REPORT

THE CORROSION OF ZERON 100 IN OIL AND GAS PRODUCTION ENVIRONMENTS.

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SUMMARY

This report summarises the corrosion test data and service experience for Zeron 100 in oil and gas production environments. The data shows that Zeron 100 can be used in a wide range of moderately sour and medium sour environments. The use of Zeron 100 is often more cost effective than competing nickel-base alloys, as well as other stainless steels.

1.0 INTRODUCTION

In the oil and gas industry there is no single corrosive fluid, but a range of fluids which can vary in corrosivity. These are described in more detail in EFC Publication 17 [1] and only a brief summary will be given here. The production fluids for oil and/or gas usually contain water, which is what causes the corrosion. In addition, there are drilling muds, completion fluids, packer fluids, acidising fluids, injection waters etc. These fluids usually contain chlorides that can vary from a few hundred mg/L to 200,000 mg/L. In addition there are often acid gases, such as CO_2 and H_2S, which reduce pH, and typical pH's range from 3 to 6 at temperature and pressure. Temperatures can also vary widely from only a little above ambient to in excess of 200°C (392°F). From this it can be seen that the corrosivity of oil and gas industry fluids can vary enormously.

There are some important factors to recognise in the oil and gas industry. The first is that retrofits are usually extremely expensive, and so it pays to get it right first time. Hence, the selection of corrosion resistant alloys (CRA) can be very cost effective and life cycle cost analyses frequently show the use of CRA's to be the most cost effective option over the life of the project.

In sour fluids it is not just general corrosion which must be considered, but also the possibility of pitting and, especially, sulphide stress corrosion cracking (SSCC), often called just sulphide stress cracking (SSC). Some guidelines about the limits of some materials are given in the standard ISO 15156 (formerly NACE MR 0175)[2]. If the service conditions are not covered by this document then testing to the guidelines in EFC 17 [1] is recommended.

This document principally examines the performance of Zeron 100 superduplex stainless steel compared with competing materials, in produced fluids.

2.0 ALLOYS

Zeron 100 is a superduplex stainless steel, combining high strength with corrosion resistance . The alloy was invented by RA Materials (formerly Weir Materials) in the 1980's and it has been used in oil and gas production environments since 1991. Table 1 shows the nominal composition of the alloy compared with 22% Cr duplex (UNS S31803) and 6% Mo austenitic (UNS S31254). Table 2 shows the minimum mechanical properties of the three alloys, and it is clear that Zeron 100 is stronger than both 6% Mo austenitic and 22% Cr duplex. Production environments frequently operate at temperatures over 100°C and at high pressures (up to 300 bar or more). The mechanical properties of Zeron 100 decrease less with temperature than both 22% Cr duplex and 6% Mo austenitic. This is demonstrated by the design stresses for the three alloys for piping to ASME B31.3, shown in Table 3. The values for 6% Mo austenitic were calculated from the B31.3 design rules for austenitic stainless steels. The data clearly show the potential for wall thickness reductions with Zeron 100. This reduces material costs, fabrication costs and reduces weight. The weight reductions possible with Zeron 100 have led to its selection for manifolds and process pipework on offshore platforms not only in preference to 6% Mo austenitic alloys but also in preference to 22% Cr duplex.

3.0 WATER COMPOSITION

If a gas field does not produce formation water, then only condensed water will be present. This will contain little chloride, but it will dissolve CO_2 readily and hence the pH will be low, typically 3.0 to 4.0. Chlorides will be very low and EFC17 [1] recommends testing corrosion resistant alloys in solutions with 1,000 mg/L chloride for this service.

When an oil or gas field produces water ("formation water") the chlorides can vary from ~ 5,000 to 200,000 mg/L but these waters usually also contain bicarbonate ions. This has the effect of buffering the pH, which is then usually in the range 4.0 to 6.0, at temperature and pressure.

Where seawater is injected to maintain well pressure, it can break through into the production fluids. The chlorides in sea water are about 19,000 mg/L, and these will mix with those in the formation water, either raising or lowering the average chloride content. However, there are also bicarbonate ions present in sea water (~ 130 mg/L) which will produce pH's above 4, as for formation waters. Hence the conditions will not necessarily be very aggressive.

Corrosion testing is often done at low pH, 3 to 3.5, with high chlorides, and if an alloy passes this test it will be suitable for either service[1]. However, it has been shown that the resistance to sulphide stress corrosion cracking of stainless steels increases as the chloride content decreases and as the pH increases. Hence, testing in an environment representative of service with either low chloride or high pH may show an alloy to be adequate even when it fails a test at low pH and high chlorides.

4.0 CORROSION

4.1 Sweet Environments

At higher temperatures and pressures, corrosion by moist CO_2 is difficult to control in carbon steels, and duplex stainless steels have traditionally been used. Both 22% Cr and Zeron 100 have excellent resistance to CO_2. Welded U-bend specimens of Zeron 100 have been tested to ASTM G30 in 9% sodium chloride solution saturated with CO_2 at 80°C. No cracking or pitting was observed after 30 days exposure.

The high strength of Zeron 100 compared with 22% Cr duplex has led to its selection for some sweet production systems because of the weight savings possible. Such a case was the Phillips Embla platform in the Norwegian sector of the North Sea. The operating temperature is 150°C at 938 bar wellhead pressure.

4.2 Sour Environments

Francis [3,4] reviewed the sulphide stress corrosion cracking resistance of duplex stainless steels and showed that susceptibility is strongly dependent on temperature.

It has been recognised for some time that the temperature for least resistance to cracking varies from alloy group to alloy group. For duplex stainless steels the critical temperature is generally found to lie in the range 70° to 110°C. Barteri [5] reviewed data from a number of sources for solution annealed and cold worked duplex alloys. The tests were not all at the same pH and chloride concentration.

Figure 1 shows data for both 22% Cr and 25% Cr alloys in the solution annealed or lightly cold worked condition (~ 825 MPa [125 ksi] 0.2% proof stress). Sulphide cracking occurs above the line for each alloy. The curves either show a minimum in the range 70° to 100℃ or they are approximately flat. Cottis & Newman [6] have suggested that this variability is caused by differences in the test methods and environmental conditions used by the different laboratories.

The results (Figure 2) for heavily cold worked material (≥ 960 MPa [140 ksi] 0.2% proof stress) show that the resistance to SSCC decreases slightly as the temperature increases, with no minimum at intermediate temperatures. The results also show that for 25% Cr duplex alloys the heavily cold worked material is considerably more susceptible to SSCC than the solution annealed alloy.

Thus it is clear that the environmental variable of temperature is closely linked to a metallurgical variable ie. cold work.

Topsides piping in Zeron 100 is in the solution annealed condition, while Zeron 100 bolting is either solution annealed or lightly cold worked (0.2% proof stress ≥ 725 MPa [105 ksi]). Zeron 100 wireline is heavily cold worked and its performance in sour brines is the subject of a separate publication.

Zeron 100 (UNS S32760) is listed in ISO 15156-3 as follows:-

a) In the solution annealed condition, both wrought and cast Zeron 100 can be used up to 0.2 bar (20/kPa) H_2S up to 232°C (Table A.24)

b) In the cold worked condition, Zeron 100 can be used up to 0.2 bar (20kPa) H_2S with up to 120,000 mg/L chloride, with a maximum hardness of 36 HRC (Table A.25).

These limits take no account of the higher H_2S levels that can be tolerated with lower chloride contents and higher pH values. However, ISO 15156 permits the use of testing to prove acceptability of a material outside the limits stated above (ISO 15156-3, 6.1).

Over the fifteen years since the commercial introduction of wrought Zeron 100, a great deal of SSCC data has been generated. Some of this is internal RA Materials data, some is by independent test houses and some is by individual oil companies. It is all collected together in Figure 3 for pH's in the range 3.3 to 3.6. The results clearly show that Zeron 100 can be used to much higher H_2S limits than specified in ISO 15156, at lower chloride contents. All the data points were derived in the temperature range 80° to 100℃ i.e. the most susceptible temperature for SSCC. Corrosion testing has been used to justify the use of Zeron 100 outside the limits of ISO 15156 in two major North Sea projects.

Figure 4 shows RA Materials data with that of Barteri el al. [7] at pH4.5. The data show that as the pH increases, Zeron 100 can tolerate even greater H_2S contents without suffering SSCC. This data has been combined into the design curves shown in Figure 5. These show that the H_2S limit increases by about half an order of magnitude for each order of magnitude decrease in the chloride content. Also the H_2S limit increases by about 50% for an increase in pH from ~ 3.5 to ~ 4.5. This means that at moderate chloride concentrations Zeron 100 is a cost effective alternative to nickel alloys such as alloy 825 and alloy 28.

Extensive testing has also been carried out on Zeron 100 welds, made with Zeron 100X consumables and tested in the as-welded condition. None of these tests has shown the welds to be more susceptible to SSCC than the parent metal. Tables 4 & 5 show some test data from Zeron 100 welds [8]. Work at TWI has confirmed these findings [9].

A recent development is the opening of hot, deep wells. These operate at temperatures from ~ 150°C to over 200°C and often contain very high chloride concentrations (>150,000 mg/l). However, the produced waters also contain bicarbonate so that the pH is greater than 4 and can be much greater. RA Materials carried out a 30 day autoclave test to EFC 17[1] in a simulated brine from a hot deep well. Both cast and wrought Zeron 100 were tested as C-rings stressed to 100% of the actual 0.2% proof stress. The total chloride content was 175,000 mg/l with 250 mg/l sodium bicarbonate. The atmosphere was 40 bar (4 MPa) CO_2 and 0.1 bar (10 kPa) H_2S at a temperature of 190°C. There was no cracking or localised corrosion seen on any of the test samples.

4.3 Pitting Corrosion

Tests have been conducted on ASTM G30 U-bend specimens of three cold worked alloys, 22% Cr duplex, a low alloy 25% Cr duplex (PREN 37) and Zeron 100 [10]. All the materials were nominally cold worked to ~ 110 ksi (750 MPa) yield strength and the specimens were stressed to about 100% of the actual yield strength. The test solution was a synthetic downhole brine containing 46,000 mg/l chloride, 93 bar CO_2 and three levels of H_2S; 0.125, 0.25 and 0.375 bar. All the tests were conducted for 30 days at 121°C.

Pitting was only observed at the highest H_2S level (0.375 bar) as shown in Table 6. Deep pitting occurred on both 22% Cr specimens and on one of the 25% Cr specimens. There were 3 shallow pits on the other 25% Cr sample. One of the Zeron 100 samples had no pitting and there were 3 shallow pits in the remaining sample. This clearly shows increasing resistance to pitting as the PREN of the alloy increased. These results demonstrate the superior resistance to pitting of Zeron 100 compared to lower alloy duplex stainless steels in sour environments.

Autoclave tests were carried out in the USA for a Middle Eastern oil company on Zeron 100. The conditions were:-

CO_2	-	41.4 bar
H_2S	-	10.3 bar
Temp	-	166°C
Chloride	-	1,000 mg/l
	-	10,000 mg/l
	-	100,000 mg/l

The pH was not reported. No stress corrosion cracking was seen on any specimen, but pitting occurred on the samples exposed with 100,000 mg/l chloride.

These results demonstrate the high resistance of Zeron 100 to pitting in sour brines.

4.4 **Erosion**

Oil and gas production environments can often include sand in addition to water, oil and gas. The presence of the sand could lead to serious erosion corrosion problems at higher velocities. While no laboratory research programme has addressed this issue there is some service data available. Zeron 100 has been in service in the environment shown below since 1991, although sand production ceased after the first two years.

CO_2	-	2.1 bar
H_2S	-	0.01 bar
Temperature	-	110°C
Sand	-	3 lbs/1000 bbls
Velocity	-	30 m/sec

The sand content of 3 lbs/1000 bbls is typical for the North Sea and is approximately equal to 10 mg/L. No problems have been reported in this environment. Inspection after four years showed the manifold, welds and pipework to be in excellent condition.

4.5 **External Corrosion**

There have been one or two instances of external chloride stress corrosion cracking (SCC) of hot process pipes in duplex and superduplex stainless steel. These have either been where seawater has become trapped under insulation or seawater has dripped onto a hot pipe. Research at the NPL, UK has shown that cracking can occur with all duplex stainless steels at temperatures greater than 70°C when stressed to 90% of the 0.2% proof stress. There is no risk of external chloride SCC up to 100°C when stressed to 70% of the 0.2% proof stress. However, the seawater ingress rate is critical as the metal surface must stay wet, but the solution must concentrate. If the seawater ingress rate is too low the metal surface dries out, while if the ingress rate is too high the seawater cannot concentrate. Hence, on a bare pipe, the seawater drip rate is critical.

In practice, the risk of cracking of bare pipes has been minimised by the use of coatings. At low temperatures this is usually done with some form of paint, while at higher temperatures thermally sprayed aluminium has been used. The Zeron 100 process pipes on the Phillips Embla platform operate at ~ 150°C, they were sprayed with aluminium in the critical areas, and no problems have occurred.

When the pipes are insulated, it is best to use non water-absorbent insulation with drainage provision at the bottom. In high risk areas the pipe can be painted or thermally sprayed with aluminium before the insulation is applied. This has also been successful with Zeron 100 in the North Sea.

When hot process pipes are used subsea it is customary to apply cathodic protection to prevent localised corrosion at coating holidays. Although a potential of - 600 mV SCE will be sufficient to protect duplex stainless steel subsea, it is more common for potentials to be ~ -1V SCE because carbon steel is also being protected. Under these conditions hydrogen can enter the metal and hydrogen embrittlement failures have occurred in a few instances. All of these have been where components were accidentally stressed well above design limits. The EEMUA 194 document, Subsea Materials Guide[11], recommends the following to avoid the risk of hydrogen embrittlement with cathodically protected duplex stainless steels.

"3. SUMMARY AND RECOMMENDATIONS

There are a large number of duplex systems installed subsea, apparently operating without problems. The main concern is with hydrogen embrittlement. The following measures are currently believed to represent best practice and should minimise the risk of cracking in service.

* Ensure that all components are supplied in the solution treated and water quenched condition, have a normal grain size and are free from precipitates.

* Ensure that all forged components have a grain orientation parallel to the pipe axis and not in the through thickness direction.

* Ensure that fabrication stresses are minimised and that pipes are not cold pulled into position to align them. Shimming of pipes and fittings should be considered to facilitate good fit-up.

* Ensure that all welds are made to qualified procedures that result in well-balanced ferrite-austenite phases across the weld zone. Autogenous welds should be avoided unless the composition of the components has been modified to ensure such a balance is achieved.

* Ensure that there are no load cases associated with subsea installation, testing, commissioning, operation (including thermal loads), future tie-ins etc which will generate stresses on the outside surfaces of the material exceeding those stresses generated during hydrotesting. This will help ensure any benefits from stress shakedown are maintained.

* Consider the use of high integrity, full life coating systems, particularly at areas of high stress concentration, to shield the material from the CP system.

* Consider the use of low voltage CP systems.

* Where practicable, consider electrical isolation and protection by iron anodes".

5.0 SERVICE EXPERIENCE

Zeron 100 has been in use in sour production environments since 1983 as castings and since 1991 as a wrought product. The alloy has been used for piping, vessels, pumps, valves and manifolds, both subsea and topsides. A large number of forgings and heavy wall pipe and fittings have been supplied for subsea wellhead hubs and flow loops. Table 7 shows a selection of projects utilising Zeron 100 components, while Table 8 shows some of the environments experienced in these projects. The list is by no means exhaustive. It is important to realise that Zeron 100 can be used outside the limits of use in ISO 15156/NACE MR0175, because of the extensive tests database that RA Materials holds on the alloy.

Figure 6 shows the Zeron 100 header and pipework on the Phillips Embla platform, while Figure 7 shows a heat exchanger for the Maersk, Harald West project. This was a high pressure (200 bar) gas cooler with the gas (200°C) inside the tubes and seawater on the outside, as the coolant. Zeron 100 was chosen for its high strength and its resistance to corrosion by both seawater and the production fluids.

Figure 8 shows the production and test manifolds for the Statoil Veslefrikk project. These were manufactured from a series of unequal tees. Figure 9 shows part of the manifold for Marathon East Brae, which was manufactured in sections by hot isostatic pressing. This produced considerable savings in both welding time and cost for the 63mm thick manifold.

6.0 CONCLUSIONS

The data and service experience show that Zeron 100 has a very high resistance to sulphide stress corrosion cracking, pitting and erosion corrosion in sour production environments. The high strength of Zeron 100 means that it can offer substantial reductions in wall thickness, cost and weight compared with both 22% Cr duplex and 6% Mo austenitic alloys.

7.0 REFERENCES

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FIGURE 1 The effect of temperature on the sulphide SCC resistance of duplex stainless steels (solution annealed and lightly cold worked) [Ref 5]

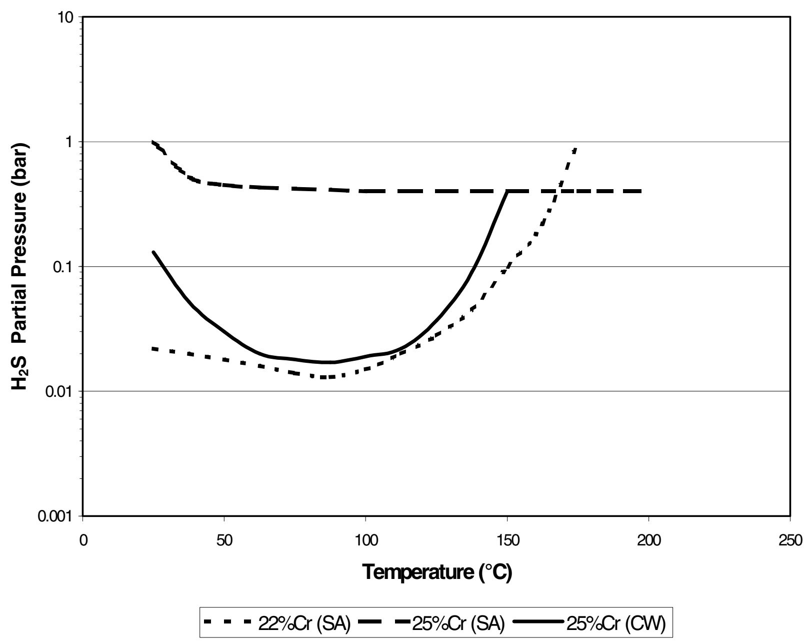


FIGURE 2 Effect of temperature on the sulphide SCC resistance of heavily cold worked duplex stainless steels [Ref 5]

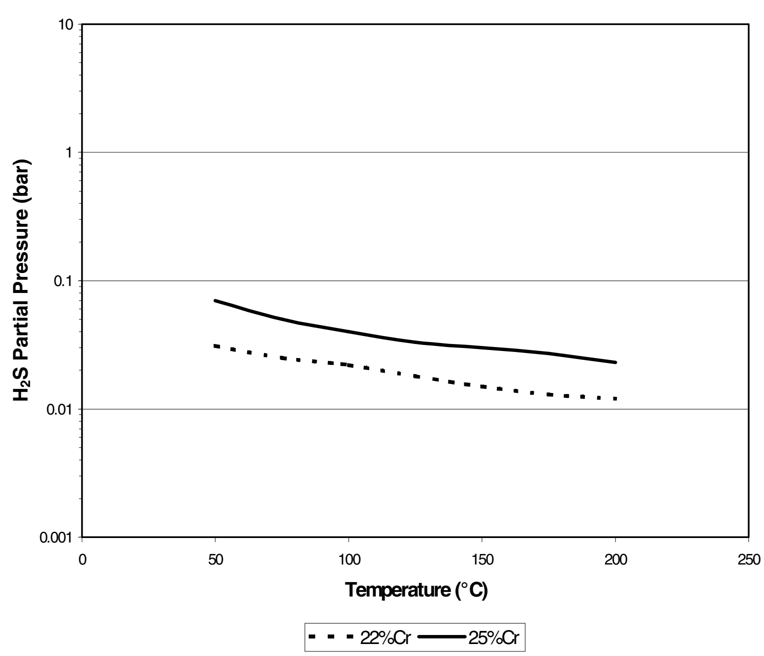


FIGURE 3 Effect of chloride on sulphide SCC of Zeron 100 at pH3.5

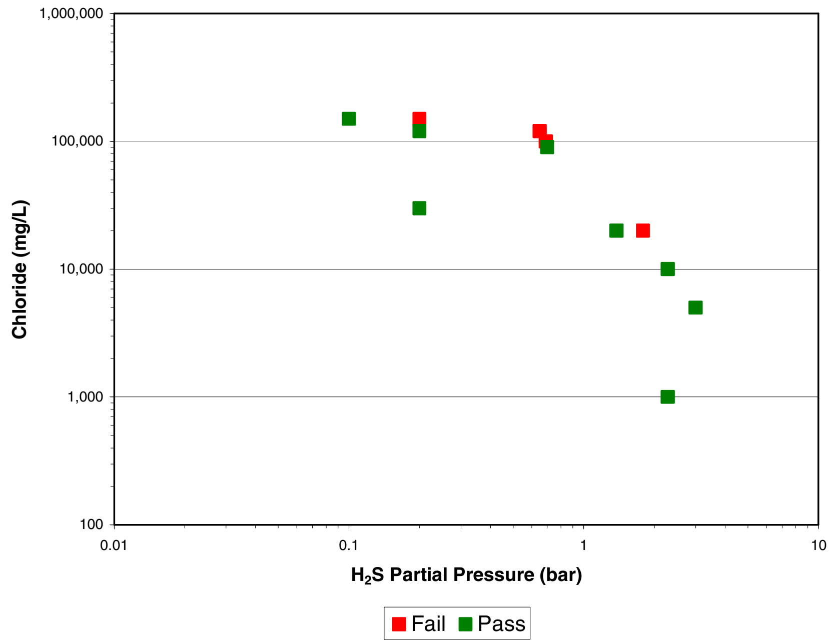


FIGURE 4 Effect of chloride on sulphide SCC of Zeron 100 at pH4.5

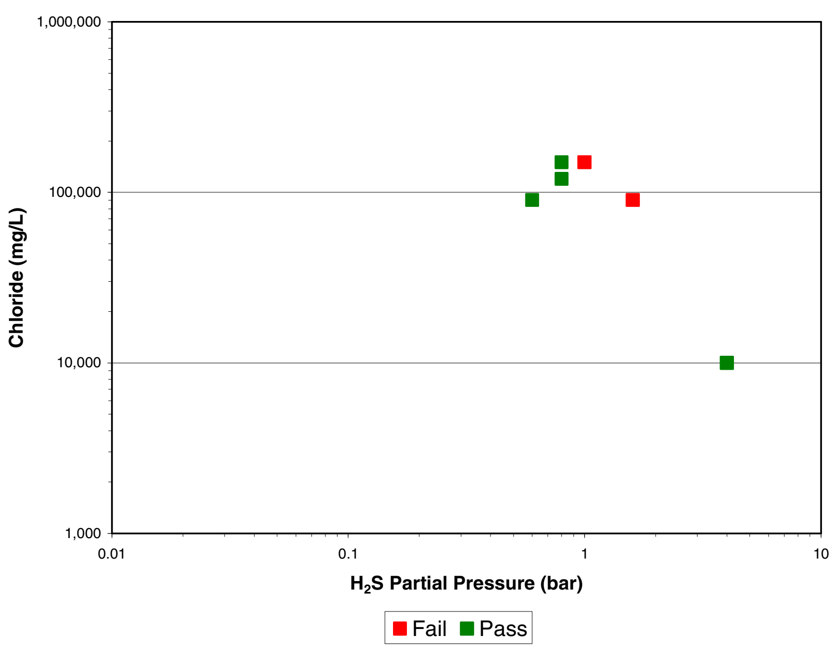
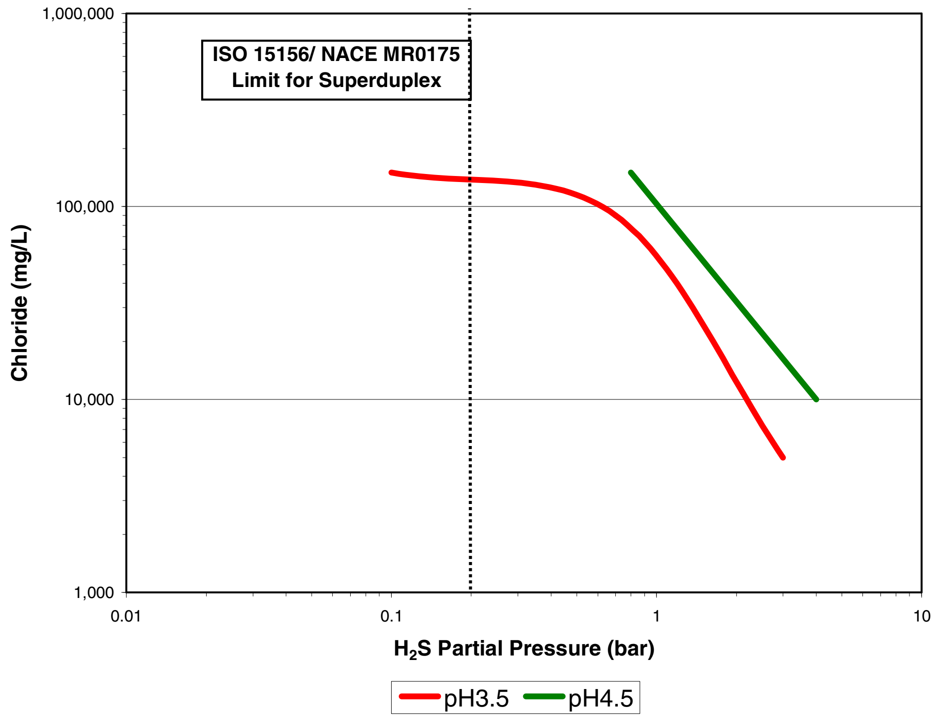


FIGURE 5 Limits of use for Zeron 100 in sour brines



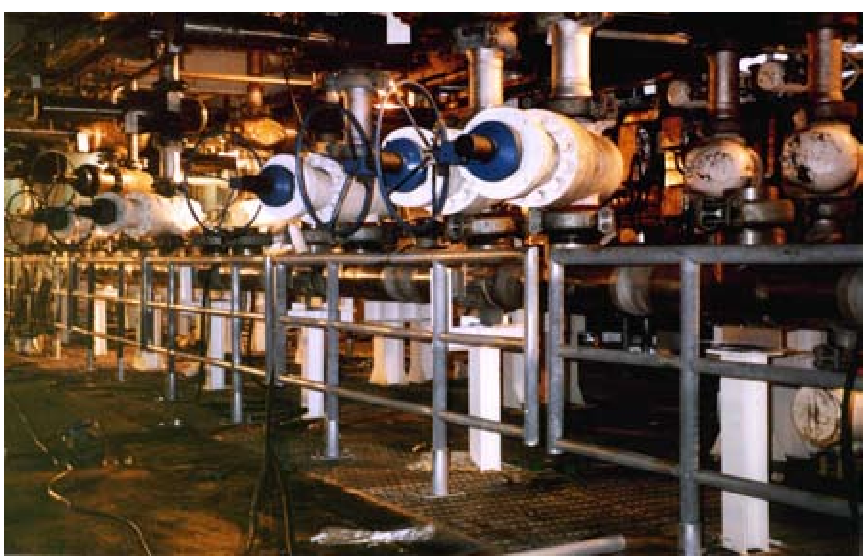


FIGURE 6 Header and pipework in Zeron 100 on the Phillips Embla Platform

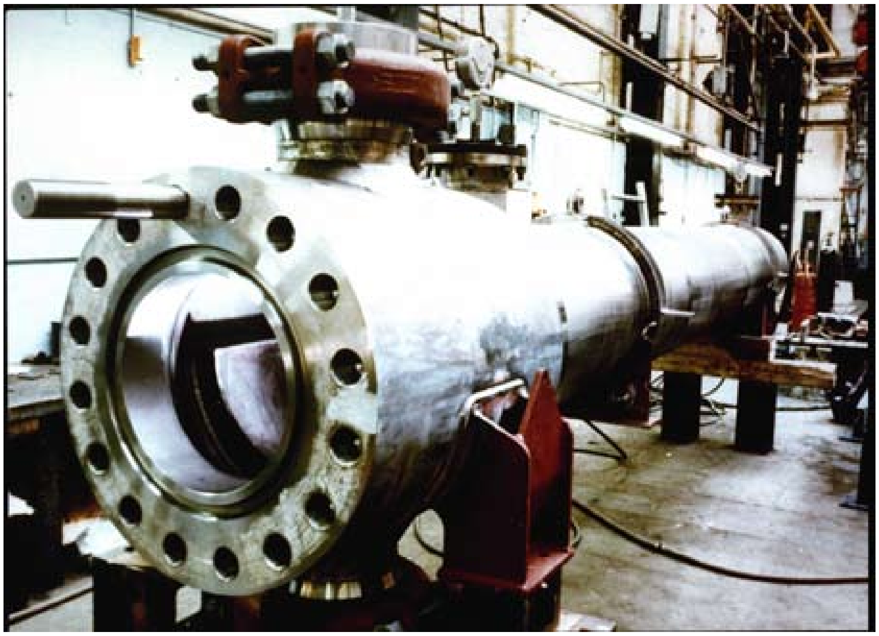


FIGURE 7 Heat exchanger supplied to Maersk Harald West project

FIGURE 8 Production and test manifolds for Statoil Veslefrikk

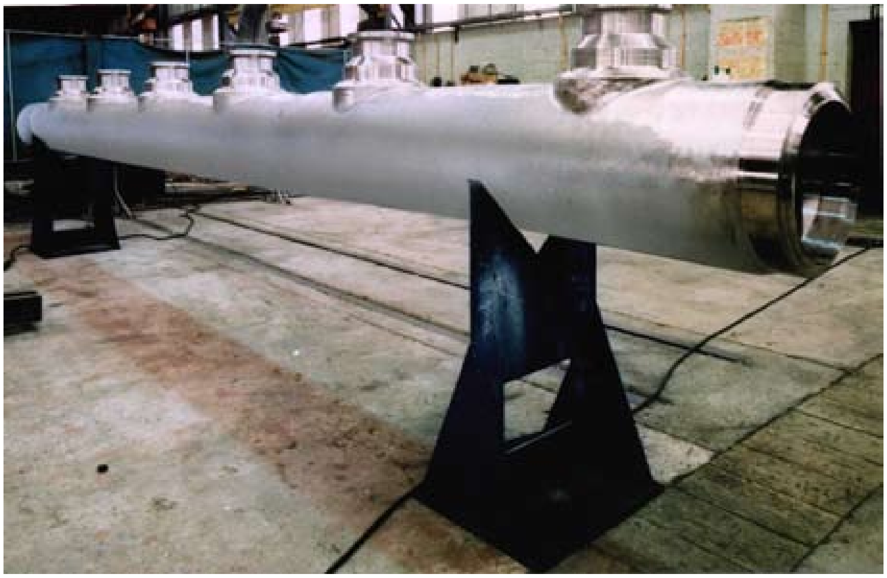


FIGURE 9 Section of Marathon East Brae manifold during Fabrication

TABLE 1 Nominal composition and mechanical properties of some stainless steels.

Alloy	Nominal Composition (wt %)							PREN*
	Fe	Cr	Ni	Mo	N	Cu	W	
22%Cr duplex (S31803)	bal	22	5	3	0.15	-	-	35
6%Mo aust. (S31254)	bal	20	18	6	0.2	0.8	-	43
ZERON 100	bal	25	7	3.5	0.25	0.7	0.7	>41

bal = balance
*PREN = %Cr + 3.3 (% Mo + 0.5x % W) + 16 x % N

TABLE 2 The mechanical properties of some common stainless steels.

Alloy	0.2% Proof Stress (MPa)	UTS (MPa)	Elongation (%)
22%Cr duplex (S31803)	450	680	25
6%Mo aust (S31254)	300	650	35
ZERON 100	550	750	25

TABLE 3 Design stresses for some stainless steels for piping to ASME B31.3.

ALLOY	DESIGN STRESS (MPa)			
	25°C	100°C	150°C	200°C
22%Cr duplex (S31803)	207	206	199	193
6%Mo Aust (S31254)	200	200	190	176
ZERON 100	250	246	236	234

TABLE 4 ASTM G30 U-bend Tests of Welded Zeron 100 (Ref 8)

Chloride Conc. (mg/l)	CO_2 Pressure (bar)	H_2S Pressure (bar)	Temp. (°C)
0	5.8	0.05	110
46000	10.5	0.05	103
46000	5.2	0.25	103

RESULTS

No Pitting
No Cracking

TABLE 5 Sulphide stress corrosion cracking tests on cross-weld tensiles of Zeron 100 (Ref 8)

ENVIRONMENT	DURATION HOURS	APPLIED STRESS (MPa)	RESULT
NACE TM-01-77 16 Bar H_2S 90°C	720	450	NO FAILURE
NACE TM-01-77 20 Bar CO_2 5 Bar H_2S 90°C	720	450	NO FAILURE
NACE TM-01-77 20 Bar CO_2 5 Bar H_2S 120°C	720	450	NO FAILURE

TABLE 6 Results of pitting tests on U-bend specimens of cold worked (~110ksi 0.2% proof stress) duplex stainless steels (Ref 10) (93 bar CO_2; 46,000mg/l chloride; 121°C)

ALLOY	H_2S PRESSURE (bar)		
	0.125	**0.25**	**0.375**
22%Cr	No Pits	No Pits	Deep Pitting/ Deep Pitting
25%Cr	No Pits	No Pits	Deep Pitting/ 3 Shallow Pits
ZERON 100	No Pits	No Pits	No Pits/ 3 Shallow Pits

TABLE 7 Some projects utilising ZERON 100 in oil and gas production systems

CLIENT	PROJECT	CONTRACTOR	SYSTEM TYPE
Statoil	Veslefrikk	Moss Rossenburg	Process Pipework
Occidental	Claymore		Flowline
British Petroleum	West sole		Flowline
Marathon Oil	Brae Central		Production Riser Pipe Components
Occidental	Piper Bravo	Brown & Root Vickers	Pipework System
Marathon Oil	East Brae	Matthew Hall	10,000 lb Gas Compression System
Statoil	Veslefrikk		Flowline
Occidental	Saltire	Brown & Root Vickers	Process Pipework System
Amerada Hess	Scott	Foster Wheeler	Process Pipework System
Phillips Petroleum	Embla		Process Pipework System
Statoil	Veslefrikk	Moss Rossenburg	Process Manifold
Amerada Hess	Scott	Foster Wheeler	Process Manifold
Marathon Oil	East Brae		Process Manifold
O.G.P.C.	Diyab Phase 2	Global	Hook Ups
Arco	Prudhoe Bay Drillsite 9		Linepipe
Q.G.P.C.	Diyab Phase 3	Global	Hook Ups
Shell	Nelson	Consafe/J P Kenny	Subsea Manifold
Phillips Petroleum	Ann	J P Kenny	Process Manifold
Phillips Petroleum	J Block	Kvaerner H&G	Process Manifold
Elf	Lillle Frigg	National Oilwell	Prod. Flowloops

TABLE 8 Some service environments being experienced by Zeron 100

PRESSURE (bar)			Temp. (°C)	Chloride (mg/L)
CO_2	H_2S	TOTAL		
2.1	0.02	31	135	80,000
6.0	0.012	240	110	10,000
1.3	0.01	138	80	***
10	0.3	103	107	16,000
7.5	0.14	225	104	20,000
25	0.2	102	102	30,000
23	0.062	300	108	19,000
4.3	0.22	145	110	120,000

*** not known