

THE FAMILY OF DUPLEX ALLOYS IN THE DESALINATION INDUSTRY

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ABSTRACT

The paper considers Multi Stage Flash (MSF), Multi Effect Distillation (MED) and Reverse Osmosis desalination processes and details the industry drivers (technical and commercial) that have led to the deployment of the family of duplex alloys in these applications. Some of the remaining technical challenges are also identified.

Focusing on sea water processing and in particular SWRO, the paper looks at the performance of duplex and austenitic grades in sea water intake, high pressure sea water feed, brine reject and energy recovery areas associated with plants. In particular the effect of water treatment on the crevice corrosion resistance of flanged and mechanical joints and the pitting corrosion resistance of welds is identified. This work explains some poor application experiences and directs end users to material selection philosophies that optimise plant reliability.

1 INTRODUCTION

The UN estimate that by 2025, 1.8 billion people will be living in countries or regions with absolute water scarcity, and two-thirds of the world population could be under stress conditions. Agriculture represents 70% of freshwater use worldwide, followed by industrial use (22%) and domestic use (8%). Demand for water from the global agricultural sector is expected to increase by between 70 and 90 per cent by 2050. This is compounded by global warming which is expected to reduce rain fall, Agriculture fed by rainfall could drop by 50% in some African countries by 2020. The problem is already manifest in Pakistan, for example, where per-capita surface-water availability for irrigation was 5,260 cubic meters per year in 1951. This has been reduced to 1,100 cubic meters per year in 2006. The water shortage will cause a wheat deficit of 12 million tonnes per year by 2012-13, (to produce 1kg of wheat requires 715 to 750 liters of water). Today the availability of clean drinking water is a major public health issue. Waterborne diseases are responsible for 80 percent of illnesses and deaths in the developing world. One child dies every eight seconds from a waterborne disease; 15 million children a year.

Industrial use of water is bimodal, wealthy countries average 59% industrial usage while low income and developing countries average 10% extraction for industrial usage. As the low income and developing countries try to build their industrial output, water availability will be a serious limiting factor. For example, it requires an estimated 237 liters of water to produce 1kg of steel, 1,000-4,000 liters of water is required to produce a liter of bio fuel, 120,000 liters of water to produce a car, and 170,000 liters of water is used in the production of 1kg of wool.

Major initiatives are already in place to conserve, recycle and reuse water. The production of drinking water from the sea constitutes a drought proof source of supply. Population growth has concentrated on costal areas so the sea constitutes a stable and convenient supply source. As water demand has increased the process technology has improved and costs have fallen.

2 DESALINATION PROCESSES

The main desalination processes are reviewed below.

2.1 Multi-Stage Flash (MSF)

A multi-stage flash distillation plant consists of a series of chambers (often 20 or more), each operating at a pressure lower than the preceding one. As heated brine flows from one chamber to the next, some of it flashes off into vapour. The vapour passes through separators to remove any entrained brine droplets and then condenses on cooler condenser tubes. The distillate then drops into collection trays and passes from stage to stage in a distillate channel, prior to distribution as drinking water. This usually involves the injection of CO₂ (sometimes in the form of non-condensable gases extracted from the distiller) to lower the pH. This distillate is then passed through limestone beds to increase hardness and finally has a small quantity of chlorinated seawater added to provide some minerals and also to disinfect the final product.

Steam heats the recirculating brine in the heat input section and the steam condensate produced is returned as feed to the boilers. The hot brine (typically 110°C) then passes through a series of flash chambers in the heat recovery section. In each chamber, some water vapour flashes off, as described above. In the last few, heat rejection, stages cold, aerated seawater is pumped through the condensers to lower the temperature for further condensation to occur and to remove the heat in the heat input section and complete the operating cycle.

Some of the raw seawater is discharged to waste and some is deaerated and dosed with chemicals to control scaling and foaming, before being added to the recirculating brine as feed make-up. The feed is necessary to replace evaporative losses and to maintain the recirculating brine concentration at acceptable levels. The brine is then heated in the heat recovery condensers before returning to the heat input section again.

2.1.1 *Materials for MSF Plants*

It is apparent from the above description that an MSF plant is quite complex and presents a range of corrosive environments. However, it can conveniently be divided into four main areas, the heat rejection section, the heat recovery section, the brine heater and the ejector section, which handles the removal of incondensable gases. The flash chambers are found in the first two areas and generally utilize the same materials of construction.

The tubes in the brine heater, the heat recovery and heat rejection sections are mostly copper alloys, although titanium is occasionally used in the heat rejection section. The experiences with these have been reviewed by Francis [1].

One possibility that has been suggested is a once-through plant using fully aerated seawater. While this offers savings in equipment, such as deaerators and brine recirculation pumps, it requires high alloy materials, such as superduplex stainless steel, for all the heat exchangers and flash chambers. A single small plant has been built using this concept at Sirte in Libya, using 6%Mo austenitic stainless steel for the most part. However, for a large plant, it has been argued that the increased cost of the heat exchangers and flash chambers, more than offsets the savings at current prices, compared to a conventional MSF plant [1].

The flash chambers are usually carbon steel with 316L cladding in the critical areas, which may include the condensing section. Older units have used 90/10 copper nickel cladding or have coated the critical areas with epoxy paint. The latter requires frequent maintenance and repair to be effective.

In addition, carbon steel flash chambers lined with 316L require regular painting of the external surfaces. In 1992, Olsson and Groth [2] examined the economics of solid stainless steel evaporators compared with carbon steel. The duplex stainless steels are the most attractive because their high strength gives the biggest reduction in wall thickness compared to carbon steel. External stiffeners are required to utilise the maximum wall thickness reduction, but with widely spaced, profiled stiffeners the cost will be low [2]. Their analysis showed that over the full 20 to 25-year life of a plant, savings of ~20% were possible by using solid 22%Cr duplex stainless steel instead of 316L clad carbon steel, which required regular external painting.

More recently, Olsson et al [3] described the use of 22%Cr duplex stainless steel flash chambers at the Wafa MSF plant in Libya. Although the designers did not take full advantage of all the savings possible, the operators still expect to make savings compared with conventional materials over the life of the plant. The introduction of lean duplex stainless steels, such as UNS S32003 and UNS S32101 offers further opportunities for cost reduction without any loss of the strength advantage of duplex stainless steel over carbon steel.

In the ejector section it is possible to get bromine in the incondensable gases [4], which greatly increases the corrosivity. Temperatures can be up to 170°C in the presence of CO₂. 316L is severely pitted when bromine is present and 904L has been used instead [1]. Superduplex stainless steel has greater corrosion resistance compared with 904L and is more readily available in a wide variety of product forms. With the high price of nickel, superduplex is also cost competitive with 904L, making it a viable alternative for ejector condensers.

MSF plants use a large number of circulation pumps and these have tended to be in nickel aluminium bronze and gunmetal for smaller pumps. Larger units have commonly had austenitic cast iron cases with stainless steel impellers and shafts. However, there have been a large number of failures of austenitic cast iron by stress corrosion cracking after 1½ to 6 years, even when the castings have been stress relieved. Research has shown that SCC of austenitic cast iron has no real threshold stress and cracking will always occur sooner or later [1]. The high number of failures has prompted a change to the case material and superduplex stainless steel is the preferred choice. In the lower temperature areas, a 25%Cr duplex alloy with a slightly lower PREN (37/38) has been used because it is easier to cast in large sections.

2.1.2 Future Developments

In MSF plants the present maximum operating temperature (~110°C) is limited by the scaling tendency at higher temperatures, even with scale control chemical additions. One method being investigated to overcome this limit is the use of nanofiltration. This removes all particles down to 0.01µm and effectively removes the ions that lead to scaling.

With brine temperatures of 160° to 180°C MSF plants would be more efficient. The question then is what materials to use for the tubes, tube plates and water boxes? It is not known whether copper alloys would still be adequate for the tubes at the higher temperatures, or whether duplex stainless steels would be better. Research is required to determine the most suitable materials under these higher temperature conditions.

2.2 Multiple Effect Distillation (MED)

MED plants, like MSF plants, require a source of heat, which can be steam or hot water (MED only) or electricity, and so are often run in conjunction with a power station. In most MED plants, a thermo-compressor or a mechanical vapour compressor is added to improve efficiency. These are known as thermo-compression distillation (TCD) and mechanical vapour compression (MVC) plants, respectively. The higher efficiency of TCD plants means that they are the most common variant.

A typical TCD plant may contain from 2 to 14 evaporator stages. Vapour at $\sim 75^{\circ}\text{C}$ is introduced into the first stage evaporator tubes, where it is condensed by externally sprayed raw water. In cooling the evaporator tubes, the raw water in stage 1 is heated and part of it vaporizes. The vapour enters the tubes of the second stage, is condensed by raw water, as in stage 1, forming more condensate. This process repeats itself in the subsequent stages. Part of the vapour produced in an intermediate stage is drawn up by the thermo-compressor, which increases its pressure and mixes it with high pressure steam to feed the first stage. The remainder of the vapour passes to the following stages and finally to a heat exchanger, where it condenses on the outside of tubes cooled internally by raw water. Part of this raw water becomes the feed to the four stages and the rest goes to waste. The product water is collected and piped away while the brine goes to blow down.

An MED plant operates in the same way, but without the thermo-compressor. In an MVC plant the thermo-compressor is replaced with a mechanical vapour compressor.

2.2.1 Materials

The raw seawater feed to an MED/TCD plant is similar to other plants requiring large volumes of cooling water. Large diameter pipe is usually GRP, rubber lined carbon steel or coated carbon steel, with valves of coated carbon steel or uncoated NAB in smaller sizes. At the intake to the unit, the feed pipes may be copper nickel or a stainless steel, if the conditions are corrosive. Alloy 904L, 6%Mo austenitic and superduplex stainless steels have all been used. This, however, is a small part of the plant.

In the heat exchanger stages the environment is aerated at the top of the unit, but oxygen levels decrease dramatically in the lower sections. In addition, the temperatures are not very high, so there is less need for exotic materials. In recent years, erosion corrosion at some plants using spray nozzles has led to the replacement of the upper two or three rows of copper alloy tubes by titanium. This has now become a trend and many plants incorporate this routinely in new construction. The remainder of the tubes are 90/10 copper nickel or aluminium brass and these generally work well. The tube plates tend to be 316L stainless steel, 90/10 copper nickel or NAB. Cathodic protection may be needed for a copper alloy tube plate if titanium tubes are fitted in some rows. Because of the low corrosivity, the shell, distillate trays, demisters etc tend to be 316L stainless steel.

In the final condenser the tubes may be titanium or 90/10 copper nickel, with 316L, titanium, copper nickel or naval brass tube plates. Cathodic protection is usually used to prevent galvanic corrosion. The water boxes are generally rubber-lined steel.

With the high price of metals such as nickel and molybdenum, there is increasing interest in low alloy duplex stainless steels for tube plates. These not only offer similar, or lower, price compared with 316L, but they can be used with reduced thickness, because of their higher strength, giving further savings. Alloy S32304 has been used for tube plates and alloys S32003 and S32101 are being considered because of their lower cost compared to 316L. These alloys are also being considered for

evaporator shells for the same reasons that they are being used for flash chambers in MSF plants, as described above.

2.2.2 Future Developments

The maximum evaporating temperature currently in MED/TCD plants is about 70° to 75°C. Above this temperature, scaling becomes a problem. If economically priced nanofiltration becomes available (see above), then the maximum temperature can be raised, to increase the efficiency. However, the temperature will probably not exceed that currently used in MSF plants, so that there will be little need to consider a major change of materials.

2.3 Reverse Osmosis

In the RO process, water from a pressurized saline solution is separated from the dissolved salts by flowing through a water-permeable membrane. The permeate (the liquid flowing through the membrane) is encouraged to flow through the membrane by the pressure differential created between the pressurized feedwater and the product water, which is at near-atmospheric pressure. The remaining feedwater continues through the pressurized side of the reactor as brine. No heating or phase change takes place. The major energy requirement is for the initial pressurization of the feedwater. For brackish water desalination the operating pressures range from 17 to 30bar (250 to 400 psi), and for seawater desalination from 55 to 70bar (800 to 1,000 psi).

In practice, the feedwater is pumped into a closed container, against the membrane, to pressurize it. As the product water passes through the membrane, the remaining feedwater and brine solution becomes more and more concentrated. To reduce the concentration of dissolved salts remaining, a portion of this concentrated feedwater-brine solution is withdrawn from the container. Without this discharge, the concentration of dissolved salts in the feedwater would continue to increase, requiring ever-increasing energy inputs to overcome the naturally increased osmotic pressure.

A reverse osmosis system consists of four major components/processes: (1) pretreatment, (2) pressurization, (3) membrane separation, and (4) post-treatment stabilization.

Pretreatment: The incoming feedwater is pretreated to be compatible with the membranes by removing suspended solids, adjusting the pH, and adding a threshold inhibitor to control scaling caused by constituents such as calcium sulphate.

Pressurization: The pump raises the pressure of the pretreated feedwater to an operating pressure appropriate for the membrane and the salinity of the feedwater.

Separation: The permeable membranes inhibit the passage of dissolved salts while permitting the desalinated product water to pass through. Applying feedwater to the membrane assembly results in a freshwater product stream and a concentrated brine reject stream. Because no membrane is perfect in its rejection of dissolved salts, a small percentage of salt passes through the membrane and remains in the product water. Reverse osmosis membranes come in a variety of configurations. Two of the most popular are spiral wound and hollow fine fiber membranes. They are generally made of cellulose acetate, aromatic polyamides, or, nowadays, thin film polymer composites. Both types are used for brackish water and seawater desalination, although the specific membrane and the construction of the pressure vessel vary according to the different operating pressures used for the two types of feedwater.

Stabilization: The product water from the membrane assembly usually requires pH adjustment and degasification before being transferred to the distribution system for use as drinking water. The product passes through an aeration column in which the pH is elevated from a value of approximately 5 to a value close to 7. In many cases, this water is discharged to a storage cistern for later use.

The duplex grade 2205 (EN1.4462, ASTM S32205) has superior resistance to pitting and crevice corrosion in comparison to 316L and 317L but has still suffered corrosion in plants in Gibraltar and on the coast of the English Channel [5, 6, 7]. One of the Gibraltar plants, Glen Rocky, was described at the EDS conference in Malta in 1991 [8] and although the paper and oral presentation claimed “no failures after 4 years operation” some pitting corrosion had actually occurred [5]. More recently rather severe pitting and crevice corrosion has been reported from another Gibraltar plant with a capacity of 2 x 240 m³/day [6]. A piece of pipe from the latter was subjected to microscopic examination, but the structure was quite normal, i.e. the corrosion was not caused by any material defects, but just insufficient corrosion resistance. There were two plants built in connection with the Eurotunnel between France and England, using 2205, but crevice corrosion has also been mentioned in this case [7]. More recently two plants in the Philippines [9] and very recently the Gold Coast Project in Australia [10] have had 2205 pipe spools suffering pitting corrosion and crevice corrosion and they have been replaced with superduplex stainless steel.

Another highly alloyed stainless steel used in some plants in the Middle East, on the Balearic Islands in the Mediterranean and on the Canary Islands is 904L (EN 1.4539, ASTM 904L). The first report of corrosion on this grade came from Kuwait already in 1991 [11]. Crevice corrosion has also been established in threaded joints at another large (45,000 m³/day) Middle East plant, but it must be emphasized that threaded connections are prone to crevice corrosion and should preferably be avoided. Severe crevice corrosion has also been established on manifolds made of 904L after only 2 months of service in plants on Mallorca. [12] and a valve in another plant on the same island. More recently 904L has suffered widespread crevice corrosion in valves, flange faces and victaulic connections at a desalination plant in Alicanti on mainland Spain.

3 POTENTIALS IN SEAWATER

3.1 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.

3.2 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 1mg/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.

3.3 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_{sat}).

Tests at RA Materials have compared the open circuit potentials of both superduplex and 6%Mo austenitic stainless steels in seawater at different redox potentials. The results showed that both alloys had the same potential and the redox potential range for the high pressure section of an SWRO plant corresponded to an open circuit potential range of +100mV to +200mv SCE.

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

4 CORROSION

Byrne et al [15] presented data showing the crevice corrosion resistance of a number of alloys that have been used in SWRO plants, as shown in Table 1. In addition 2205 and Zeron 100 superduplex stainless steels were tested in the welded condition. These tests were conducted at a range of different potentials and the critical crevice corrosion temperature (CCT) was determined for all the parent metals. The critical pitting temperature (CPT) was determined for the welded samples.

| 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

$$* PREN = \% Cr + 3.3 \times \% Mo + 16 \times \% N$$

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

The effect of pickling the welds was also investigated, to determine what increase in CPT could be realized.

Figure 1 shows the relative CCT of various stainless steels in seawater as a function of potential. The arrows on the 316L curve indicate that corrosion occurred at ambient temperature and the true CCT was at a lower temperature.

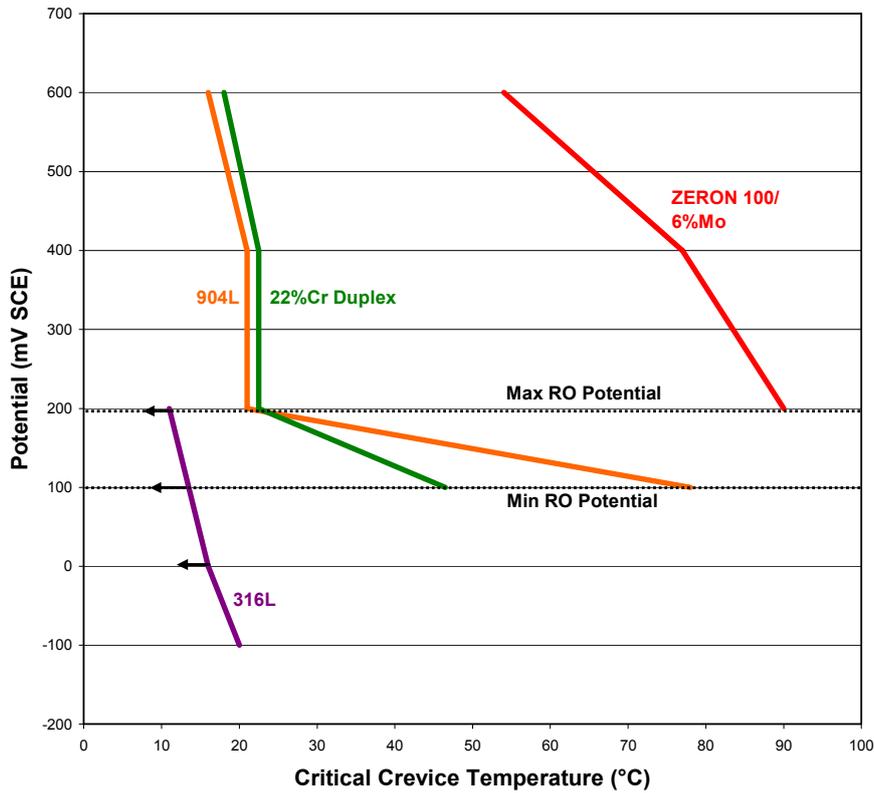


Figure 1 Effect of electrochemical potential in seawater on CCT of some stainless steels.

Figure 2 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 3 shows the effect of acid pickling on the relative CPT of welds of Zeron 100, while Figure 4 shows the effect of chloride content on the relative CCT of the duplex stainless steels.

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 5). The internal surface of all samples was pickled to try and ensure that corrosion initiated on the external face. Figure 6 shows the effect of surface finish on the relative CCT of ZERON 100.

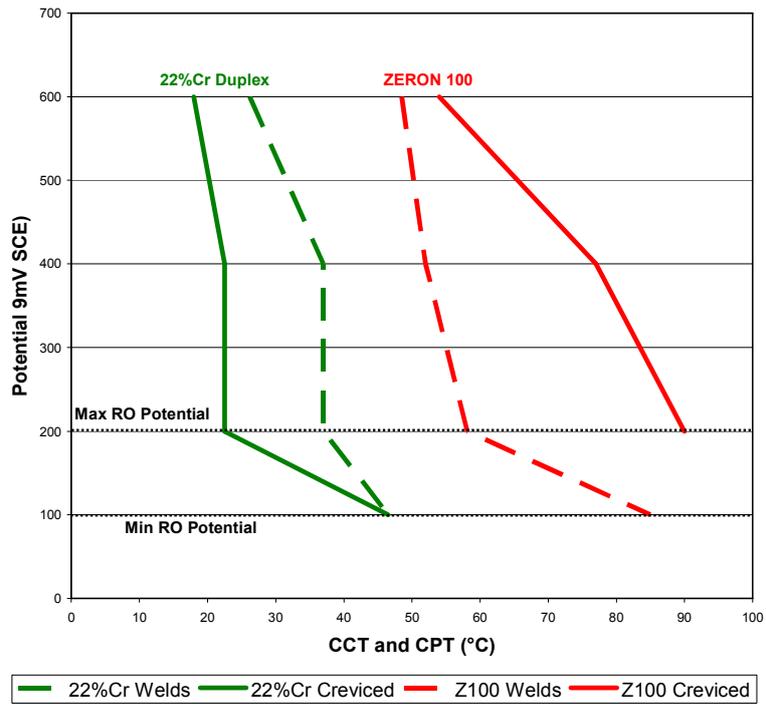


Figure 2 Comparison of CCT (parent) and CPT (welds) as a function of potential in seawater.

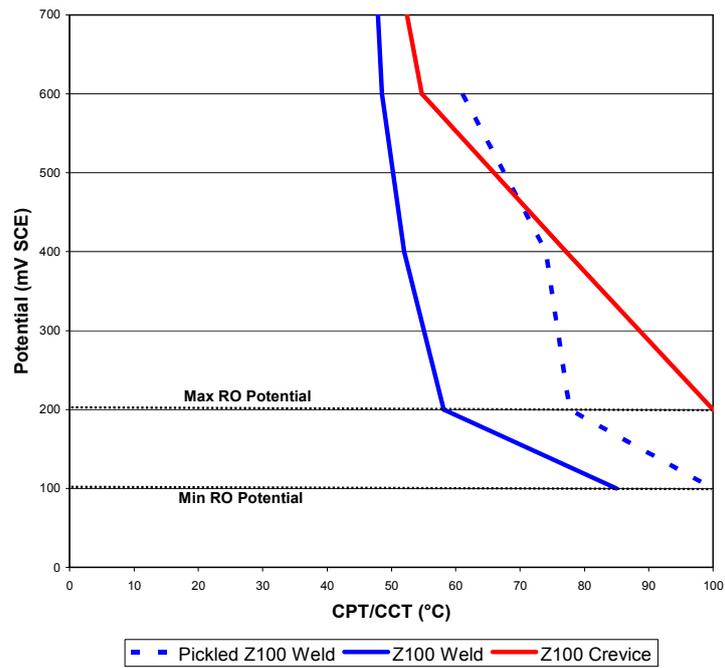


Figure 3 Effect of pickling on the CPT of Z100 welds in seawater.

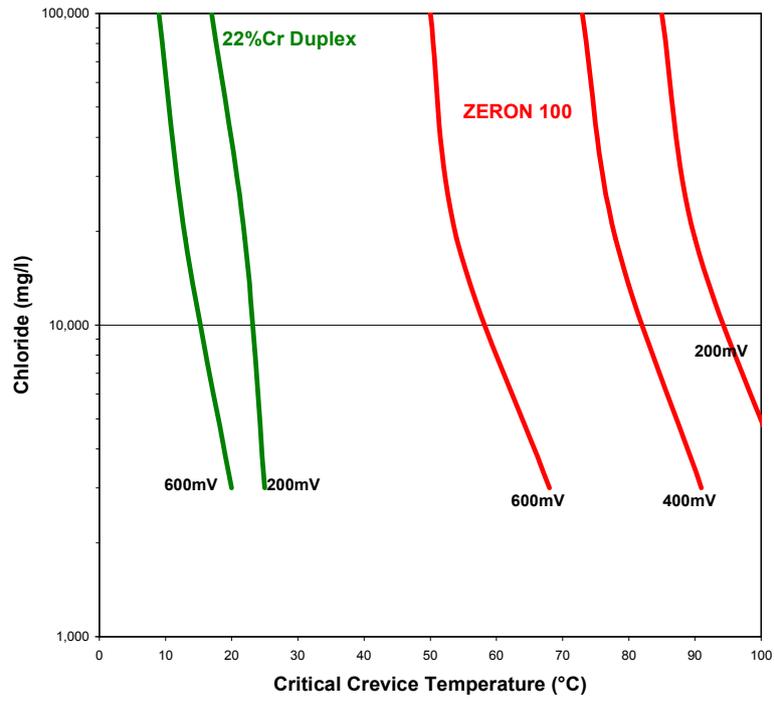


Figure 4 The effect of chloride on the CCT of duplex stainless steels in seawater.



Figure 5 Appearance of creviced pipe sections, A) as received; B) machined.

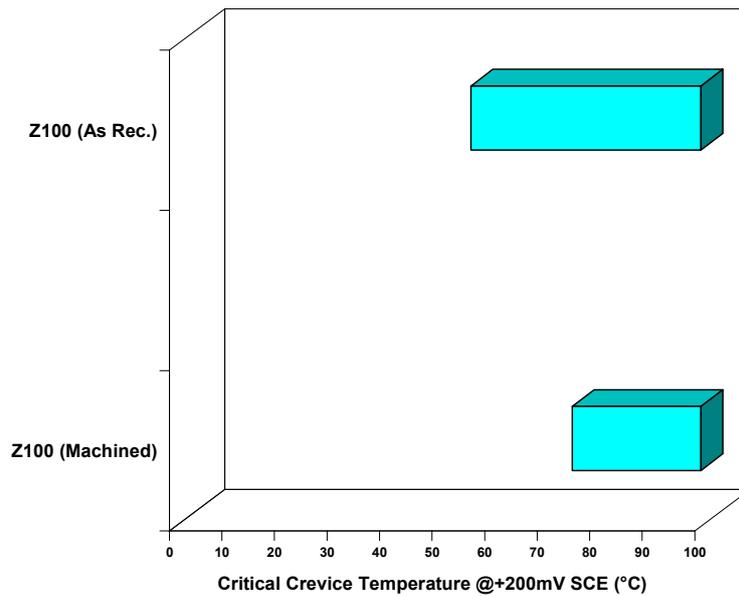


Figure 6 Effect of surface finish on the CCT of Z100 pipe at +200mV SCE in seawater.

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 1 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 potentials 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 [16, 17]. 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 2 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) [18]. This limit can be further increased by pickling [19], as shown in Figure 3.

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 4 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 6 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 ovality 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

5 CONCLUSIONS

- 1 There are clear, cost-effective applications for lower alloy and lean duplex stainless steels in the evaporators and flash chambers of thermal desalination plants. These are as alternatives to both 316L and coated carbon steel.
- 2 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.
- 3 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 assemblies in the service temperature range. This is supported by service experience.
- 4 The weld joint critical pitting temperature of ZERON 100 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)
- 5 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 is ideal for the reject brine and energy recovery section in terms of corrosion resistance and strength.

- 6 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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