride ion concentration has only a small effect on the CCT over the concentration range of interest in SWRO plants, Even at the high chloride concentrations (~45,000 mg/l) in the reject brine lines and energy recovery section, ZERON 100 has adequate resistance to crevice corrosion (parent) and pitting (welds) to give corrosion-free service. However, 22% chromium duplex steels and 904L austenitic steels do not. CCT's at or below design temperatures prevail and the favourable effect of lower potentials is much reduced.

Crevice corrosion at victaulic joints is not uncommon for low and intermediately alloyed stainless steels in SWRO systems. In a few cases there has been crevice corrosion reported under the rubber boot of Victaulic high pressure couplings in high alloy steels too. The results in Figure 10 show that the CCT of as-manufactured pipe surfaces was variable and could be significantly inferior to machined surfaces. The results show that not all pipes had inferior crevice corrosion resistance, but there was no obvious factor indicating inferior surfaces. However, machining a small amount of metal from the land for the rubber seal is a simple, low cost operation and enhances the level of crevice corrosion resistance. This may be attributable to either
a) less ovailty in the OD of the pipe and a more even force at the crevice former /metal interface
b) removal of alloy denuded regions on the pipe surface
c) a smoother surface

V.   CONCLUSIONS

1   In natural and chlorinated seawater, only ZERON 100 and 6%Mo austenitic alloys have sufficient corrosion resistance. Alloys 316L, 22% Cr duplex and 904L are not adequate and have corroded in service.

2   In the treated water used in the high pressure sections of SWRO plants, ZERON 100 and 6%Mo have good corrosion resistance at temperatures above those seen in service. Alloy 316L is totally unsuitable, while 904L and 22% Cr duplex are marginal and may corrode in service and are process sensitive and lack performance margin to accommodate more aggressive crevice assembly in service temperature range. This is supported by service experience.

3   The weld joint critical pitting temperature of ZERON100, significantly exceeds normal SWRO design temperatures. The pitting resistance of the welds can be further increased by acid pickling. In this case the pitting resistance of the weld becomes similar to the crevice corrosion resistance of the parent material. We consider acid pickling to be best practice especially for application in warm seawaters (i.e. Middle East sea water intake or intake from power station cooling water out lets)

4   The CCT and CPT of duplex stainless steels are not much affected by the chloride ion concentration over the range of interest in SWRO plants. Again 22% Cr duplex steels are not sufficiently resistant to pitting or crevice corrosion in brines exceeding 3000ppm chloride. Super duplex stainless steel ideal for the reject brine and energy recovery section in terms of corrosion resistance and strength.

5   The surface condition on pipes can increase the susceptibility to crevice corrosion under the rubber seal in high pressure couplings. This can be prevented by machining the land on which the rubber seal sits. Machining also improves pipe ovality and eliminates surface chemistry effects.

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