Galvanic corrosion of high alloy stainless steels in sea water

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The galvanic corrosion data for couples between high alloy stainless steels and other metals in both natural and chlorinated sea water are reviewed. Recommendations for preventive measures are made for the major items used in sea water systems, i.e. valves, heat exchangers, and piping. Some service experiences are presented to show the kind of galvanic problems which can arise and the solutions adopted.

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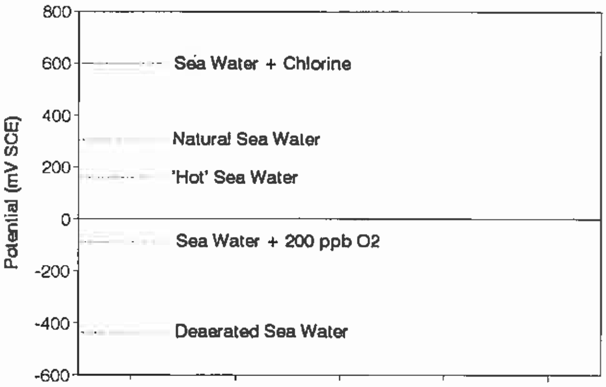
INTRODUCTION

The coupling of dissimilar metals in conducting, corrosive solutions, such as sea water, can lead to the accelerated corrosion of one metal and protection of the other more noble metal.[1] The extent of corrosion depends on the area ratio of the two metals, the difference in potential, and the cathodic efficiency of the more noble metal. In many media there are only limited data on the performance of various metal couples, but sea water is widely used for cooling purposes and a large database has been accumulated. Authors such as La Que[2] have constructed tables showing the open circuit potentials of many metals in sea water. However, this on its own is not sufficient to enable a satisfactory materials selection free from galvanic corrosion problems because it does not take cathodic efficiency into account. The present paper reviews the data from a range of sources, showing the effects of coupling common alloys to high alloy stainless steels in sea water. These alloys are widely used in sea water systems both from new and as replacements for less corrosion resistant alloys. The data cover the temperature range from ambient North Sea (~10°C) to approximately 40°C. At higher temperatures there are no known data, but the general principles for lower temperatures are still expected to apply.

Work has been carried out by organisations such as Sintef[3] which has shown that both the potential and cathodic efficiency of all high alloy stainless steels in sea water are similar. Figure 1 shows the typical potentials obtained with both 6%Mo austenitic and super duplex stainless steels in sea water. In ambient temperature sea water a biofilm forms over a period of 1–4 weeks which depolarises the cathodic reaction. This produces potentials in the range 250–350 mV(SCE) and a high cathodic efficiency. When chlorine is added to the sea water (typically 0·5–1·0 mg L^{-1}) to control fouling, the reduction of hypochlorite ions to chloride provides a fast cathodic reaction. Potentials are typically in the range 550–650 mV(SCE), but the cathodic efficiency is not as high as in natural sea water.[4] As the sea water temperature is increased a point is reached at which the biofilm is not viable and lower potentials, in the range 100–200 mV(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 average sea water temperature.[5]

The corrosion that is observed on the least noble or anodic metal depends on its corrosion behaviour in sea water. Carbon steels mostly suffer general corrosion which is increased when the steel is coupled to a more noble metal. The same is generally true for copper alloys, although they can suffer localised corrosion if the conditions are suitable for its initiation. Type 300 stainless steels suffer pitting/crevice corrosion in sea water and this becomes deeper, and sometimes more widespread, when they are coupled to more corrosion resistant alloys.



1 *Potentials obtained with high alloy stainless steels in sea water*

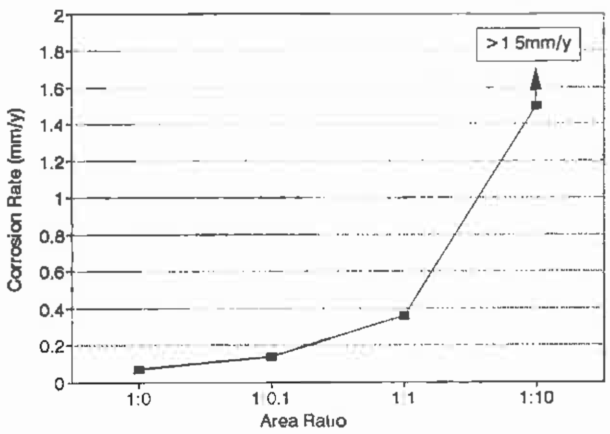
ALLOYS

It is necessary to specify not only which alloys are covered by this review, but also which alloys are specifically excluded. High alloy stainless steel covers both the super austenitic and super duplex alloys and the most commonly used ones, along with their nominal compositions, are given in Table 1. There are some other stainless steels which are specifically excluded from the class of super stainless steels. The principal ones are 316 stainless steel (UNS S31600), 22%Cr duplex stainless steel (UNS S39225) and alloy 825 (UNS N08825), all of which are susceptible to crevice corrosion in sea water at ambient temperature[6]

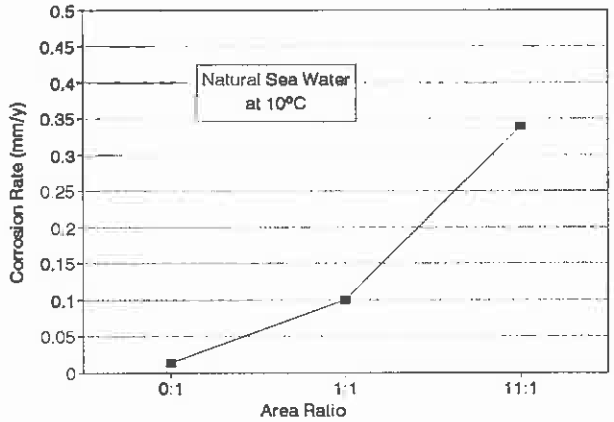
Table 1 Commonly used super stainless steels and their nominal compositions, wt-%

UNS no.	Common name	Cr	Mo	Ni	Cu	N	W
Super duplex							
S39276	Zeron 100*	25	3·5	7	0·7	0·25	0·7
S39275	SAF2507†	25	4	7	...	0·28	...
S39274	DP3W‡	25	3	7	0·5	0·28	2
Super austenitic							
S31254	254SMO§	20	6	18	0·7	0·2	...
N08926	1925hMo¶	21	6	25	1	0·2	...
N08367	AL6XN‖	20	6	25	...	0·2	...

* Trademark of Weir Materials Ltd.
† Trademark of AB Sandvik Steel.
‡ Trademark of Sumitomo Metal Industries Ltd.
§ Trademark of AB Avesta.
¶ Trademark of Krupp VDM GmbH.
‖ Trademark of Allegheny Ludlum.



2 *Graph of corrosion rate versus area ratio (carbon steel/stainless steel) for carbon steel coupled to high alloy stainless steel in natural sea water*



4 *Graph of corrosion rate versus area ratio (stainless steel/Cu–Ni) for 90Cu–10Ni coupled to high alloy stainless steel in natural sea water*

and so cannot be included in the present class of high alloy stainless steels.

LABORATORY DATA

Coupled to carbon steel

The potential difference between carbon steel and high alloy stainless steel is large and substantial increases in the corrosion rate of carbon steel can result when the area of carbon steel is low compared with that of stainless steel. Wallen and Anderson[7] looked at the corrosion of carbon steel coupled to various areas of high alloy stainless steel in natural sea water and the results are shown in Fig. 2. A small area of stainless steel (0·1 : 1) produces only a doubling of the corrosion rate, whereas at equal area ratios the increase is about a factor of 5.

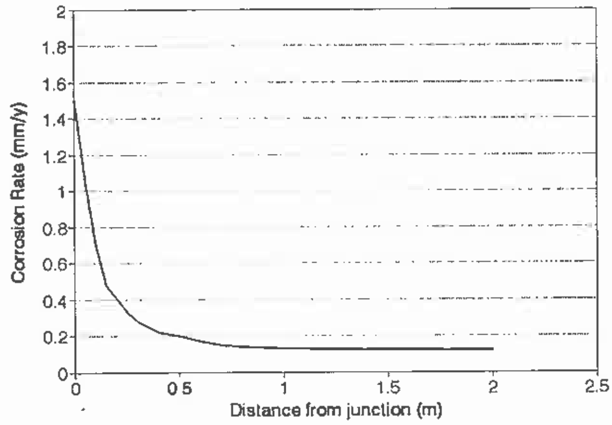
Gartland and Drugli[8] modelled the couple between stainless steel and carbon steel pipes using polarisation data from long term exposure tests in chlorinated sea water. They showed that directly coupled corrosion rates for a NPS 10* pipe gave a corrosion rate of ~1·5 mm/year at the junction, decreasing to normal values at ~1·5 m from the junction (Fig. 3). Where the pipe sizes at the junction are different, the corrosion rate is modified. If the carbon steel pipe is larger than the stainless steel pipe, the corrosion rate is reduced (e.g. NPS 3 stainless steel/NPS 6 carbon steel gives a maximum corrosion rate of 0·5 mm/year). If the carbon steel pipe is smaller than the stainless steel pipe, the corrosion rate is increased (NPS 4 stainless steel/NPS 2 carbon steel gives a maximum corrosion rate of 5·8 mm/year). Hence preventive measures are needed to preserve the carbon steel (*see* below).

Coupled to copper alloys

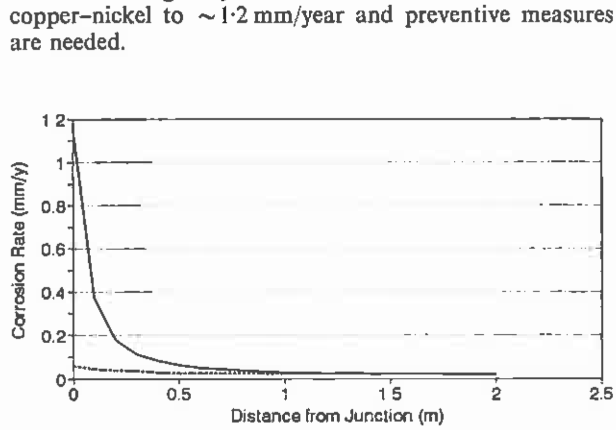
Copper alloys in sea water do not have a truly passive layer but rely for protection on a very tenacious oxide layer, which limits the rate of metal dissolution, and a thin film beneath limiting the cathodic efficiency. Coupling to stainless steel increases the corrosion rate by providing a more active cathode. Wallen and Anderson[7] showed that most copper alloys increase their corrosion rate by a factor of about 7 when coupled to an equal area of stainless steel in natural sea water. However, as the free corrosion rate is very low, the increase can often be acceptable on thick walled items. Higher area ratios of stainless steel increase the corrosion rate of the copper alloys even further. Figure 4 shows a plot of corrosion rate versus area ratio for stainless steel coupled to 90Cu–10Ni.

Bardal *et al.*[9] modelled the galvanic corrosion of 90Cu–10Ni pipes coupled to stainless steel. They found that there was a significant difference between natural and chlorinated sea water, as shown in Fig. 5. The results show that in chlorinated sea water the corrosion rate for directly coupled pipes will be 0·06 mm/year, which should be acceptable for most applications. However, in natural sea water without chlorine, the high cathodic efficiency of the stainless steel greatly increases the corrosion rate of the copper–nickel to ~1·2 mm/year and preventive measures are needed.

*NPS = nominal pipe size as described in BSI 1600, Part 2, 1970 and ANSI/ASME B36.19M, 1985.



3 *Graph of corrosion rate versus distance from junction for carbon steel coupled to high alloy stainless steel for NPS 10 pipe in chlorinated sea water*



—— in natural sea water; – – – in chlorinated sea water

5 *Graph of corrosion rate versus distance from junction for 90Cu–10Ni coupled to high alloy stainless steel for NPS 10 pipe*

Coupled to other alloys

The most commonly used alloys in sea water, not already covered above, are nickel based alloys, titanium, and low alloy stainless steels.

Research in natural sea water by Wallen and Anderson[7] and by Shone *et al.*[6] in chlorinated sea water has shown that no galvanic corrosion occurs, even in crevices, when super stainless steels are coupled to intrinsically corrosion resistant nickel based alloys and titanium. Such nickel based alloys are alloys 625 (N06625) and C-276 (N10276), but not alloy 825 (N08825) which can suffer localised corrosion in sea water. This would be exacerbated by coupling to a more resistant alloy such as super duplex stainless steel.

Nickel–copper alloys such as alloys 400 (N04400) and K-500 (N05500) cause concern. Although they have been used for many years in sea water applications, they have generally been coupled to less noble metals, such as copper alloys or carbon steel, which would protect them. Evidence is beginning to accumulate that shows nickel–copper alloys to have less satisfactory intrinsic corrosion resistance in sea water than was previously thought. Gallagher *et al.*[10] reported severe corrosion of an alloy 400 sea water piping system, particularly at welds. Wallen and Anderson[7] carried out galvanic corrosion tests for 12 months on alloy 400 coupled to a super austenitic stainless steel. The results were very similar to those for 90Cu–10Ni, except that in the uncoupled state the corrosion rate of alloy 400 was three times that of 90Cu–10Ni. When alloy 400 was coupled to stainless steel, not only did the general corrosion rate increase, but pitting up to a depth of 0·3 mm was observed.

The 300 series of stainless steels has been used in sea water for many years, particularly the 316/316L grades. Although these alloys are susceptible to pitting and especially crevice corrosion in sea water, they have been very successful when coupled to less noble alloys such as carbon steel, copper alloys, or austenitic cast iron. If these low grade stainless steels are coupled to a high alloy super stainless steel, the risk of localised corrosion initiation is not usually increased, but the rate of propagation could be increased if a substantial increase in cathodic area were made available.

Although the super stainless steels are the cathodes in the galvanic couples described above, it is still possible for them to suffer corrosion. This can occur when they form a crevice with a lower alloy material which suffers attack in the crevice. This leads to a lowering of the pH and an increase of the chloride concentration in the crevice. If the conditions become severe enough it is possible for corrosion also to initiate on the super stainless steel. This has been reported by Wallen and Anderson[7] for super stainless steel coupled to alloy 400 in a crevice, and by Shone *et al.*[6] for a couple between super stainless steel and 316 stainless steel.

Coupled to graphite

Graphite is very noble to most metals in sea water, as well as being a good cathode. Hence it is likely to stimulate attack even on high alloy materials, especially in crevices. It is not uncommon to find graphite loaded seals or gaskets specified for flanges, valve seals, and pump seals. These should be avoided in all areas wetted by sea water as they can cause rapid localised attack of most alloys, including super stainless steels. The seals and gaskets can usually be successfully replaced with non-graphite versions which generally give trouble free performance.

PREVENTIVE MEASURES

There are a number of measures which can be considered to prevent accelerated corrosion in a galvanic couple in sea water piping systems.

Valves

With a valve there are usually only two options. One is to add a sufficient corrosion allowance to the anodic component such that its life is adequate. The second is to replace the anodic element with an alloy compatible with the high alloy stainless steel. Coating of the stainless steel to reduce the cathodic current is not usually practicable, and coating the anode should be avoided because the corrosion rate at defects in the coating will be very high due to the high cathode to anode area ratio, leading to rapid failure. Note that where the area ratio of cathode to anode is small, little acceleration of corrosion will occur.

Heat exchangers

The critical part of a heat exchanger is the tubing, and where corrosion of the tubing has occurred it is often desired to retrofit in a high alloy stainless steel. It is then necessary to prevent corrosion of the tube plates and water boxes if these are not also changed. Water boxes are usually cast iron or carbon steel with coatings such as coal tar epoxy, neoprene, or glass flake, and this is usually adequate even with stainless steel tubes. It is desirable to change the tube plate to high alloy stainless steel, but where this has not been done the plate is usually a copper alloy. This must be prevented from suffering galvanic corrosion around the tubes. Tube plate coatings have been used with some success by the CEGB, but it is more common to use cathodic protection. This can be satisfactorily achieved with soft iron anodes. Where impressed current is used, a potential of -600 to -700 mV(SCE) is adequate to prevent corrosion and this will demand less current than a system designed to protect carbon steel.

Piping

There are three ways of protecting the anodic part of a galvanic couple in a piping system.

Sacrificial spool pieces

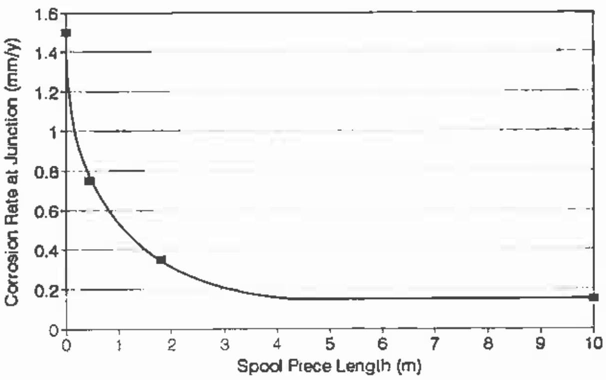
Sacrificial spool pieces have been considered for preventing the corrosion of copper alloy piping in contact with stainless steel. A carbon steel spool piece about five to six pipe diameters long is inserted between the copper alloy and stainless steel. The carbon steel requires a corrosion allowance such that frequent replacement is not necessary. These spool pieces can last for 1 to 2 years but routine replacement is required. Their use also results in iron corrosion products in the system, although this is not usually a problem as the products are usually soft and form films up to $\sim$1 mm thick on the piping downstream.

Isolation flanges

If the two pipe materials are electrically isolated from each other, no corrosion will occur on the anodic material. This can be done with an isolation flange: a thick, non-conducting insert between the two flange faces with special sleeves on the bolts to prevent electrical contact between the flange faces. However, there are two disadvantages to this approach. One is that the isolation sleeves on the bolts require careful assembly to work properly and must not be damaged in any way, i.e. skilled fitters are required. Second, in many plants electrical engineers require all piping to be earthed, especially on offshore platforms. Hence the use of an isolation flange will be completely negated when both pipes are strapped to the earthing line. This is a common occurrence in practice.[4]

Insulated spool pieces

An alternative method of preventing galvanic corrosion is to use a spool piece of the more noble metal, i.e. stainless



6 *Corrosion of carbon steel with different length spool pieces for NPS 10 pipe in natural sea water*

steel, and coat it both along the bore and on the flange face connecting to the less noble material. A wide range of coatings can be considered, such as neoprene, polyurethane, fusion bond epoxy, or glass flake. The critical factor is the length of the spool piece to ensure that any acceleration of corrosion of the anodic member of the couple is minimised. The data of Bardal *et al.*[9] show that for 90Cu–10Ni pipe in chlorinated sea water, it is possible to manage without a spool piece. However, in practice one is usually used in case the system operates without chlorine, in which case corrosion of the copper–nickel greatly increases.[9] It is common to use a spool piece five to six pipe diameters long and experience has shown this to be satisfactory.

Gartland and Drugli[8] looked at spool pieces for carbon steel to stainless steel pipe joints and found that a somewhat longer spool piece was required than for copper–nickel. Figure 6 shows how the maximum corrosion rate of the carbon steel (at the closest point to the stainless steel) is reduced as the spool piece length is increased. In practice, it is not necessary to completely prevent corrosion of the carbon steel, and the small increase in corrosion with a 2–2·5 m spool piece is usually acceptable.

The advantage of coating the stainless steel for the spool piece is that, even if the coating has defects in it, the increase in the cathodic area will be negligible and no extra corrosion will result. The use of an insulated spool piece is the most widely used method of joining dissimilar pipe materials, particularly on offshore platforms.

SERVICE EXPERIENCE

The following section relates some practical examples of galvanic corrosion from service.

The influence of graphite in seals and gaskets was described above. Amerada Hess experienced crevice corrosion of Zeron 100 (S39276) flanges with graphite loaded gaskets in a sea water system on the Ivanhoe/RobRoy platform. The flange faces were cleaned and replaced with non-graphite gaskets and the system has now been running for several years with no further problems.

Johnsen and Olsen[4] report the coupling of a copper-nickel column pipe to a super austenitic chlorinated sea water piping system on a North Sea platform. An insulation flange had been used, but the pipes were all earthed and so connected. After 5 years of operation no excessive corrosion of the copper–nickel had occurred.

An oil company has reported corrosion of copper–nickel pipes coupled to a titanium plate heat exchanger on a supertanker. Titanium is a more efficient cathode than stainless steel, but the problem was solved by using insulated spool pieces on the inlet and outlet which were lined with neoprene and were five pipe diameters in length. (The pipe size was NPS 12.)

Weir Pumps has supplied sea water pumps in super duplex stainless steel for many years. In the early days it was common to use castings for the casing and impeller, but the shaft was often made out of alloy K-500 (UNS N05500) and corrosion problems with some of these shafts led to failure. Initially these were in polluted water, to which K-500 is not resistant, but corrosion has also been seen on shafts handling clean sea water. Weir Pumps now considers that alloy K-500 is not galvanically compatible with super duplex stainless steel in sea water, and the shafts are now made of wrought Zeron 100.

An interesting case of galvanic corrosion concerned a duplex stainless steel pump with carbon steel end covers. To prevent corrosion of the carbon steel, both end covers had been coated. However, one of the end covers contained a drain plug which was also made of carbon steel. This corroded very rapidly and failed after a very short time. There was no simple solution to this problem: the use of a duplex stainless steel plug would transfer the corrosion to the threads on the carbon steel cover leading to a second failure. The problem was essentially one of design, and the end covers and plug should all have been duplex stainless steel.

OTHER MEDIA

This paper has so far been concerned solely with sea water. There are few data in other media, but recently Wilhelm has reported galvanic corrosion data for a number of alloys in process brines.[11] These covered four conditions: sweet brine, sour brine, packer fluid, and acidising fluid. The conclusions were similar to those in sea water, i.e. the coupling of alloys resistant to the fluid resulted in no galvanic corrosion. Coupling of duplex stainless steels to carbon steel produced only small increases in corrosion above uncoupled rates, e.g. an increase of 0·01–0·05 mm/year, in sweet brine with an anode to cathode area ratio of 1:4. Where both metals in the couple were corroding, large increases in corrosion of the metals occurred in addition to pitting. The component with the most severe corrosion was generally the one with the smallest area. Duplex stainless steels remained passive in sweet brine, sour brine, and packer fluid.

CONCLUSIONS

1. From a galvanic coupling point of view, the corrosion behaviour of all the high alloy stainless steels in sea water is similar.
2. High alloy stainless steel can be coupled to other passive alloys in sea water without galvanic corrosion.
3. Corrosion of copper–nickel pipes connected to high alloy stainless steels can be prevented by an insulated spool piece five to six pipe diameters long.
4. Corrosion of carbon steel pipes coupled to high alloy stainless steels can be prevented by an insulated spool piece 2–2·5 m long.

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