Experiences with superduplex stainless steel in seawater

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Introduction

The authors' company has been heavily involved with the offshore oil and gas industry since the development of the North Sea oil and gas fields in the 1970's. In particular there was a requirement for seawater injection pumps to maintain production rates. As the fields became larger and the pressures higher, austenitic stainless steel pumps became large and heavy and duplex stainless steels offered weight saving due to their higher strength. However, the 25Cr duplex stainless steels available in the 1970's did not meet all the requirements in terms of strength and corrosion resistance. An alloy development programme resulted in a cast alloy named ZERON 100 (1), the first of the superduplex stainless steels[1]. This alloy became very successful for injection, seawater lift and firewater pumps and this created a demand for a wrought counterpart. The authors' company developed production routes for all the commonly used wrought product forms (plates, pipes, forgings etc.) and the wrought version first entered service in the late 1980's. UNS numbers were ultimately obtained for the wrought (S32760) and cast (J93380) versions and the alloy was submitted for entry in the appropriate ASTM standards. It is also listed in the vessels codes ASME VIII division I (cast and wrought) and III (cast) and ASME B31.3 (wrought) for pipes. Zeron 100 has become widely used in many industries in addition to the oil and gas sector. Zeron 100 has been in service in seawater for up to 16 years, with few reported problems. This paper discusses these problems and shows how combining these problems with laboratory data have enabled the limits of use to be more accurately defined.

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The alloy

The compositions of the cast and wrought versions of the Zeron 100 are shown in Table 1. The alloys are made to give a 50/50 ferrite/austenite microstructure, which combines high strength with corrosion resistance. The additions of chromium, molybdenum and nitrogen give good resistance to localized attack by chlorides. Tungsten has a similar effect to molybdenum, while copper improves the corrosion resistance in sulphuric acid. Table 2 shows the mechanical properties of the alloy compared with some other common stainless steels. The use of the high strength results in reductions in wall thickness that reduces not only materials cost, but also fabrication time and costs.

Applications

Pumps

In the North Sea, nickel aluminium bronze (NAB) was originally used for seawater lift and firewater pumps, but there have been severe corrosion problems on some platforms, which has lead to replacement by superduplex stainless steel. The main corrosion problem with NAB has been severe pitting by sulphides during idle time, although erosion corrosion with high chlorine dosing has also been a problem.

The first Zeron 100 injection pumps entered service in 1982 and are still working well after 20 years. The first seawater lift pumps were installed on a Shell platform in the North Sea in 1986. Most of the injection pumps in the North Sea are now superduplex stainless steel and it is also the preferred alloy for seawater lift and firewater pumps. This is because the alloy gives high reliability with minimum maintenance. Figure 1 shows one of several large seawater circulation pumps supplied to BOC Cantarell, where the seawater also contains substantial suspended solids.

In the Middle East a common combi-

ALLOY	0.2% PROOF STRESS (MPa)	TENSILE STRENGTH (MPa)	ELONGATION (%)
Zeron 100 (cast)	450	700	25
Zeron 100 (wrought)	550	750	25
316L	213	500	45
6 Mo Aust	300	650	35

Table 2.
Minimum mechanical properties of some common stainless steels.

FORM	UNS No.	NOMINAL COMPOSITION (wt%) Fe	C	Cr	Ni	Mo	Cu	W	N
Cast	J93380	bal	0.02	25	8	3.5	0.7	0.7	0.25
Wrought	S32760	bal	0.02	25	7	3.5	0.7	0.7	0.25

Table 1.
Nominal composition of Zeron 100 superduplex stainless steel.

Figure 1. Zeron 100 seawater pump supplied to BOC to handle seawater with a high solids burden (up to 50,000mg/l)

Figure 2. Zeron 100 fasteners and clamps used as part of a buoyancy system on oilfield riser pipes.

nation for seawater pumps has been an austenitic cast iron case with a 316L or 25Cr duplex stainless steel impeller. There have been a number of failures of austenitic cast iron cases by stress corrosion cracking, and some companies are now specifying only the more SCC resistant superduplex stainless steel for all the components in such pumps.

Piping

The authors' company supplied the first superduplex stainless steel offshore cooling system to Amerada Hess (Table 3) in 1989 and it is still in service and has proved extremely reliable. Table 3 shows some of the applications for Zeron 100 in seawater service since that time. These show the widespread use of Zeron 100 by major oil and gas operators and engineering design contractors. The table also shows that the alloy is also now widely accepted for piping in reverse osmosis desalination plants. Because the alloy is available in all product forms, it is also used for valves, flanges and bolting. Mounting brackets and bolts in Zeron 100 are widely used in dockyards (e.g. Devonport, UK) and in the seawater intakes of multi-stage flash desalination plants in the Arabian Gulf (e.g. Jebel Ali G, Dubai).

CLIENT	CONTRACTOR	PROJECT	APPLICATION
Amerada Hess	Brown & Root	Ivanhoe Rob Roy	Seawater Systems
Mobil	Davy	Beryl A	Firewater
British Gas	Global	Morecambe Bay	Seawater Discharge
BP	Brown & Root	Bruce	Seawater Firewater
Amerada Hess	Foster Wheeler	Scott	Seawater System
GSPC	Global Eng	Dipah	Hook-up System
Hamilton Oil	Brown & Root	Liverpool Bay	Seawater Firewater
EE Caledonia	Brown & Root	Piper Bravo	Seawater Firewater
ONGC	Hyundai	Neelam	Column Pipes
Johnston Hunt	–	Forth	Heat Exchanger
Maersk	–	Harald West	Heat Exchanger
ADP	Wim Voorbij	Tiffany	RO Sulphate Removal
Ministry of Environment (Spain)	FCC/SPA	Adeje-Arona	RO Plant
Tampa Bay Desalination	–	Tampa Bay	RO Plant
BOC	OEL Teknik	Carrerd	Heat Exchangers

Table 3.
Some applications for Zeron 100 in seawater service.

PROBLEMS

Galvanic corrosion

When high alloy stainless steels were first used in the North Sea there were a number of corrosion problems due to galvanic corrosion. Many of these manifest themselves as crevice corrosion. One of these involved graphite loaded gaskets. Kain[2] carried out tests on a range of gaskets, including graphite loaded ones, and found crevice corrosion similar to that seen with PTFE gaskets. However, Rogne and Drugli[3] showed that the severity of crevice corrosion with a gasket depends on its ability to absorb water. Synthetic fibre gaskets absorb a lot of water and dilute the strong crevice solution, while PTFE gaskets absorb no water and are more likely to cause crevice corrosion. Rogne et al[3] also pointed out that graphite only caused a galvanic problem when the covering of the graphite is damaged, exposing the graphite to water. Unfortunately this is an occurrence that is frequent on offshore platforms. Figure 3 shows crevice corrosion of a Zeron 100 flange in contact with a graphite gasket in service. Turnbull[4] showed why graphite coupled to high alloy stainless steel would be detrimental in chlorinated seawater but not in natural seawater. Because of this graphite gaskets are now banned by many oil companies[5] and synthetic fibre gaskets are preferred for low pressure (10 bar) seawater system[5].
Leaks have also occurred with Ni-Cu alloy 400 (UNS N04400) spiral wound gaskets. High alloy stainless steels are cathodic to alloy 400 and stimulate rapid corrosion of the Ni-Cu alloy in chlorinated seawater, leading to leakage. Zeron 100 belongs to a family of high alloy materials that can be safely connected together[5]. There are superduplex stainless steel, superaustenitic stainless steel (6 Mo), titanium, alloy 625 (N06625), alloy C-276 (N10276) and other nickel - chromium - molybdenum alloys where Mo>7%. There have also been galvanic corrosion problems with superduplex piping systems fitted with NAB valves. These corrode rapidly coupled to high alloy stainless steel and closing them becomes a problem. These failures and the solution (to use superduplex valves) were explained by Francis[6].

Crevice corrosion

No crevice corrosion has been seen in any Zeron 100 system supplied by the authors' company, and these systems operate up to 40°C discharge temperature. This excludes the galvanic corrosion problems discussed above. Crevice corrosion problems with 6Mo austenitic stainless steel have been reported at 30° to 35°C[7,8], while the experience with superduplex stainless steel has been good[9]. There has been some crevice corrosion on Zeron 100

Figure 3.
Corrosion of a Zeron 100 flange caused by the use of a graphite-filled gasket.

flanges that reached temperatures of 60°C or more during dewaxing of heat exchangers offshore. This temperature is above that recommended for superduplex stainless steels in seawater. Despite this the operators who have experienced this corrosion report that repassivation occurs readily on restoring normal operating conditions and actual leaks are rare.

Both superduplex and superaustenitic stainless steels have shown a small amount of crevice corrosion in laboratory exposure tests[10]. At first sight this appears to contradict the service experience, but the reason is probably to do with the crevice formers. In a seawater cooling system the crevices are mostly flanges with synthetic fibre gaskets, while exposure tests usually use INCO type crevice washers in PTFE or a similar polymer. As explained above, these polymers absorb little or no water and so create a more severe crevice than fibre gaskets, which do absorb water[3].

Welds

Severe corrosion occurred at the welds in the firewater system on the Goodwyn 'A' platform off the north west coast of Australia. These were initially due to poor quality welding that resulted in the formation of large quantities of sigma phase (>10%). This phase produces a large, local reduction in corrosion resistance and the problem was largely solved by qualifying new weld procedures to avoid sigma formation. Since that time there have been some additional problems on this platform with superduplex:

1. There have been a few failures of welds subsequently, but these are believed to be in areas exposed to direct strong sunlight, where pipe temperatures can reach ~70°C. Superduplex stainless steel is not generally suitable for use at these temperatures in seawater (see below).
2. There has been corrosion of flanges due to the use of alloy 400 spiral wound gaskets (see galvanic corrosion above).
3. Corrosion of sprinkler heads in the firewater system occurred soon after start-up. These were brass and the problem was corrected by fitting sprinklers in Zeron 100.
4. Corrosion of the threads of Zeron 100 sprinkler heads occurred in the accommodation module at ~20°C. This was caused by a depolarization of the cathodic reaction (reduction of dissolved oxygen) due to the presence of metallic copper. This had formed by the reduction of copper corrosion products from the previous brass sprinkler heads. This problem can be prevented by thorough cleaning to remove the copper deposits.

Temperature (C°)	Chlorine (mg/l)
10	200
20	5.0
30	1.0
40	0.7

Table 4.
Recommended maximum chlorine levels at different seawater temperatures.

Chlorine

All high alloy stainless steels suffer fouling in natural seawater. Hence, it is usual to chlorinate the seawater in a cooling system at the intake. The chlorine residual decreases through the system as the chlorine reacts with organic material in the seawater. In offshore cooling systems it is usual to measure the chlorine residual at the top of the pump column pipe or in the ring main close to the intake. The level is usually from 0.5 to 1.0 mg/l with 0.7 mg/l being typical.

When the Scott platform started up in 1993 there were seven leaks at welds after the heat exchangers. The seawater temperature was 43°C and the chlorine residual at this point was measured as 2 mg/l. This was far too high, and no further leaks occurred after the chlorine dosing was brought under proper control. There have been no further problems with the seawater system since that time.

The Scott failure and laboratory testing showed that the tolerable chlorine dose is a function of the seawater temperature. This data was combined to give the maximum safe chlorine levels shown in Table 4. This shows that in cold seawater alloy Z100 can tolerate high chlorine levels and this is borne out by our experiences with seawater lift pumps in the North Sea where strong hypochlorite has sometimes been injected directly into the pump suction intake and no corrosion has occurred.

Temperature

When high alloy stainless steels were first introduced, laboratory tests by Shell suggested that Zeron 100 would be OK up to at least 40°C in chlorinated seawater[11]. There are several installations in the North Sea where seawater temperatures after heat exchangers approach this (e.g. Scott ~ 38°C currently) as well as installations in the Arabian Gulf (Jebel Ali G ~ 40°C in summer), and no corrosion problems have occurred.

Shortly after start up of the Liverpool Bay platform, there were a few failures at welds immediately after three gas coolers. The seawater temperature was ~ 45°C and the chlorine concentration was ~ 0.5 mg/l. There were no failures further downstream, where the seawater temperature was below ~ 40°C. The failures were put down to the seawater temperature being above the design limit (40°C). However, leaks also occurred in other welds, exposed in hot dead legs or discharge lines that see intermittent high temperatures (~60°C) during de-waxing. All the replacement welds have had 100% radiography and portable arc monitoring system (PAMS) monitoring of the welding parameters. To date there have been no leaks in any of the replacement spools.

Similar leaks at welds have also been seen on the BP Bruce and ETAP platforms in areas that see intermittent high temperatures, above the recommended limit. All the operators seeing leaks in hot discharge lines said that once normal operating conditions were restored no further leaks occurred. This is believed to be due to the ability of Zeron 100 to repassivate readily when normal temperatures are restored. This was demonstrated in laboratory tests12, where Zeron 100 repassivated more readily than other superduplex and

superaustenitic stainless steels.
The Piper Bravo platform installed a superduplex stainless steel seawater cooling system, and the initial discharge temperature from three gas coolers was ~20°C for several months. The gas intake then increased and discharge temperatures rose to ~55°C. Concern was raised about corrosion, but after 2 years there were no leaks and the discharge temperature was further increased to 65°C. After a further 4 years there have still been no leaks. This demonstrates the advantage of a "soft" start up.
Laboratory tests13 showed that pickling welds increased the critical pitting temperature (CPT) in synthetic seawater at +600mV SCE by ~20°C. In piping, where pickling is not possible, a "soft" start up improves the corrosion resistance. A recommended procedure is:

1. Start in cold seawater for 2 days (min)
2. Run in cold, chlorinated seawater for 5 days (min)
3. Turn on heat exchangers.

N.B.The longer the start up, the better.

Hence it is possible to run superduplex seawater systems at temperatures above 40°C, provided appropriate precautions are taken.

Conclusions

1. Zeron 100 superduplex stainless steel 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.
2. Laboratory tests and service experience have enabled the safe chlorination/temperature limits to be determined.
3. A slow start up increases the performance of welds in seawater.
4. Trained and qualified welders 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. ◀

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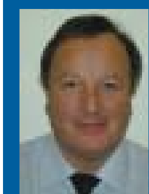
References

1. C.V. Roscoe and K. J. Gradwell, "All that Glisters is not Gold : The History and Development of Duplex Stainless Steels", Duplex Stainless Steels '86. The Hague, Holland. Oct.1986.
2. R.M Kain, Paper 702, Corrosion '98, San Diego, CA, USA. March 1998, NACE.
3. T. Rogne and J.M Drugli, Stainless Steel World '99 Conference, The Hague, Holland. Nov. 1999, page 527, published by KCI.
4. A. Turnbull, Corrosion 55, 2 (1999) 206.
5. R. Francis Galvanic Corrosion - A Practical Guide for Engineers. Published by NACE, 2001
6. R. Francis Brit. Corr. J. 34, 2 (1999) 139.
7. R. Lye, Paper No.2 Engineering Solutions to Industrial Corrosion Problems, June 1993. Sandefjord, Norway. Published by NACE.
8. O Strandmyr, "Seawater Materials: Norwegian Experience" 12th International Symposium on Corrosion and Materials Offshore, Stavanger, Norway, Jan 1999, NITO (Norwegian Society of Engineers).
9. S Shrive, "Seawater Materials: British Experience" ibid.
10. D.M. Aylor, R.A Hays, R.M Kain and R.J Ferrara Paper 329, Corrosion '99 San Antonio, TX, USA. April 1999. NACE.
11. P. Gallagher, A. Nieuwhof and R.J.M. Tausk, Marine Corrosion of Stainless Steels: Chlorination and Microbial Effects European Federation of Corrosion Publn. No. 10, Page 73, published by IOM.
12. R Francis, J. Irwin and G Byrne Brit. Corr. J. 30, 3 (1995) 237.
13. R Francis and G R Warburton, Paper 630 Corrosion 2000. San Antonio, TX, USA. March 2000. NACE.

About the author



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Dr. Byrne obtained his Ph.D. from the University of Sheffield, UK and joined CAPCIS, the industrial corrosion and protection arm of the University of Manchester Institute of Science and Technology, UK. He worked on a variety of corrosion problems from several different sectors, including the marine and oil and gas industries. In 1988 he joined Weir Materials and Foundries as Sales and Technical Director and since that time he has directed the marketing of the company's flagship alloy, Zeron 100, into a wide range of industries.

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Dr Francis has been a corrosion engineer for over 25 years. He is currently the Corrosion Services Manager for Weir Materials and Foundries, Manchester, which he joined in 1991. His duties include organisation and supervision of external R&D, in-house corrosion testing, advice on materials selection to the Weir Group worldwide and the examination of service failures. He has been employed as a consultant by several large companies, investigating major failures. He was a Director of NACE International from 2000 to 2003 and is currently Chairman of NACE Europe for the second time. He sits on the EFC (European Federation of Corrosion) Working Parties on Marine Corrosion and Corrosion in the Oil and Gas Industry. He also sits on more committees than he cares to remember.