



## REPORT

### Marine Corrosion Resistance of ZERON<sup>®</sup> 100 Superduplex Stainless Steel.

**Prepared by:** R Francis  
Corrosion Manager

**Approved by:** G Warburton  
Technical Director

#### CIRCULATION

<b>Division</b>	Engineering
<b>Job No.</b>	
<b>Reference No.</b>	
<b>Report No:</b>	TN779
<b>Iss No.</b>	4
<b>Date:</b>	Dec 2008

Confidential		Copyright © Rolled Alloys 2008	Rolled Alloys Company Ltd co. registered in USA (Delaware)-#37-1540008, PO Box 1287, Northbrook, Illinois 60065. UK Company Number FC027795 VAT Reg No. GB 803 8704 36
General Release	Y	Rolled Alloys is the owner of the Copyright in this document. The document and its text, images, diagrams, data and information it contains must not be copied or reproduced in whole or in part, in any form or by any means, without the prior written consent of Rolled Alloys	



## MARINE CORROSION RESISTANCE OF ZERON® 100 SUPERDUPLEX STAINLESS STEEL.

### TABLE OF CONTENTS

<u>SECTION</u>	<u>DESCRIPTION</u>
	SUMMARY
1.0	INTRODUCTION
2.0	ALLOY COMPOSITIONS
3.0	LABORATORY PITTING TESTS
4.0	CORROSION TESTS
	4.1 Potentials in Sea Water
	4.2 Natural Sea Water
	4.3 Chlorinated Sea Water
	4.4 Repassivation
	4.5 Galvanic Corrosion
	4.6 Chloride Stress Corrosion Cracking
	4.7 Gaskets
	4.8 Start up
5.0	SERVICE EXPERIENCE
6.0	CONCLUSIONS
7.0	REFERENCES
<b><u>TABLES</u></b>	
Table 1.	The nominal compositions of some high alloy stainless steels.
Table 2.	Alloy groupings for galvanic compatibility in seawater at ambient temperature (Ref 22).
Table 3.	Installation list for seawater pumps in Zeron 100.
Table 4.	Major seawater, firewater and RO desalination systems in Zeron 100.
<b><u>FIGURES</u></b>	
Fig 1.	Relationship between PREN and critical crevice temperature (ASTM G48B).
Fig 2.	Typical critical pitting temperature in ASTM G48C ferric chloride test.



- Fig 3. Some possible potentials for stainless steel in seawater.
- Fig 4. Maximum depth of crevice corrosion in natural seawater at 8°C (Ref 1).
- Fig 5. Maximum depth of crevice corrosion in natural seawater at three sites (Refs 1, 9 & 10).
- Fig 6. Depth of crevice corrosion in seawater + 1mg/L chlorine at 16°C.
- Fig 7. Depth of crevice corrosion in seawater + 1mg/L chlorine at 40°C.
- Fig 8. Threshold temperature for chloride SCC in 3% sodium chloride.
- Fig 9. Zeron 100 firewater pump for the South Arne project.
- Fig 10. Spooling of the Zeron 100 seawater piping for the Saltire project.
- Fig 11. Replacement Zeron 100 firewater system on Mobil Beryl 'A'.
- Fig 12. Heat exchanger shell in Zeron 100 for the Fulmar project.
- Fig 13. Seawater filter vessel in Zeron 100 for the BP Bruce project.
- Fig 14. Zeron 100 riser clamp bolts for Balmoral.



## SUMMARY

This report summarises the current data available on the corrosion of ZERON<sup>®</sup> 100 in the marine environment and compares it with that for some other stainless steels. There is over twenty years successful service experience in a wide range of marine applications.

<sup>®</sup> - ZERON is a registered trademark of Rolled Alloys.



## 1.0 INTRODUCTION

The use of high alloy stainless steels for sea water cooling and fire water systems is very attractive, particularly offshore, where high alloy stainless steels can offer substantial weight savings over copper-nickel, and hence reduce the quantity of structural steel needed to support the structure <sup>1</sup>.

Over the last twenty years two main classes of stainless steel, the super austenitic and the superduplex alloys, have been developed for marine applications. This paper reviews corrosion data for both these families of alloys, and assesses how Zeron 100 superduplex stainless steel compares with other alloys.

## 2.0 ALLOY COMPOSITIONS

Zeron 100 is a proprietary alloy developed by RA Materials (formerly Weir Materials) during the 1980's. It falls within the composition limits of UNS S32760 (wrought) and UNS J93380 (cast). However, the composition limits of these two UNS numbers are very wide while the melting specification for Zeron 100 covers a very narrow range. This is to ensure a balanced microstructure to give the optimum physical and mechanical properties and corrosion resistance. The differences between Zeron 100 and alloys purchased only to UNS specifications have been demonstrated by Byrne et al <sup>2</sup>, who showed that generic alloys can have a substantially reduced corrosion resistance.

There are two main types of austenitic alloy containing 6% molybdenum. UNS S31254 contains 18% nickel (e.g. Avesta 254 SMO) and UNS N08367/N08926 contain 25% nickel (e.g. VDM 1925 hMo). The superduplex alloys all contain 25% chromium, 3 to 4% molybdenum and about 0.25% nitrogen. Zeron 100 contains slightly less molybdenum than S32750 (SAF 2507), but it also contains tungsten and copper. Tungsten has similar properties to molybdenum, contributing to repassivation kinetics, while copper improves resistance to non-oxidising acids. Cast versions of these alloys are also produced, although the compositions are slightly different to the wrought ones to improve castability. The 6%Mo alloys do have a tendency to suffer from hot cracking and grain growth in the cast form and 25% Cr superduplex alloys are generally preferred. The compositions of all the alloys are shown in Table 1.

The corrosion resistance of stainless steels in chloride – containing media is often assessed by use of the pitting resistance equivalent number or PREN value. This is usually calculated by use of the empirical formula:-

$$\text{PREN} = \% \text{Cr} + 3.3x\% \text{Mo} + 16x\% \text{N}$$

Table 1 shows that the super austenitic and superduplex alloys have PREN values in excess of 40.

Zeron 100 is the only alloy that is made to a guaranteed minimum PREN of 40, to provide a guaranteed level of corrosion resistance. At first sight, the other alloys in Table 1 might be thought to be more corrosion resistant than Zeron 100 because of their somewhat higher PREN values. However, the PREN number is only a guide to corrosion resistance as it addresses only the chromium, molybdenum and nitrogen contents with no regard for other elements, microstructure, surface finish etc., all of which contribute to the corrosion performance.

As the PREN increases above 40, properties such as formability and weldability decrease. Zeron 100 is made to a minimum PREN of 40 because this gives good resistance to localised corrosion in seawater, while retaining good formability and weldability.

Kovach and Redmond<sup>3</sup> showed that stainless steels that passed an ASTM G48B test at 35°C had good resistance to crevice corrosion in warm seawater. They related the critical crevice temperature in the G48B test to the PREN, as shown in Figure 1. This indicates that separate lines are produced for ferritic, duplex and austenitic stainless steels. Thus to give a CCT of 35°C a duplex alloy requires a minimum PREN of about 40, while an austenitic alloy requires a minimum PREN of about 43.

Zeron 100 contains tungsten, which is not included in the PREN equation, but which is believed to influence breakdown and repassivation of the protective film in the same way as molybdenum. Nagano et al<sup>4</sup> showed that tungsten increases the immunity potential to crevice corrosion of duplex alloys in high temperature chloride solutions. Recent work by Barteri et al<sup>5</sup> showed that the addition of 0.3% tungsten to a 25% Cr duplex stainless steel gave a marked improvement in resistance to sulphide stress corrosion cracking in H<sub>2</sub>S environments. Okamoto<sup>6</sup> showed that tungsten additions of up to 4% to a 25% Cr duplex stainless steel gives a marked improvement in resistance to pitting in chloride solutions. A further advantage of tungsten is that the kinetics for sigma precipitation are much slower than with molybdenum thus reducing the risk of third phase precipitation after hot working operations or welding. The effects of tungsten on the properties of Zeron 100 are discussed in detail elsewhere<sup>7</sup>.

The results in these papers support the opinion on the similarity of the roles of molybdenum and tungsten in stainless steels. Okamoto<sup>6</sup> suggested that tungsten be included in the PREN formula at half the value of molybdenum (i.e. 1.65) and this modification has been adopted by standards such as ISO 15156/NACE MR0175. If tungsten is included in the PREN formula along with the molybdenum, the PREN of Zeron 100 exceeds 41.

### 3.0 LABORATORY PITTING TESTS.

The ASTM G48C ferric chloride test is commonly used as a quick method of assessing the resistance of stainless steels to localised corrosion. The critical pitting temperature (CPT) is a function of a number of variables including metallurgical condition and surface preparation as well as composition. Hence the CPT values for different heats and production routes for any alloy cover a range of values.

Figure 2 shows typical CPT values for some common stainless steels. The results show that variations of 5° to 10° C in CPT values are common. Also the CPT values of 6%Mo austenitic and Zeron 100 superduplex are very similar. The 25% Cr duplex material is an older alloy with a PREN of ~36.

While CPT values give a guide to the relative resistance to localised corrosion, they are not in any way a guide to performance in any particular environment. At the present time, only exposure tests or loop tests give a reliable indication of likely service performance. Results from tests of this kind are described in the next section.

## 4.0 CORROSION TESTS

### 4.1 Potentials in Sea Water

When high alloy stainless steels are immersed in seawater they can adopt a range of potentials depending on the conditions, as shown in Figure 3. In ambient temperature natural seawater a biofilm forms over a period of 1-4 weeks, which depolarises the cathodic reaction. This produces potentials in the range 250-350mV SCE and a high cathodic efficiency. In simple chloride solutions stainless steels are not very good cathodes. This means that if the passive film breaks down it is difficult to support much in the way of corrosion. The presence of a cathodically efficient biofilm makes the propagation of localised attack more likely.

When chlorine is added to seawater (typically 0.5-1.0mg/L) to control fouling, the reduction of hypochlorite ions to chloride provides an alternative cathodic reaction to the reduction of dissolved oxygen. Potentials are typically in the range 550-650mV SCE, but the cathodic efficiency is not as high as in natural seawater.

As the temperature of natural seawater is increased, a point is reached at which the biofilm is not viable and lower potentials, in the range 100-200mV SCE, result. The cathodic efficiency is then much lower than in the presence of the biofilm. It has been shown that the critical temperature for the prevention of a biofilm is approximately 25° to 30°C above the ambient seawater temperature. As the oxygen content of the water is reduced, the potential becomes more electronegative, but even low oxygen contents still produce potentials around -100mV SCE (Figure 3).

### 4.2 Natural Sea Water

Natural, unchlorinated seawater is somewhat less corrosive than chlorinated seawater. Shone et al<sup>1</sup> carried out crevice tests on a wide range of stainless steels and nickel alloys. Figure 4 shows the maximum depth of attack after 60 days for several common stainless steels. Only alloys with a PREN>40 resisted crevice corrosion. Tests have been conducted in a number of locations at different ambient temperatures. Figure 5 compares the results of Shone et al<sup>1</sup> (~8°C), Francis<sup>9</sup> (~15°C) and Kain<sup>10</sup> (~25°C). Although the maximum depth of attack varied from site to site, only alloys with a PREN > 40 resisted attack.

Consideration has been given to the resistance of Zeron 100 to corrosion in stagnant seawater at high temperature and particularly at welds. Two test vessels were fabricated from NPS 6 pipe with a flange and blanking plate welded on one end and an end cap on the other. One vessel was totally filled with seawater and the other was half filled. In addition to the vessel welds, welded coupons were exposed inside the vessels, both fully immersed and in the gas space. The vessels were left filled with stagnant seawater outside in a yard fully exposed to the elements in Dubai for eighteen months. The external temperature of the vessels reached 70°C during the summer. At the end of the test no corrosion was observed on any of the welds.

One concern over the more corrosion resistant alloys is their resistance to microbiological attack (MIC). This could occur either beneath fouling in aerated seawater, or due to sulphate reducing bacteria (SRB) in anaerobic, bottom mud. In either case the reactive products would be sulphides, either as H<sub>2</sub>S or a reactive organic sulphur compound such as cystine<sup>11</sup>. Superduplex stainless steels, such as Zeron 100, have been extensively

used in oilfield production systems, where H<sub>2</sub>S levels of up to several hundred mg/L have been handled successfully, at temperatures over 100°C. Zeron 100 has also been tested in NACE solution. This contains 5wt% sodium chloride plus 0.5wt% acetic acid, which is saturated with H<sub>2</sub>S. No pitting or cracking was observed after 30 days of testing. Hence it is not expected that the concentration of H<sub>2</sub>S likely to be encountered under fouling or in bottom mud will cause any corrosion problems with superduplex stainless steel.

Trials have been carried out in the mud flats at Hayling Island on the UK South Coast. Pipes of carbon steel, 316L stainless and Zeron 100 have been buried in an aggressive, anaerobic mud for several years. Samples removed after 5 years showed corrosion and pitting of the carbon steel (max depth = 0.64mm) and pitting on the 316L (max depth = 0.37mm)<sup>12</sup>. The Zeron 100 showed no corrosion either at the mudline, below the mudline or at welds. Zeron 100 has been deployed subsea by BHP on the Jibaru Project specifically to combat a microbiological corrosion problem with good success<sup>13</sup>.

Under flowing conditions Zeron 100 also has excellent resistance to erosion corrosion in high velocity seawater. While 90/10 copper nickel has a maximum design velocity of 3 to 3.5 m/sec, tests on Zeron 100 in seawater at 30 m/sec and 30°C showed no detectable weight loss after 30 days<sup>14</sup>. The maximum practical velocity for seawater systems is about 10m/sec because of considerations of noise and vibration. The strength of Zeron 100 means that erosion corrosion resistance is retained even in the presence of particulates such as small amounts of silt or sand. The resistance of Zeron 100 to erosion corrosion is discussed in more detail elsewhere<sup>15</sup>.

#### 4.3 Chlorinated Sea Water

The main concern over the corrosion resistance of super stainless steel piping systems in seawater is crevice corrosion. Chlorine or hypochlorite is generally added to the seawater to prevent fouling. As this is a powerful oxidising agent, the risk of crevice corrosion is increased. Francis<sup>9, 16</sup> reported the results of 90 day exposures in natural chlorinated sea water using "INCO" crevice washers<sup>17</sup>. The results, in Figure 6, show the maximum depth of attack for a range of stainless steels at 16°C, and in particular that 22% Cr and ordinary 25% Cr duplex (PREN 37) can suffer from crevice corrosion. Only the 6%Mo austenitic alloys and Zeron 100 were immune from attack. Similar results were obtained by Shone et al<sup>1</sup> with 0.8mg/L chlorine.

As the seawater temperature increases, eg. downstream of heat exchangers or in tropical waters, the risk of crevice corrosion increases. Figure 7 shows the maximum depth of attack in chlorinated seawater at 40°C for several stainless steels. Not only did the lower alloy stainless steels suffer attack, but so did the 6%Mo austenitic alloy and only Zeron 100 resisted attack. This has been confirmed by other workers. Wallen et al<sup>18</sup> recommended a maximum service temperature of 30° to 35°C in chlorinated seawater for 6%Mo austenitic stainless steel. Francis and Byrne<sup>19</sup> pointed out that superduplex stainless steels are limited to a maximum seawater temperature of about 40°C by the pitting resistance of the welds, rather than by crevice corrosion.

Loop tests have also been carried out by Shell<sup>1</sup> in chlorinated seawater (0.5 – 0.8 mg/L chlorine) at ambient temperature (7°-18°C). These utilised standard pipe, fittings flanges, etc., fabricated by welding, in a configuration with dead ends and stagnant zones. These tests were conducted at normal flow velocities and Zeron 100 showed no signs of corrosion after six months of loop operation.

#### 4.4 Repassivation

Of concern for some applications, where stainless steel is being used for seawater cooling piping, is the effect of temperature transients on the crevice corrosion performance. Normal discharge temperatures from seawater cooling lines are 20° to 40°C. However, upsets in process conditions can lead to much higher temperatures (up to 70°C) for short periods. Under such conditions localised corrosion can initiate and propagate and may or may not repassivate when normal operation conditions are restored. Francis et al<sup>20</sup> reviewed some service failures observed in 6%Mo austenitic alloys due to temperature excursions. They also described<sup>20</sup> laboratory tests to compare the resistance of 6%Mo austenitic with Zeron 100 under upset conditions.

Crevice specimens polarised to +600 mV SCE were allowed to stabilise at ambient temperature for an hour or two and were then taken rapidly up to 70°C. After 22 hours they were allowed to cool and the repassivation temperature was recorded.

The results showed that all the 6Mo specimens suffered extensive crevice corrosion at 70°C and the repassivation temperature varied from 33.5° to 47°C. Only 50% of the Zeron 100 samples suffered crevice corrosion and all of these repassivated readily on cooling. The repassivation temperature varied from 42°C to 65°C. There was also much less corrosion on those Zeron 100 samples which were attacked, compared with the 6%Mo specimens. The results show the much greater resistance of Zeron 100 to high temperature excursions.

#### 4.5 Galvanic Corrosion

As can be seen from Figure 3, the potential of Zeron 100, and other high alloy stainless steels, is considerably more electropositive than that of some other materials that are often used in seawater systems. This raises the possibility of galvanic corrosion. It has been shown that there is a range of high alloy materials that behave similarly in seawater. These include the superduplex and super austenitic stainless steels, titanium and the nickel alloys, such as C-276 and 625. These can safely be connected together in seawater without any risk of galvanic corrosion<sup>21</sup>.

Francis<sup>22</sup> showed that alloys can be divided into 5 main groups (Table 2). Alloys within each group can be safely coupled together. Coupling alloys from different groups may result in attack, depending on the area ratio, cathodic efficiency and a number of other factors. It can be seen that Zeron 100 is in Group 1 as are the other alloys listed above. Zeron 100 should not be coupled to nickel alloys 400, K-500 or 825 unless there is a very small area of Zeron 100. Where there is a potential for galvanic corrosion, Francis<sup>22</sup> describes methods that can be used to prevent problems.

Zeron 100 is available in a wide range of product forms and it is possible to obtain most components for seawater systems in a single alloy, thus avoiding galvanic corrosion problems.

#### 4.6 Chloride Stress Corrosion Cracking

Duplex stainless steels have superior resistance to chloride stress corrosion cracking (SCC) compared with austenitic alloys such as 316L. Figure 8 shows the temperature at which chloride SCC has been observed in 5% sodium chloride solution for several stainless steels. Tests on Zeron 100 have shown no cracking at 250°C. Seawater

temperatures, even from heat exchanger discharge lines, rarely exceed 40° to 45°C and so external stress corrosion cracking is not a concern.

#### 4.7 Gaskets

A common crevice in seawater systems is that at flanged joints. Previously, compressed asbestos fibre (CAF) was the main gasket material and this caused few problems. Since CAF was banned a number of alternative materials have been tried and tested, such as neoprene, PTFE and mineral fibres. Some of these, e.g. PTFE, give more problems than others and it has been suggested<sup>23</sup> that the gaskets that tend to absorb some water give least problems, because the water in the gasket dilutes the aggressive solution in the crevice.

There are two other types of gasket that can cause problems in seawater. The first is gasket materials containing graphite. When the gasket is wetted the graphite will be more electropositive compared with Zeron 100 and could stimulate localised corrosion by creating a galvanic cell<sup>22</sup>. Graphite loaded gaskets were used with Zeron 100 flanges on the seawater cooling system on the Rob Roy platform in the North Sea. Pitting occurred on the flanges beneath the gaskets after some time in service. The flange faces were repaired and the flanges were reassembled with non-graphite gaskets. No corrosion has subsequently occurred. Similar problems have occurred with graphite-containing gaskets and 6%Mo stainless steel flanges<sup>22</sup>. Following such experiences, graphite-containing gaskets are not permitted for seawater flanges by some oil companies.

A second type of gasket that causes concern are metallic ones formed either as a “V” seal or spirally wound. These are frequently made of 316L stainless steel, which suffers severe attack in crevices in seawater, and this can lead to attack on super stainless steels adjacent to the 316. The reason for this is that when the 316 stainless steel corrodes the pH of the localised water drops sharply. The solution can eventually become sufficiently acid (pH<1) to promote attack on both super austenitic steels and superduplex steels<sup>1</sup>.

Where spirally wound gaskets are to be used with Zeron 100 it is important to select a metal for the spirals that is compatible with Zeron 100 in seawater. In addition the spirals need to be relatively soft so that they can be compressed to give a seal. Alloy 400 (UNS N00550) and alloy 825 (N08825) are not regarded as being galvanically compatible with Zeron 100 in seawater<sup>22</sup>. Alloys which could be considered for the windings are:-

- Superduplex
- Alloy 625 (UNS N06625)
- Alloy C-276 (UNS N10276)
- 6%Mo austenitic (UNS S31254/N08926)
- Titanium

i.e. alloys from Group 1 of Table 2.

The choice will depend on price and availability.

The selection of gaskets for use with high alloys stainless steels was reviewed by Francis and Byrne<sup>24</sup>

#### 4.8 Start up

It has been observed by several workers (e.g. Ref 25) that when stainless steels are progressively subjected to an increasingly aggressive environment, e.g. increasing temperature, they are more resistant to crevice corrosion than when they are immersed immediately in the most aggressive environment. The mechanism for this increased corrosion resistance is not known, but Rogne et al<sup>25</sup> suggested that a gentle start up of high alloy stainless steel cooling systems would give the alloys more resistance to crevice corrosion in the hottest sections downstream of the heat exchangers.

This suggestion was first adopted in the Norwegian sector of the North Sea and is standard start up practice for some oil companies. A typical start up regime is:-

- (1) Cold, natural seawater for 48hrs minimum.
- (2) Cold, chlorinated seawater for 5 days minimum.
- (3) Start up heat exchangers as slowly as possible.

#### 5.0 SERVICE EXPERIENCE

Zeron 100 castings have been used for seawater lift pumps and firewater pumps since 1986. The alloy has also been used for high pressure feed pumps in reverse osmosis desalination plants. These have performed very well with no reports of any corrosion problems. Table 3 shows some of the numerous applications of Zeron 100 for pumps handling seawater, while Figure 9 shows a typical Zeron 100 firewater pump.

A number of seawater cooling systems, firewater systems and reverse osmosis (RO) desalination plants has been supplied in Zeron 100. Table 4 shows some of these projects. The oldest is Rob Roy/Ivanhoe, which has been in operation since 1990 with no reported problems since start up.

There have been a number of problems reported with 6%Mo austenitic stainless steel systems, some of which have occurred in seawater with temperatures reported to be as low as 15°C<sup>26</sup>. The 6%Mo alloy has been most widely used for sea water systems in the Norwegian sector of the North Sea and the problems were summarised by Strandmyr<sup>27</sup>. They mainly concerned crevice corrosion at threaded joints and flanges. On some platforms this had led to considerable down time while repairs were undertaken.

At the same conference Shrive<sup>28</sup> reported on the British experience, which has largely been with superduplex stainless steel rather than 6%Mo austenitic, and much of it Zeron 100. Shrive stated that problems as described by Strandmyr were not seen and, although there were usually a few problems at start up associated with over chlorination or temperature transients, once these were rectified the systems were generally very reliable. This experience confirms the good results with Zeron 100 in laboratory tests.

Figure 10 shows the Zeron 100 sea water pipes being spooled for the Elf Saltire seawater system, while Figure 11 shows the firewater system on Mobil Beryl 'A'. The latter system was a retrofit, replacing a corroding carbon steel system and the Zeron 100 piping was welded into position around the existing fixtures and piping without problems. Figure 12

shows a heat exchanger shell for the Shell Fulmar platform, where Zeron 100 proved more cost effective than titanium. The seawater filter vessel in Figure 13 was built to replace a glass flake lined carbon steel vessel, which failed due to detachment of the coating on the BP Bruce Platform. Although superduplex filter vessels are several times the price of glass flake lined carbon steel, stainless steel is preferred because of the difficulty of access to the filter vessels offshore for maintenance or replacement. The cost of one replacement of lined carbon steel is many times that of a single superduplex vessel.

Even on platforms where 6%Mo austenitic stainless steel has been chosen for the piping it is very common to find superduplex stainless steel selected for the valves and pumps. This is because it is much easier to make large castings in superduplex compared with 6%Mo austenitic, because of the problems described in Section 2.

Zeron 100 piping has been used for both seawater and firewater systems on the Woodside Goodwyn "A" Platform. Soon after start up in 1990 a series of leaks appeared, associated with welds, in the firewater system. RA Materials was involved in the investigation that was carried out in Australia. All of the welds were very dark on the root side, and many were covered with thick, black oxide. The corrosion occurred at the low temperature heat affected zone as extensive pitting. The microsections showed extensive sigma phase precipitation in the HAZ, with levels of not less than 10% and in some cases up to 20%. The samples with dark films clearly indicate the use of excessive heat inputs, above those specified in the weld procedure. It is well documented that the use of high heat inputs results in the precipitation of sigma phase. The welds with heavy coking on the root side also suggest little or no argon purging occurred. Under these circumstances the weld pool becomes very sticky and greater heat input is necessary to complete the weld. Excessive heat inputs in schedule 10S pipes (2" to 6") are well known to result in sigma phase precipitation.

There was little radiography carried out on the welds compared with North Sea practice. In addition parts of the flooded firewater piping were exposed at temperatures up to, and probably exceeding, 60°C. This demonstrates the need for qualified welders and approved procedures when welding Zeron 100. Following these failures new welding procedures were qualified, welder training was improved and awareness of the importance of heat input and interpass temperature control was heightened among the fabricators.

It is recognised that with thin wall, small diameter pipework some third phase HAZ precipitation may be inevitable. However, this is usually in the low single figure percentage range. There is laboratory data and much service experience to show that such a level of precipitate in no way impairs performance<sup>29,30</sup>.

The Piper Bravo platform ran at 20°C seawater discharge temperature for two or three months until full production started. The seawater discharge temperature from three gas coolers then rose to ~60°C and stabilised at ~50°C. After 2 years operation no leaks had occurred in the piping at flanges or welds. The gas flow has been further increased and the discharge temperature is now ~65°C. There have been no leaks after over 10 years at the highest temperature. These results show the excellent resistance of Zeron 100 to crevice corrosion at elevated temperatures in seawater and the advantages of a gentle start up.

In addition to offshore oil and gas piping Zeron 100 has found two other areas of use where its combination of high strength and good corrosion resistance give it an

advantage over competing materials. The first application is for bolting and Zeron 100 fasteners have been extensively used for column pipes, flanges, subsea clamps and similar applications. No corrosion problems have been reported in environments varying from the North Sea to the Arabian Gulf. Figure 14 shows Zeron 100 bolting used by Balmoral to retain buoyancy floats on an offshore riser.

The second application is for high pressure feed and brine reject pumps and piping in reverse osmosis (RO) desalination plant. Zeron 100 has excellent corrosion resistance in seawater up to at least 40°C and gives similar or better performance than 6%Mo austenitic alloys. However, the pressure in these lines is typically around 70 bar and for many pipe sizes this can be accommodated with schedule 10S pipe in Zeron 100, while schedule 40S is required for 6%Mo austenitic. Thus there is the scope for substantial cost savings. This is discussed in more detail by Byrne et al <sup>30</sup>.

## 6.0 CONCLUSIONS

1. The PREN value is only a guide to corrosion resistance and factors such as the other alloying elements, microstructure, and surface finish need to be taken into account.
2. ZERON 100 has excellent resistance to localised corrosion in chlorinated seawater in flanged pipework systems, with considerable good service experience up to and including 40°C. Experience above 40°C is limited but some operators have advised of successful continuous operation at 60° to 65°C for a number of years without corrosion.
3. The resistance of ZERON 100 superduplex stainless steel to localised corrosion in seawater at ambient temperature is similar to or better than that of the 6%Mo austenitic alloys.
4. At elevated seawater temperatures ZERON 100 shows superior performance to 6%Mo austenitic alloys under both short term transient conditions and longer term exposures.
5. The service experience with ZERON 100 shows its excellent corrosion resistance in seawater, the weight savings that can be achieved over copper-nickel systems, and the cost savings over 6%Mo austenitic in high pressure RO systems.
6. Trained and qualified fabricators working to approved and qualified welding procedures are essential if the optimum seawater corrosion resistance is to be achieved. The necessary disciplines to achieve these requirements have been applied by fabricators around the world with good success.



## 7.0 REFERENCES

1. E B Shone, R.E. Malpas and P Gallagher  
Trans Inst Mar Eng 100 (1988) 193
2. G Byrne, R Francis and G Warburton  
“Variation in Mechanical Properties and Corrosion Resistance of Different Alloys within the Generic Designation UNS S32760”.  
Duplex America 2000, Houston, TX, USA, Mar 2000, KCI.
3. C.W Kovach & J.D Redmond, Paper 267, Corrosion '93. New Orleans, LA, USA, March 1993. NACE International
4. H Nagano, T. Kudo, Y. Inada and M Harada, Metaux Corrosion Industrie  
No 667 p23.1 1981
5. M Barteri, G Rondelli, L Scopio and A Tamba,  
Duplex Stainless Steels 91, Beaune, France, Oct 1991; les editions de physique, page 1203.
6. H Okamoto, Applications of Stainless Steels '92 June 1992, Stockholm, Sweden,  
Published by Jernkontorets, Page 360.
7. WM&F Technical Report, TN1120R1, June 2000.
8. R Francis, Brit. Corr. J. 29, 1 (1994) 53
9. R Francis, Stainless Steel '87  
York UK. Sept 1987. IOM, p192.
10. R M Kain, Duplex Stainless Steel '97  
Maastricht, Holland. Oct 1997. KCI, p627.
11. T H Rogers, J Inst Met 75 (1948) 19.
12. R Francis, G Byrne and HS Campbell  
Paper 313, Corrosion 99', San Antonio, TX, USA.  
April 1999, NACE, International.
13. A Polomka, BHP, Private Communication
14. R.M Kain, L.S. Marshall, D.G Melton, D.M Aylor, R.A Hays and R.J Ferrara.  
Stainless Steel World, Dec 2000, p28.
15. WM&F, Technical Report, TN781R2, Nov 2002.
16. R Francis, Confidential BNF Metals Technology Centre,  
Report; R592/2 Feb 1988.
17. D B Anderson, Statistical Aspects of Crevice Corrosion,  
ASTM STP 576, 1976.

18. B Wallen and S Henrikson, Paper 403, Corrosion' 88. St. Louis, MO, USA. March 1988, NACE International.
19. R Francis and G Byrne, Stainless Steel World 16, June (2004) 53.
20. R Francis, J Irwin and G Byrne  
Brit. Corr. J. 30, 3 (1995) 237
21. E.B. Shone and P Gallagher  
"Galvanic Compatibility of Selected Alloy Stainless Steels in Seawater Corrosion in Seawater Systems", Chapter 4, Ed. A.D. Mercer, 1990. Pub Ellis Horwood, page 40
22. R Francis, Galvanic Corrosion – A Practical Guide For Engineers, NACE International, 2001.
23. R.M Kain, Paper 702 Corrosion '98  
San Diego, CA, USA. March 1998; NACE International
24. R Francis and G Byrne, Mat Perf. 46, 10 (2007) 50
25. T Rogne and U Steinsmo "European Workshop on Sea Water Corrosion of Stainless Steels – Mechanisms and Experiences." EFC Publication No.19, IOM; Page 55.
26. R Lye, Paper No. 2  
Engineering Solutions to Industrial Corrosion Problems June 1993. Sandefjord, Norway. Published by NACE International.
27. O Strandmyr " Seawater Materials: Norwegian Experience"  
12<sup>th</sup> International Symposium on Corrosion and Materials Offshore, Stavanger, Norway, Jan 1999, NITO.
28. S Shrive " Seawater Materials: British Experience"  
ibid.
29. R Francis and G Warburton.  
Stainless Steel World 1999 Conference  
The Hague, Holland. Nov 1999. KCI page 711.
30. P L Bowden and J L Ward "Experiences welding 25Cr super duplex stainless steels for topsides hydrocarbon piping" OTC, May 1993, Houston, TX, USA
31. 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.



TABLE 1. The nominal compositions of some high alloy stainless steels.

TYPE	DESIGNATION	NOMINAL COMPOSITION (wt%)							PREN*
		C	Cr	Ni	Mo	N	Cu	W	
Wrought	S31254	0.02	20	18	6	0.2	0.7	-	43
	N08367	0.02	20	25	6	0.2	-	-	43
	N08926	0.02	20	25	6	0.2	1.5	-	43
	S32550	0.02	25	6	3.7	0.25	1.5	-	41
	S32750	0.02	25	7	3.7	0.25	-	-	41
	<b>ZERON 100</b>	<b>0.02</b>	<b>25</b>	<b>7</b>	<b>3.5</b>	<b>0.25</b>	<b>0.7</b>	<b>0.7</b>	<b>&gt;40</b>
Cast	CN3MN	0.02	21	24	6	0.2	0.5	-	43
	CK3MCuN	0.02	20	18	6	0.2	0.7	-	43
	<b>ZERON 100</b>	<b>0.02</b>	<b>25</b>	<b>8</b>	<b>3.5</b>	<b>0.25</b>	<b>0.7</b>	<b>0.7</b>	<b>&gt;40</b>

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



**TABLE 2. Alloy groupings for galvanic compatibility in seawater at ambient temperature. (Ref 22).**

CATEGORY	TYPE	ALLOY
1	Noble; passive	Nickel-chrome-molybdenum alloys (Mo>7%) 6% Mo austenitic stainless steel Superduplex stainless steel Titanium and its alloys.
2	Passive; not truly Corrosion resistant	Alloy 400/K-500 904L 22% Cr duplex Alloy 825 Alloy 20 316L
3	Moderate Corrosion Resistance	Copper Alloys Austenitic cast iron
4	Poor Corrosion Resistance	Carbon Steel Cast iron
		Aluminium alloys



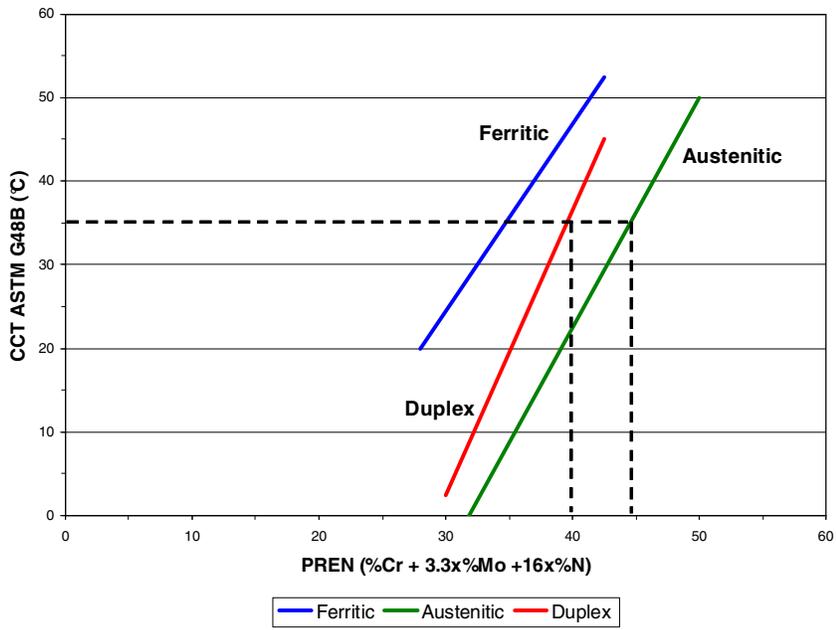
TABLE 3: Installation list for seawater pumps in Zeron 100.

Application	Type	Delivery Date
Shell	Vertical in-line	1986
Shell Oman	Booster pump	1987
Amerada Hess (Ivanhoe/RobRoy)	Lineshaft Pumps	1987
Global/RDS (South Morecambe)	3-stage submersible	1989
Shell (Brent Charlie)	2-stage tank pumps	1989
PDO Oman	Injection	1991
QGPC (Dukhan)	Injection	1991
BP (Gyda)	Seawater lift	1992
Adma Opco (Zakum)	Seawater lift	1992
Petronas Garigali (Dulang)	3-stage submersible	1994
Agip Tiffany	High pressure feed (RO)	1994
Zadco (Upper Zakum)	3-stage submersible	1996
ESSO Falcon & Xicomba	Seawater lift	2001
Petrobras Brasil	Seawater lift	2002
ESSO Safiro	Seawater lift	2002
Conoco Jade	Firewater	2002
BOC Cantarell	Circulation and make-up pumps	2003
Carigali Triton, Cakerwala	Seawater lift	2003

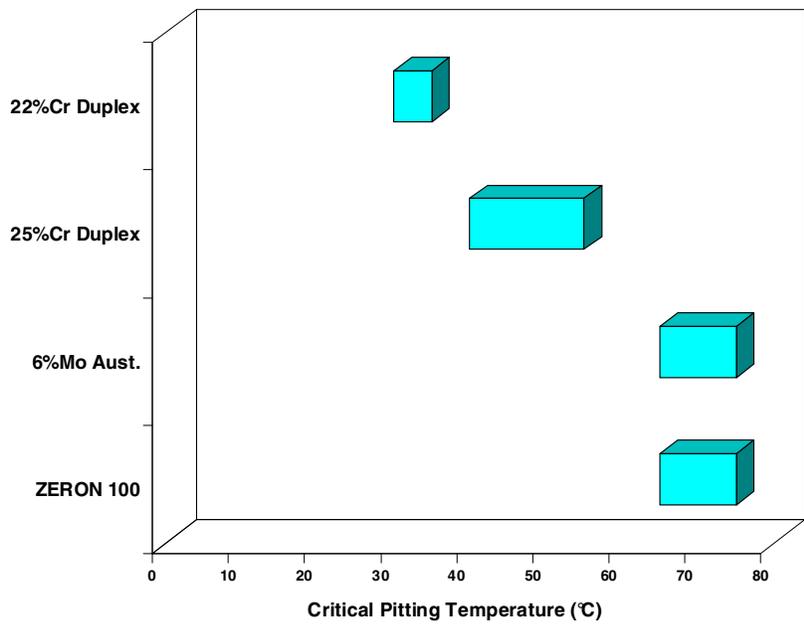
TABLE 4: Major seawater, firewater and RO desalination systems in Zeron 100.

CLIENT	CONTRACTOR	PROJECT
Amerada Hess	Brown & Root	Ivanhoe/Robroy (Seawater system)
Mobil	Davy McKee	Beryl A (Firewater/Deluge system)
British Gas	Global	Morecambe Bay (Seawater discharge)
BP	Brown & Root Vickers	BP Bruce (Firewater/seawater)
Amerada Hess	Foster Wheeler	Scott (Seawater system)
QGPC	Global Eng.	Diyab (Hook up system)
Hamilton Oil	Brown & Root	Liverpool Bay (Seawater/firewater)
EE Caledonia	Brown & Root	Piper Bravo (Seawater/firewater)
ONGC	Hyundai	Neelam (Column pipes)
Maersk	-	Harald West (Heat Exchanger)
AGIP	Weir Westgarth	Tiffany (Sulphate RO removal)
Ministry of Environment (Spain)	FCC/SPA	Adege-Aronas (RO plant)
Hyundia Heavy Industries	Haliburton	Terra Nova (Seawater System)
BOC	BOC	Nitrogeno de Cantarella (Heat Exchangers)
Tampa Bay Desalination	Covanta	Tampa Bay (R.O. Plant)

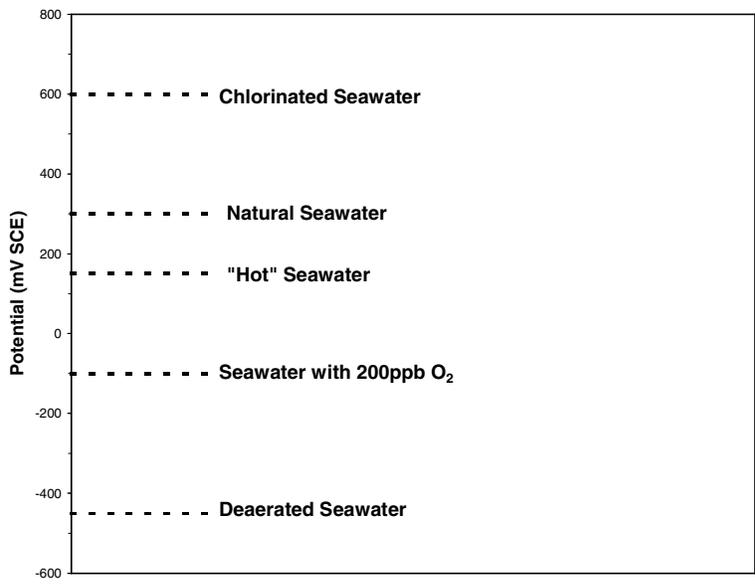
**FIGURE 1 Relationship Between PREN and Critical Crevice Temperature (ASTM G48B)**



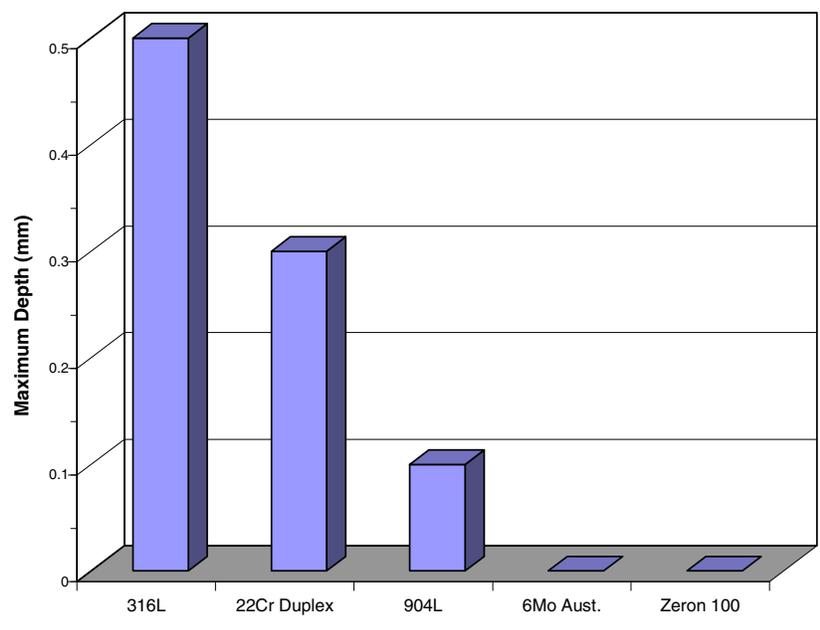
**FIGURE 2 Typical critical pitting temperature in ASTM G48C ferric chloride test**



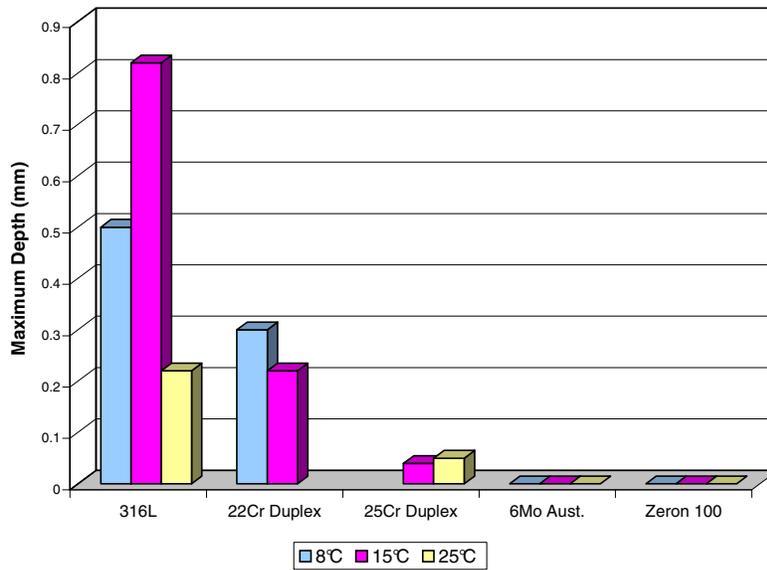
**FIGURE 3 Some possible potentials for stainless steel in seawater**



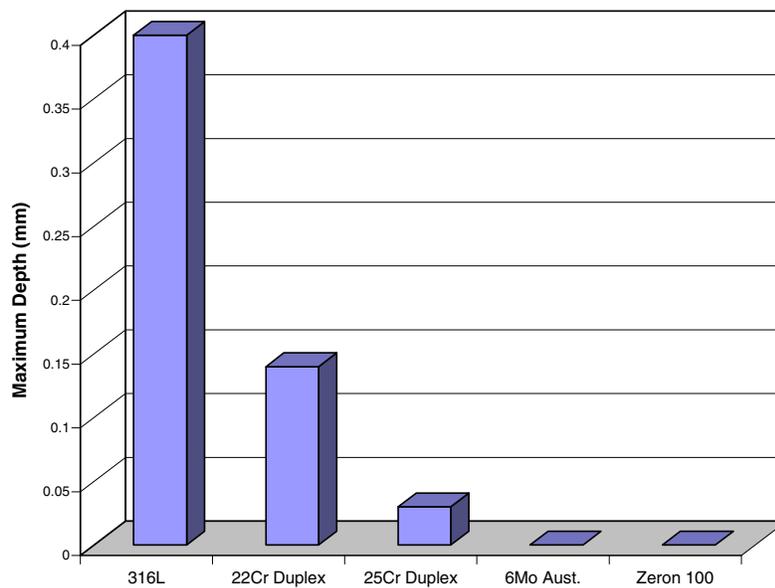
**FIGURE 4 Maximum depth of crevice corrosion in natural seawater at 8°C (Ref 1)**



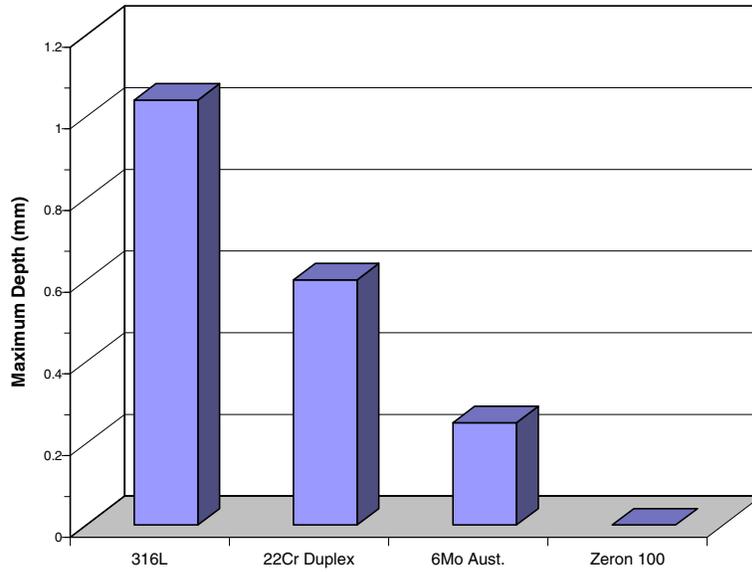
**FIGURE 5 Maximum depth of crevice corrosion in natural seawater at three sites (Refs 1, 9 & 10)**



**FIGURE 6 Depth of crevice corrosion in seawater + 1mg/L chlorine at 16°C**



**FIGURE 7 Depth of crevice corrosion in seawater + 1mg/L chlorine at 40°C**



**FIGURE 8 Threshold temperature for chloride SCC in 5% sodium chloride**

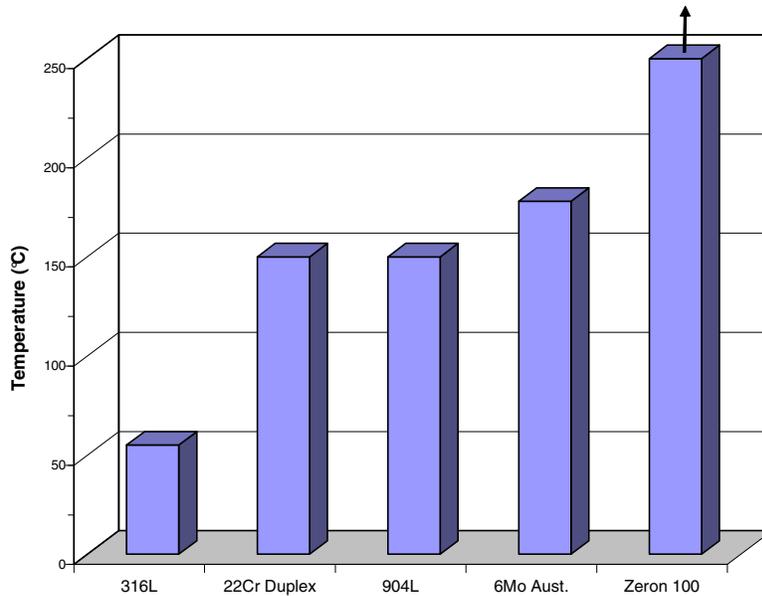




FIGURE 9 Zeron 100 firewater pump for the South Arne project.

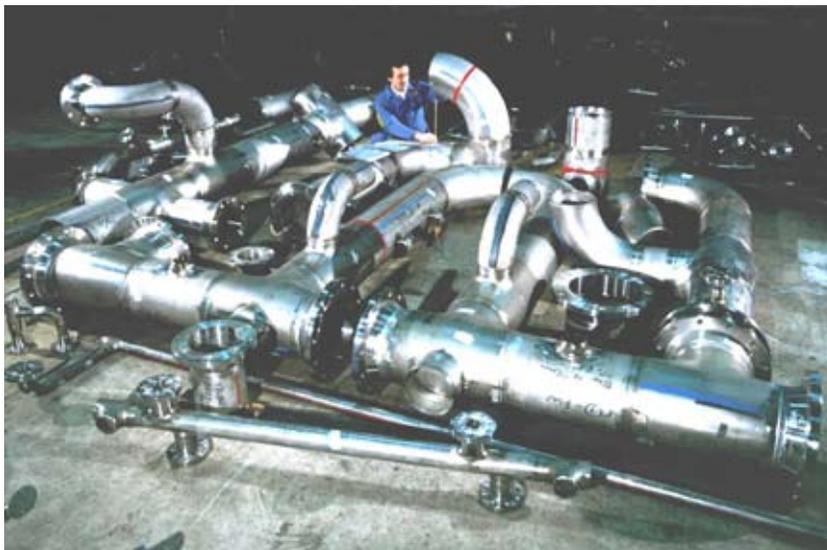


FIGURE 10 Spooling of the Zeron 100 seawater piping for the Saltire project.



FIGURE 11 Replacement Zeron 100 firewater system on Mobil Beryl 'A'.



FIGURE 12 Heat exchanger shell in Zeron 100 for the Fulmar project.

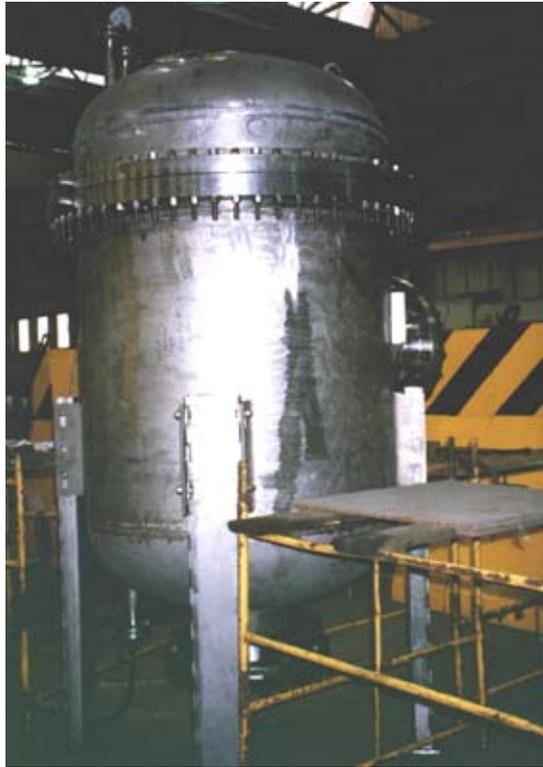


FIGURE 13 Seawater filter vessel in Zeron 100 for the BP Bruce project.



FIGURE 14 Zeron 100 riser clamp bolts for Balmoral.