

Coupling of superduplex stainless steel and cast nickel–aluminium bronze in sea water

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Tests have been performed at about 25°C in both natural and chlorinated sea waters on couples of nickel–aluminium bronze (NAB) and Zeron 100 (Z100) superduplex stainless steel. Two NAB/Z100 area ratios (1:1 and 1:10) were used in exposures of 60 days. The results in natural sea water showed severe localised corrosion of NAB both in the crevices and on open surfaces at both area ratios. In chlorinated sea water there was no corrosion at a 1:1 area ratio. The attack is explained in terms of the different cathodic reactions occurring in natural and chlorinated sea waters, and the metallurgical structure of NAB. Service experiences with couples of NAB and superduplex stainless steel are described and recommendations are given for the avoidance of problems.

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INTRODUCTION

Zeron 100 (Z100) is a superduplex stainless steel manufactured by Weir Materials and Foundries that has been used for sea water and firewater piping systems on offshore platforms since 1989. The results have been very good with no serious corrosion problems.

Historically the offshore oil and gas industry has used 90–10 copper nickel piping with nickel–aluminium bronze (NAB) valves. The lower cost of NAB valves compared with superduplex stainless steel has led to queries as to the compatibility of NAB with superduplex in ambient temperature sea water cooling systems. Tube plates of NAB have been used with both titanium and stainless steel tubes in sea water cooled heat exchangers, and so there is a possibility of this combination being viable. This report presents the results of tests to investigate the risk of galvanic corrosion between Z100 and cast NAB in sea water.

EXPERIMENTAL

Materials

Z100 coupons were cut from 3.4 mm sheet with a shot blasted finish. The coupons were of two sizes, 50 × 50 mm and 100 × 270 mm, i.e. a tenfold increase in surface area. The NAB was cast to BS 1400 AB2 in the form of two cylindrical bars of about 100 mm length and 62 mm o.d. The bars were turned to 57 mm o.d. and discs 3 mm thick were parted off. The discs had a good quality machined finish typical of that found on a flange face or a machined surface of a valve. This gave NAB/Z100 area ratios of 1:1 and 1:10. The composition of both alloys and the relevant standards are shown in Table 1.

Holes of 9 mm diameter were drilled 12 mm from the edge of each specimen so that they could be bolted together in pairs. The couples were bolted together with M8 polypropylene screws, thus creating a metal/metal crevice

between the plates and two metal/polymer crevices between the bolt head or nut and each plate.

Exposure conditions

All specimens were exposed in sea water for 63 days at a test facility at Holyhead, on Anglesey, UK. The sea water at the site is clean and has the typical composition

Chloride	20 900 mg L ⁻¹
Sulphate	2720 mg L ⁻¹
Bromide	63 mg L ⁻¹
Bicarbonate	150 mg L ⁻¹
Calcium	480 mg L ⁻¹
Magnesium	1270 mg L ⁻¹
Sodium	10 800 mg L ⁻¹
pH	7.9

Two conditions were investigated, i.e. natural sea water and chlorinated sea water both at about 20–25°C. The temperature was chosen as being the maximum encountered in UK waters. This temperature was above ambient and so the specimens were suspended in two plastic tanks fitted with heaters and constantly refreshed with sea water. The chlorine and temperature were monitored daily. A nominal chlorine concentration of 0.5–1 mg L⁻¹ was chosen as being typical of that used on offshore platforms.

Each tank contained the following specimens

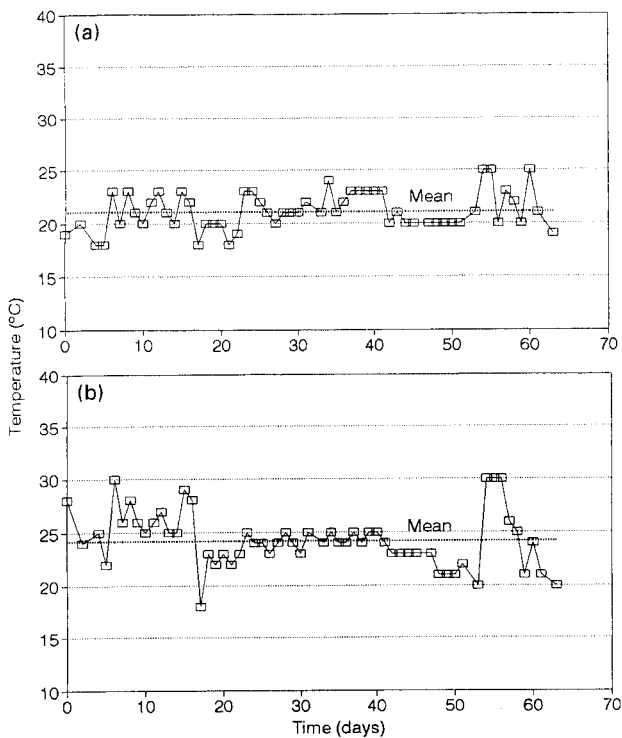
Couple	Area ratio	No. of specimens
NAB/NAB	1:1	2 off
Z100/Z100	1:1	2 off
Z100/NAB	1:1	3 off
Z100/NAB	10:1	3 off

This provided reference specimens showing the intrinsic resistance to crevice corrosion of both materials.

After testing, the specimens were removed, photographed, and then examined closely for signs of corrosion. Micro-sections were prepared of some of the corroded specimens.

Table 1 Composition of test alloys and their standards

Alloy	Standard	Composition, wt-%												
		Cu	Al	Ni	Fe	Mn	C	Cr	Mo	N	W	Zn	Si	
Nickel–aluminium bronze	BS 1400 AB2	Min.	...	8.8	4.0	4.0	
		Max.	Bal.	10.0	5.5	5.5	1.5	0.5	0.1	
		Actual	Bal.	9.9	5.18	4.65	1.30	0.03	0.03	
Zeron 100	UNS S32760	Min.	0.5	...	6.0	24.0	3.0	0.2	0.5	
		Max.	1	...	8.0	Bal.	1.0	0.03	26.0	4.0	0.3	1.0	...	1.0
		Actual	0.59	...	7.37	Bal.	0.58	0.026	25.33	3.67	0.23	0.58	...	0.27



1 Temperature variation with time for (a) natural sea water and (b) chlorinated sea water

RESULTS

During testing, the average chlorine content was 0.7 mg L^{-1} in the chlorinated tank, with extreme values of 0.6 and 0.8 mg L^{-1} . The variation in temperature with time is shown in Fig. 1a and b for natural sea water and for chlorinated sea water respectively. The mean values were 21 and 24°C .

Upon removal, the specimens exposed to natural sea water looked as shown in Fig. 2a and b. The photographs clearly show the presence of fouling slime (grey/brown) and large quantities of green and brown corrosion products on some couples. Figure 3a and b shows the specimens from the chlorinated tank. These clearly show less corrosion and no fouling.

Visual appearance

All the couples were separated and the specimens were examined under a low power microscope for indications of corrosion.

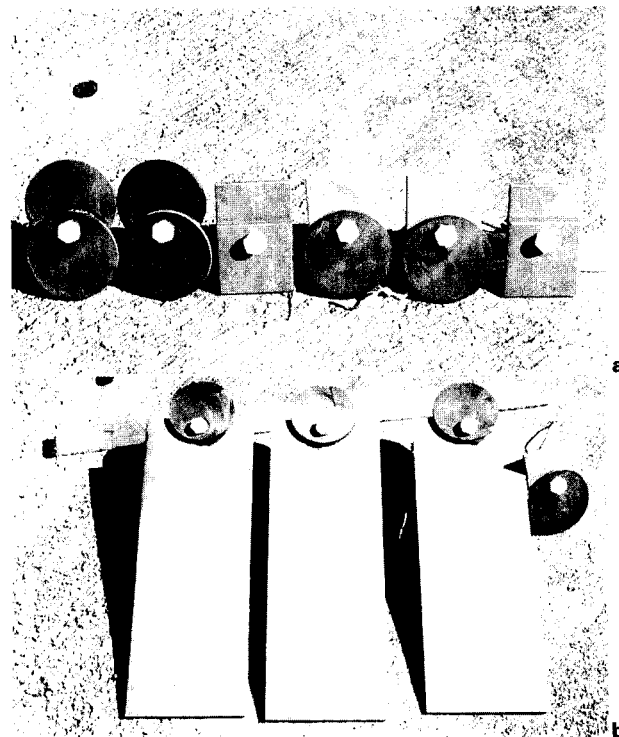
Natural sea water

The NAB/NAB couples had a covering of slime but showed only general corrosion with no signs of crevice attack. The NAB specimens coupled to Z100 at a 1:1 area ratio all showed thick corrosion products around the crevice area, with a deep trough just outside the crevice. The outer layer of corrosion products was a green colour with an orange-brown product beneath the outer layer. In addition to the crevice corrosion there were broad pits on the open surface on one side of each NAB specimen. The depth appeared similar to that in the crevice, but the corrosion product beneath the green outer layer was white, not orange as in the crevice areas.

The NAB specimens coupled to Z100 with a 1:10 area ratio were similar in appearance to those described above. The corrosion outside the crevice area appeared deeper than with the smaller area ratio and copper crystals were clearly visible inside the crevice on the NAB surface. There

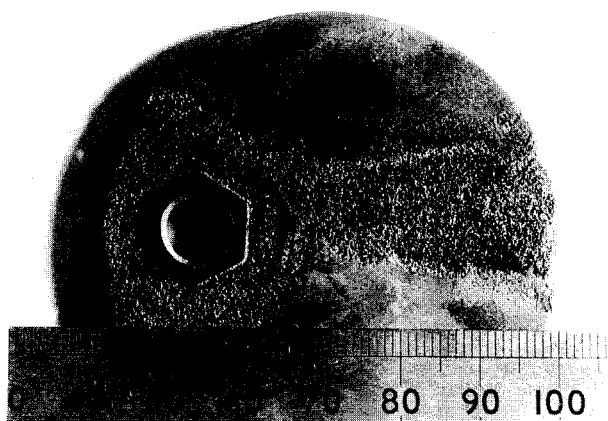


2 Appearance of galvanic couples exposed for 63 days in natural sea water



3 Appearance of galvanic couples exposed to sea water plus 0.7 mg L^{-1} chlorine for 63 days

was also crevice attack around the polypropylene nut and screw head which was not seen at the lower area ratio. Figure 4 shows the appearance of an NAB specimen coupled to Z100 with an area ratio of 1:10 in natural sea water. The specimen was pickled in cold 10% sulphuric acid to remove the corrosion products. The extensive attack



4 Appearance of corrosion on NAB outside crevice after coupling to Z100 in natural sea water

around the crevice created by the nut and elsewhere is clearly visible.

There was no attack on the Z100 coupled either to itself or to NAB. The Z100 specimens coupled to NAB all had a hard, white, crystalline deposit on them. This effervesced vigorously when a drop of 10% sulphuric acid was placed on it, indicating the presence of carbonate.

Chlorinated sea water

In general there was far less corrosion product on the NAB specimens exposed to chlorinated sea water compared with those exposed to unchlorinated sea water. The NAB specimens coupled to NAB showed some corrosion products at the edge of the crevice, but the corrosion was only superficial.

The NAB specimens coupled to Z100 at an area ratio of 1:1 also showed corrosion products around the crevice, but again the attack was only superficial. The NAB specimens coupled at the higher area ratio (1:10) showed deep attack at the crevice, similar to that seen in unchlorinated sea water. In addition there was some lesser attack at the crevices created by the polypropylene fastener. Although no significant pitting was observed on the NAB outside the crevices, there were tiny mounds of corrosion product on the open surface which could have been 'incipient' pits.

The Z100 specimens had the same appearance as those in unchlorinated sea water, except for the absence of the biological slime film.

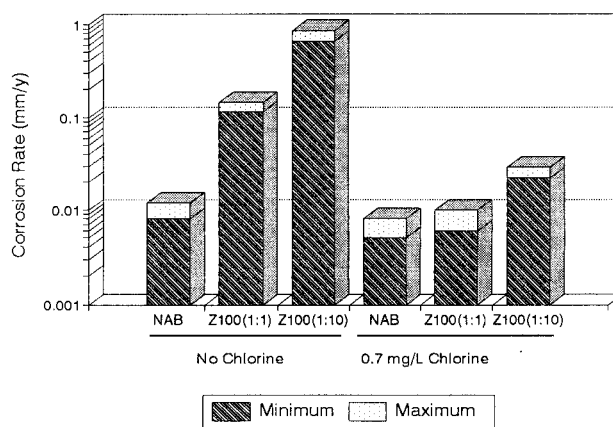
Corrosion measurements

After visual examination, all of the specimens were cleaned in cold 10% sulphuric acid and weighed. The depth of any pitting was also measured to an accuracy of ± 0.01 mm.

Figure 5 shows the minimum and maximum corrosion rates calculated from the weight losses for all exposure conditions. No corrections have been made for metal loss due to localised corrosion, and so some of these figures, particularly in natural sea water, are higher than the 'true' general corrosion rate. The results show only the typical amount of scatter for this kind of test.

A number of points are immediately apparent. In natural sea water the corrosion rate of NAB is very low, typical of copper alloys, but coupling to Z100 greatly accelerates the rate of metal loss. Increasing the area of Z100 coupled to the NAB has the effect of increasing the corrosion rate by a factor of ~ 5 . Much of this is probably accounted for by the increase in localised corrosion outside the crevice.

In chlorinated sea water the corrosion rate for NAB coupled to itself was less than in natural sea water and hardly increased when coupled to an equal area of Z100. Coupling to ten times the area of Z100 produced a



5 Corrosion rate of NAB galvanic couples in sea water at $\sim 25^\circ\text{C}$

substantial increase in the corrosion rate, but still much less than seen in natural sea water. Most of the increase appears to be due to localised rather than general corrosion.

The depths of attack are shown in Table 2. This differentiates between pitting at the metal/metal crevice, pitting at the propylene/metal crevice, and pitting on open surfaces. No significant pitting was observed on couples with NAB coupled to NAB in both waters, or on NAB coupled to an equal area of Z100 in chlorinated sea water. Significant corrosion was observed on NAB coupled to Z100 at both area ratios in natural sea water, and on NAB coupled to Z100 at an area ratio of 1:10 in chlorinated sea water. The depths of attack under all three exposure conditions were similar, ranging from 0.2 to 0.49 mm. The exception was one specimen coupled to Z100 in natural sea water, where a depth of over a millimetre was recorded.

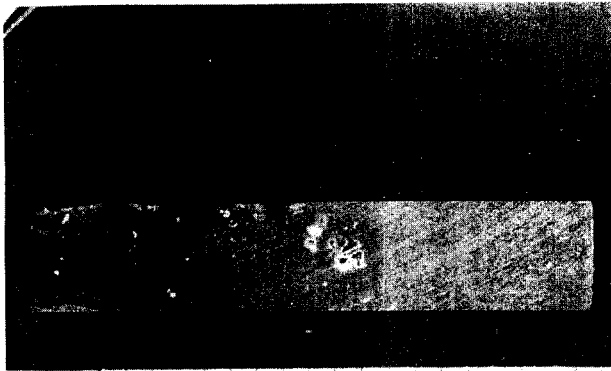
Where pitting had occurred it was usually at the metal/metal crevice and on open surfaces, with very little attack at the crevice created by the nut. The exception was the 10:1 Z100 to NAB couples in chlorinated sea water, where attack only occurred at the metal/metal crevice.

Microsections

To obtain a more detailed picture of the pitting/crevice attack, microsections were prepared through corroded

Table 2 Depth of attack of NAB after 60 days exposure in sea water

Sample no.	Couple alloy	Area ratio	Chlorine, mg L^{-1}	Depth of attack, mm		
				Crevice	Nut	Open surface
1	Z100	1:1	0	0.27	0.03	1.19
2	Z100	1:1	0	0.35	0.01	0.29
3	Z100	1:1	0	0.27	0	0.22
4	Z100	1:1	0.7	0	0	0
5	Z100	1:1	0.7	0	0	0
6	Z100	1:1	0.7	0	0	0
7	NAB	1:1	0	0	0	0
8	NAB	1:1	0	0.01	0	0
9	NAB	1:1	0	0	0	0
10	NAB	1:1	0	0	0	0
11	NAB	1:1	0.7	0	0	0
12	NAB	1:1	0.7	0	0	0
13	NAB	1:1	0.7	0	0	0
14	NAB	1:1	0.7	0	0	0
15	Z100	10:1	0	0.35	0	0.46
16	Z100	10:1	0	0.36	0	0.47
17	Z100	10:1	0	0.39	0	0.27
18	Z100	10:1	0.7	0.2	0.01	0
19	Z100	10:1	0.7	0.22	0	0
20	Z100	10:1	0.7	0.49	0.01	0



6 Macrosection of NAB specimen after coupling to Z100 in natural sea water



7 Microsection ($\times 50$) of specimen shown in Fig. 6, etched electrolytically in 1% chromic acid

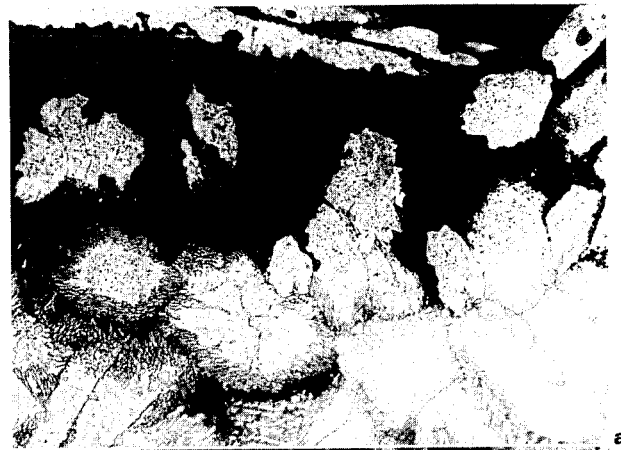
areas of specimens 1 and 20. Figure 6 shows a macrosection of specimen 1.

Not only is the corrosion clearly visible, but so is the extensive porosity in the casting. The apparent great depth of the pitting seems to be because corrosion opened up a large pore or series of pores in the casting. Porosity was also visible on specimen 20, although not to the same extent as on specimen 1. The pitting had not opened up any pores on specimen 20.

Both specimens were electrolytically etched in 1% chromic acid to show the structure at the corrosion sites. Figure 7 shows a low magnification picture of the attack on specimen 1. The corrosion is broad and shallow, with an open series of casting pores beneath. Figure 8a and b shows details of the corrosion in the pits on specimens 1 and 20 respectively. These show that the α phase particles are being removed by corrosion of the long, thin needles of κ_{III} phase around them.

DISCUSSION

Table 1 shows that the composition of both alloys falls within the standards for BS 1400: AB2 and UNS S32760 respectively. Currently it is usual to ensure that the nickel content exceeds the iron content in NAB, typically by about 0.5 wt-%, as is the case for the NAB used in this investigation. This is not written into the British Standard, but it is believed to optimise the corrosion resistance of the NAB. Although some porosity in castings is quite usual,



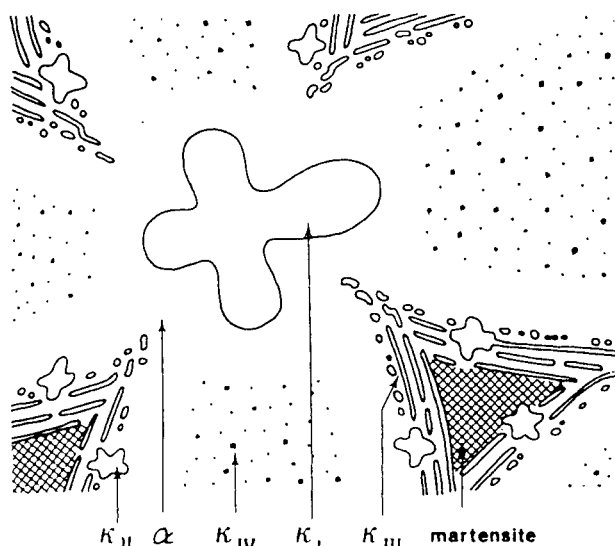
8 Microsections ($\times 500$) of corroded NAB after coupling to Z100 in (a) natural sea water and (b) chlorinated sea water (area ratio 1:10), etched electrolytically in 1% chromic acid

the extent shown in the present tests, of which Fig. 6 is an extreme example, is rather excessive. Microsections showed that by and large the porosity was not giving rise to unreal pit depths, except for specimen 1. The Z100 composition is typical for this alloy.

The microstructure and composition of the phases in nickel-aluminium bronze (AB2) are complex, and were only explained in detail relatively recently.^{1,2} On cooling, the high temperature β phase transforms to α and κ phases. Four distinct κ phases have been identified, and a schematic of a typical microstructure is shown in Fig. 9 (from Ref. 2). The κ phases are all intermetallics, enriched in aluminium and iron and/or nickel.² Figure 9 also shows a martensite phase. This is what is often referred to as 'residual β ' phase, and it is produced when the alloy is cooled too rapidly after thermal processing and the β phase does not fully transform into α and κ .

The martensite or 'residual β ' phase is highly cathodic to the α phase and corrodes rapidly in sea water.² It is usual to specify a heat treatment such as that in Royal Navy Specification NES 747, i.e. 675°C for 6 h followed by air cooling, to ensure the optimum microstructure and mechanical properties after thermal processing. There have been a few spectacular corrosion failures due to corrosion of welds that had not been post-weld heat treated. This heat treatment is, at present, only in NES 747, but it is increasingly regarded as essential if the optimum performance is to be achieved.

The corrosion of NAB was studied in detail by Rowlands *et al.*³ following some corrosion problems of NAB experienced by the Royal Navy. In extended tests they found that exposure to normal flow conditions ($> 1.5 \text{ m s}^{-1}$) resulted in the formation of a protective film and no

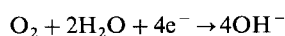


9 Schematic representation of microstructure of NAB (from Ref. 2)

significant problems. However, exposure to continuous slow flow ($\sim 0.06 \text{ m s}^{-1}$) or alternating stagnant and flowing conditions led to localised corrosion. The attack was on the κ_{III} phase and corrosion rates of over 1 mm/year could occur. There was also a rather variable incubation time which could be anywhere from 3 to 9 months.

Detailed electrochemical studies of the individual phases³ showed that at neutral pH (7 to 8) the κ_{III} phase was cathodic to the α phase while at pH 3 it was strongly anodic. This suggested that, once an occluded cell formed and the local pH decreased significantly, selective attack along the rods of κ_{III} would occur. This mechanism explains the somewhat erratic incubation time under slow flow conditions and the lack of attack under more turbulent flow conditions, where occluded cells are less likely to form.

In order to explain the corrosion observed in the present tests it is necessary to combine the above observations with the known electrochemical behaviour of NAB and Z100. The cathodic reaction occurs principally on the Z100 and in natural sea water it takes the form of the reduction of dissolved oxygen, i.e.

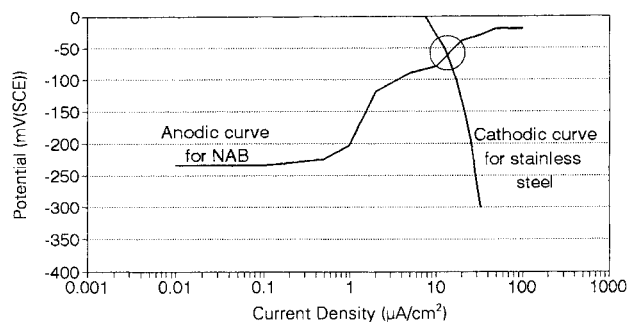


The production of hydroxyl ions leads to a local increase in pH and the precipitation of calcium and magnesium carbonate scales, as was observed on the Z100 specimens. At the same time a biofilm forms on the Z100 in natural sea water and this has the property of significantly depolarising the cathodic reaction.⁴ The anodic reaction is the dissolution of metal, primarily copper, i.e.

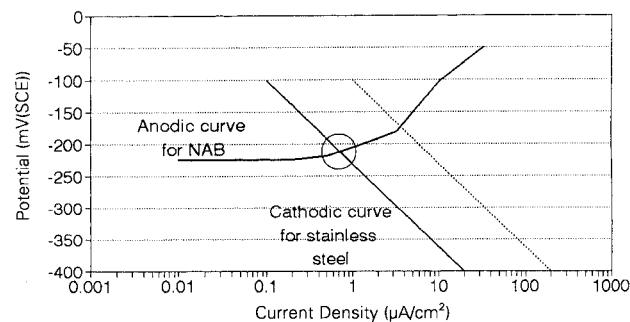


The copper ions react with dissolved oxygen or hydroxyl ions to form copper oxide or hydroxy chlorides. Where an occluded cell is created there is very limited access of oxygen and cuprous chloride is created. This hydrolyses to form HCl and the pH decreases, producing more metal dissolution, and then the cycle repeats, further decreasing the pH and so on.

To explain the behaviour in natural sea water the cathodic curves for stainless steel from Scotto *et al.*⁴ have been combined with the unpublished anodic curves for NAB of Maselkowski and Francis.⁵ This is shown in Fig. 10. The solid lines are for equal specimen areas and it can be seen that the net result, indicated by the circle, is an increased potential for the NAB to about -70 mV(SCE) and a high current in excess of $10 \mu\text{A cm}^{-2}$. When localised



10 Polarisation curves showing corrosion of NAB coupled to Z100 in natural sea water: area ratio 1:1



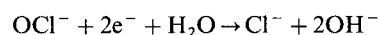
— 1:1 area ratio; 1:10 area ratio

11 Polarisation curves showing corrosion of NAB coupled to Z100 in chlorinated sea water

corrosion of NAB is occurring at the κ_{III} phase, the potential is typically observed to increase to about -50 mV(SCE) .⁶ The corrosion rate at $12 \mu\text{A cm}^{-2}$, as shown in Fig. 10, is about 0.2 mm/year, using Faraday's law. However, as the attack is confined principally to the κ_{III} , an increase in the corrosion penetration rate by a factor of ten could occur, assuming 10% of the exposed surface is κ_{III} , i.e. 2 mm/year.

The attack on the NAB when coupled to ten times the area of Z100 hardly increased in depth compared with a 1:1 area ratio. This is probably because the efficiency of the cathode with the biofilm is so great that an increase in area makes only a small difference to an already high corrosion rate. When the area of the cathode is increased, the effect is to push the cathodic curve in Fig. 10 to the right. This results in a more positive potential and a higher corrosion current.

In chlorinated sea water the behaviour is clearly different. No biofilm forms on the Z100 but the open circuit potential of stainless steel increases from about $+300 \text{ mV(SCE)}$ with a biofilm to about $+600 \text{ mV(SCE)}$ in chlorinated sea water.^{4,7} The stainless steel is much less efficient as a cathode, even though the hypochlorite provides an alternative cathodic reaction to the reduction of dissolved oxygen, i.e.



The anodic curve for NAB in chlorinated sea water from Ref. 5 has been combined with a composite cathodic curve for high alloy stainless steel derived by Sintef⁷ in Fig. 11. The solid lines are for an area ratio of 1:1 and it can be seen that the potential is hardly increased from that of freely corroding NAB. The current is very low, giving an average corrosion rate of 0.011 mm/year. Selective phase attack of the κ_{III} phase did not initiate, probably because the corrosion rate was so low that an occluded cell could not easily form. Even in the crevice areas there was no indication of localised attack.

When the area of the cathode is increased tenfold this effectively increases the cathodic curve by an order of magnitude as shown by the dotted line in Fig. 11. This results in a small ennoblement of potential of about 50 mV but increases the current by a factor of about 5. This produces an average corrosion rate of 0.056 mm/year, which would be equivalent to a penetration rate of 0.56 mm/year if only 10% of the exposed surface were κ_{III} . The potential ennoblement seems to be insufficient to initiate selective phase corrosion outside the crevices.

The electrochemical data combined with Rowland's data³ explain the observations in the present tests. The results suggest that NAB should not be connected to Z100 in natural sea water under any circumstances. In chlorinated sea water no attack was observed with equal area ratios, although it did occur at a 10:1 area ratio. Unfortunately, in real piping systems the current can throw a long way down a stainless steel pipe⁸ and hence any NAB valve would invariably be effectively connected to a large area of stainless steel.

One important factor to remember is that the exposures were only for 60 days and it is possible that NAB might suffer localised attack after prolonged exposure (say 12 months) when coupled to an equal area of Z100 in chlorinated sea water. A further complication could arise with an NAB valve in sea water service when it is left closed for an extended period. The chlorine in the water will be consumed within a few hours at most, and the aerobic bacteria will consume the dissolved oxygen in a day or two. If the anaerobic bacteria, such as sulphate reducing bacteria (SRB), become sufficiently active, then significant quantities of sulphide could be produced. Nickel–aluminium bronze is well known to have poor resistance to sulphides in sea water and accelerated attack could occur when the valve is subsequently opened. Frequent use of the valve to flush it with fresh sea water should prevent this potential problem.

SERVICE EXPERIENCE

In order to determine whether the observations in the present tests would be borne out by service experience, enquiries were made among offshore operators. However, only two users of NAB valves with high alloy stainless steel piping were found.

The first of these was on the Goodwyn 'A' platform off North West Australia. The inlet sea water temperature varies from 20 to about 40°C, which is somewhat higher than in the present tests, and the sea water is also chlorinated. During the first year, problems were experienced with some of the NAB valves in the main sea water lines, which would not close properly. It is believed that no actual leaks occurred. The valves have not been inspected by Weir Materials and Foundries, but the operator reports that there was excessive corrosion of the NAB, preventing proper valve closure. These valves are gradually being replaced with cast Z100 valves. Although the sea water was chlorinated, galvanic corrosion of the NAB still occurred, probably because of the higher water temperature compared with the present tests.

The BP Andrew platform in the North Sea has also used NAB valves in stainless steel lines but with natural sea water. The sea water inlet temperature is much lower than on Goodwyn 'A', being 4–15°C, which should reduce the risk of localised corrosion of the NAB. Problems were reported after a year in operation, which took the form of isolation valves failing to close and seal properly. Examination showed extensive corrosion of the NAB bodies and seats. The valves are now being replaced with superduplex stainless steel valves. These failures are what

would be expected in natural sea water from the present tests.

The BP ETAP project is using a similar sea water cooling system to that on the BP Andrew platform, but the sea water is chlorinated. The project will begin production shortly, and success or failure with the valves will depend on the area ratio in service and whether the creviced areas have been protected.

CONCLUSIONS

1. In natural sea water, nickel–aluminium bronze corrodes rapidly at localised areas, both at crevices and on open surfaces, when coupled to an equal area of Zeron 100 superduplex stainless steel.

2. When the NAB/Z100 area ratio is changed from 1:1 to 1:10 in natural sea water the attack of the NAB becomes much more widespread but not much deeper.

3. In chlorinated sea water, NAB did not suffer any significant accelerated corrosion when coupled to an equal amount of Z100.

4. When the area of Z100 was ten times that of NAB in chlorinated sea water, pitting occurred at the creviced areas of NAB.

RECOMMENDATIONS

Based on the data described above, the following recommendations are made. Note that these are only for a maximum sea water temperature of 25°C, and they are based on exposures of 60 days. They take no account of any corrosion with a long incubation time.

1. Nickel–aluminium bronze should not be coupled to Z100 in natural sea water unless the area of NAB greatly exceeds that of the stainless steel (e.g. a stainless steel pump shaft or a valve stem).

2. Nickel–aluminium bronze can be coupled to Z100 piping in chlorinated sea water (0.5–1.0 mg L⁻¹ chlorine) provided the crevice areas are protected and the temperature is ≤25°C. The flanges are normally cast-in and form a substantial crevice with the gasket. These can be protected with a high integrity coating such as coal tar epoxy, fusion bond epoxy, etc. The stem and seat need to be compatible with the pipework so that no corrosion occurs in this area and the valve will always close properly. Suitable alloys for this area are Z100, C-276, alloy 625, and wear resisting alloys such as Stellite 6 and Ultimet. Although there will be some increase in the corrosion rate of the valve body, this should not be serious as the valve body will be of substantial thickness (>15 mm). Regular refreshment of the water in closed valves would be beneficial to prevent sulphide attack.

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