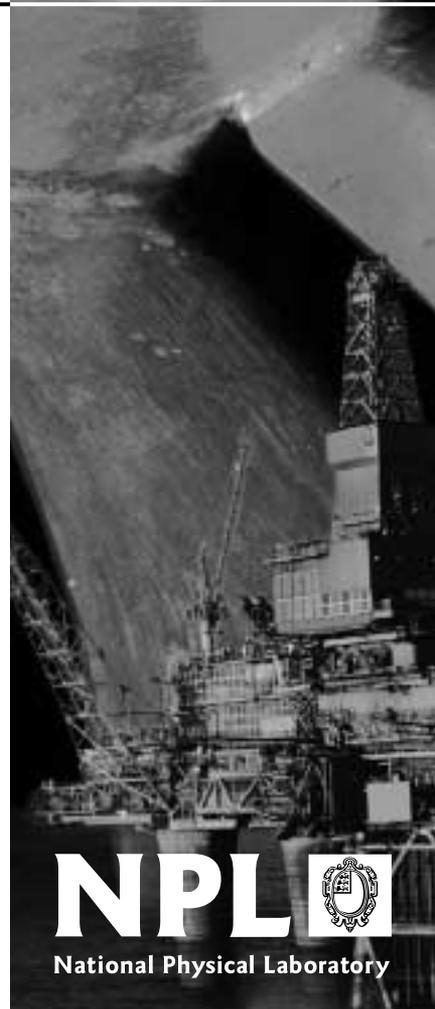Guides to Good Practice

in Corrosion Control

Bimetallic
Corrosion

NPL
National Physical Laboratory

Bimetallic
Corrosion

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1.0 Introduction

The purpose of this guide is to provide general information about bimetallic corrosion. More detailed information can be obtained from British Standards Institution Published Document PD6484: 1979 (1). Further advice on specific issues can be obtained from the organisations listed at the end of this guide.

When a metal is immersed in a conducting liquid it takes up an electrode potential (also known as the corrosion potential). This is determined by the equilibrium between the anodic and cathodic reactions occurring on the surface and it is usually measured with reference to a standard electrode such as the saturated calomel electrode (SCE).

Bimetallic corrosion occurs when two metals, with different potentials, are in electrical contact while immersed in an electrically conducting corrosive liquid, Because the metals have different natural potentials in the liquid, a current will flow from the anode (more electronegative) metal to the cathode (more electropositive), which will incease the corrosion on the anode, see Figure 1.
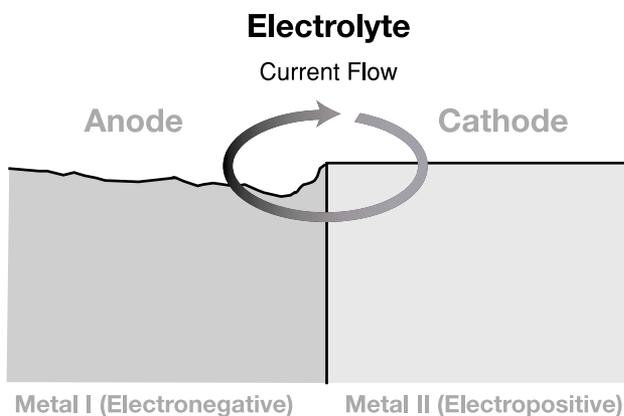
Electrolyte
Current Flow

Figure 1. Method of bimetallic corrosion

This additional corrosion is bimetallic corrosion. It is also referred to as a galvanic corrosion, dissimilar metal corrosion or contact corrosion.

In general, the reactions which occur are similar to those that would occur on single, uncoupled metal, but the rate of attack is increased, sometimes dramatically. With some metal combinations the change in the electrode potential in the couple potential can induce corrosion which would not have occured in the uncoupled state (e.g. pitting). In some environments the change in potential of the cathode in the couple can also introduce problems (e.g. hydrogen embrittlement).

The effect of coupling the two metals together increases the corrosion rate of the anode and reduces or even suppresses corrosion of the cathode. Hence, coupling a component to a sacrificial anode can prevent corrosion, and this is the principle of cathodic protection, which is discussed in a separate publication in this series.

When a metal is corroding two processes occur. One is the dissolution of metal at the anode (e.g. iron):

$$Fe \rightarrow Fe^{2+} + 2e$$

This must be balanced by a cathodic reaction. Most practical cases of bimetallic corrosion occur in solutions containing dissolved oxygen and in most neutral and alkaline liquids the primary cathodic reaction is the reduction of dissolved oxygen:

$$O_2 + 2H_2O + 4e \rightarrow 4OH$$

In acid liquids the cathodic reaction is often the reduction of hydrogen ions to hydrogen gas:

$$2H^+ + 2e \rightarrow H_2$$
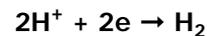
Other Cathodic reactions can occur in deaerated environments and one example is liquids containing hydrogen sulphide. There is a range of partially oxidised sulphur species (e.g. thiosulphate, dithionate etc.) and reduction of one or more of these species can be the principle cathodic reaction in corrosion e.g. in sour process brines in the oil and gas industry.

Under uncoupled corrosion the anodic and cathodic reactions occur at small, local areas on the metal. In a bimetallic couple the cathodic reaction is more, or totally, on the electropositive member of the couple and the anodic reaction is mostly, or totally, on the electronegative component of the couple.

In this guide reference is made to a number of common alloys in general engineering use. For those unfamiliar with these, the alloys are listed in Table 1 by alloy group, common name and nominal composition.

Table 1. Nominal composition of some common engineering alloys

Ferrous Alloys

NAME	NOMINAL COMPOSITION (wt%)						
	Fe	C	Cr	Ni	Mo	N	Others
Austenitic cast iron (flake)	Balance	2	2	15	-	-	Cu
Austenitic cast iron (spheroidal)	Balance	2	2	20	-	-	
13/4 martensitic	Balance	0.08	12.5	4	0.5	-	
17/4 martensitic	Balance	0.5	16.5	4	-	-	Cu
304 stainless steel	Balance	0.03	18	10	-	-	
316 stainless steel	Balance	0.03	17	10	2	-	
Alloy 20	Balance	0.03	20	28	2.5	-	Cu
Super Austenitic	Balance	0.02	20	18/25	6	0.2	(Cu)
22Cr duplex	Balance	0.02	22	5	3	0.16	
Super duplex	Balance	0.02	25	7	3.5	0.25	(Cu, W)

Copper Alloys

NAME	NOMINAL COMPOSITION (wt%)						
	Cu	Ni	Zn	Al	Fe	Sn	Others
Naval Brass	61	-	Balance	-	-	1	
CZR Brass	Balance	-	36	-	-	-	As, Pb
Aluminium Brass	76	-	Balance	2	-	-	As.
Gun metal (LG2)	Balance	-	5	-	-	5	Pb
Gun metal (LG4)	Balance	-	3	-	-	7	Pb
Phosphor bronze	Balance	-	-	-	-	5	P
Tin Bronze	Balance	-	-	-	-	10	P
Nickel aluminium bronze	Balance	5	-	10	4.5	-	
90/10 copper nickel	Balance	10	-	-	1.5	-	Mn
70/30 copper nickel	Balance	30	-	-	0.7	-	Mn

Nickel Alloys

NAME	NOMINAL COMPOSITION (wt%)						
	Fe	Cr	Ni	Mo	Cu	Al	Others
Alloy 400	2	-	65	-	Balance	-	
Alloy K-500	1.5	-	65	-	Balance	3	Ti
Alloy 825	Balance	2.1	40	3	2	-	Ti
Alloy 625	3	21	Balance	9	-	-	Nb
Alloy C-276	5	15.5	Balance	16	-	-	W
Alloy B-2	1	0.5	Balance	28	-	-	-

Aluminium Alloys

There are too many to list individually but the main groups of alloys and the chief alloying additions are listed below:-

1000 series - low alloy aluminium
2000 series - Al-Cu
3000 series - Al-Mn
5000 series - Al-Mg

6000 series - low alloy aluminium
7000 series - Al-Cu
8000 series - Al-Mn

2.0 Conditions necessary for bimetallic corrosion

The basic requirements necessary to cause bimetallic corrosion are:

1   An electrolyte bridging the two metals - which may not always be aggressive to the individual metals when they are not coupled, and may be in the form of a bulk volume of solution, a condensed film, or a damp solid such as soil, salt deposits, or corrosion products.

2   Electrical connection between the metals. This usually involves direct physical contact but it can also arise where electrical continuity is established between two metals, for example, by an insulation-coated conductor, by structural metal work or electrical earthing. It is not necessary for the metal junction to be immersed in the electrolyte.

3   A sufficient difference in potential between the two metals to provide a significant galvanic current.

4   A sustained cathodic reaction on the more noble of the two metals by one of the mechanisms described in the previous section; in most practical situations this is the consumption of dissolved oxygen.

3.0 Factors that effect the rate of corrosion

3.1 Electrode potential

The electrode potential is determined by many factors but the only fluid for which these factors are really well documented is sea water.

The value of the potential for any alloy, even in sea water, can be changed by a variety of factors such as temperature, velocity, biocide treatment etc. However, the relative ranking of alloys remains largely unchanged by these factors. A simplified version of the galvanic series is shown in Table 2. Alloys which are coupled to metals which have more electropositive potentials are the ones which may suffer bimetallic corrosion. Stainless steels, such as 316, have a thin, protective film and while this is intact corrosion rates are very low and the alloy is said to be in its passive state. When breakdown of the film occurs, usually localised, such as crevice corrosion, then the stainless steel is said to be active. Table 2 shows that the potentials of low alloy stainless steels,

Table 2
Simplified Galvanic Series in Sea Water

Electro Positive	Graphite	
	Platinum	
	Gold	
	High Alloy Stainless Steels	{Super Austenitic} {Super Duplex}
	Titanium	
	Nickel Chrome Molybdenum Alloys	{625; C-276}
	Low alloy stainless steels (eg 316)	(PASSIVE)
	Alloy 400/Alloy K-500	
	Silver	
	Nickel Aluminium Bronze	
	Copper nickel (70/30; 90/10)	
	Gunmetals/Tin Bronzes	
	Brasses	
	Tin	
	Lead	
	Austenitic Cast Iron	
	Low alloy stainless steels (eg 316)	(ACTIVE)
	Cast Iron	
Electro Negative	Carbon Steel	
	Aluminium alloys	
	Zinc	
	Magnesium	

such as 316, are very different in the active and passive states. Although the ranking in Table 2 was derived for sea water, it is very similar for many other near neutral aerated aqueous solutions, and thus may be used to assess the risk of bimetallic corrosion in these liquids.

However, the magnitude of the potential difference alone is not sufficient to predict the risk of bimetallic corrosion. For instance, metals with a potential difference of only 50 mV have shown bimetallic corrosion problems, while other metals with a potential difference of 800 mV have been successfully coupled together. The potential differences between the metals provides no information on the kinetics of bimetallic corrosion which depend upon the current flowing between them. There is a wide range of factors which affect the severity of bimetallic corrosion such as area ratio, temperature, flow rate, composition of the electrolyte etc. The important ones are discussed below.

A general idea of the qualitative risk of bimetallic corrosion can be gained by putting these effects together into a form such as Figure 2. This is not meant to be rigorous but gives a guide to acceptable and potentially dangerous combinations.

Metal being considered (a) \ Metal in Contact	Magnesium	Zinc	Aluminium alloys	Carbon Steel	Cast iron	Lead	Tin	Austenitic Cast Iron	Brasses	Gunmetals / Tin Bronzes	Copper Nickel Alloys	Nickel Aluminium Bronze	Alloy 400/K-500	Low alloy stainless steel	Nickel-chrome moly alloys	Titanium	High Alloy Stainless Steel	Graphite
Magnesium																		
Zinc																		
Aluminium alloys																		
Carbon Steel																		
Cast iron																		
Lead																		
Tin																		
Austenitic Cast Iron																		
Brasses																		
Gunmetals / Tin Bronzes																		
Copper Nickel Alloys																		
Nickel Aluminium Bronze																		
Alloy 400/K-500																		
Low alloy stainless steel																		
Nickel-chrome moly alloys																		
Titanium																		
High Alloy Stainless Steel																		
Graphite																		

Legend: Additional corrosion unlikely | Additional corrosion may occur | Additional corrosion possible

Figure 2. Risk of additional corrosion from bimetallic contact in neutral aqueous electrolytes.
[Each of the two metals must be read aginst the other. the degree of corrosion always refers to the metal on axis A]

Even potentially dangerous combinations may be made to work in service if appropriate steps are taken at the design stage to minimise the risk. More details on the likely behaviour of bimetallic couples are given in the extensive tables in reference 1. Note: Unalloyed aluminium is anodic towards most copper containing aluminium alloys. At the junction between the two, the alloy is often protected at the expense of the aluminium.

3.2   Electrode efficiency

Current flow between the two metals in contact is accompanied by a shift in the potential of the anode to a more electropositive value and in the potential of the cathode to a more electronegative value. These changes, called polarisation, result in the two metals approaching the same potential, any potential difference between them being equal to the product of the current and the resistance through the electrolyte. The extent of polarisation depends upon both the metal and the environment. In neutral electrolytes the cathode is almost always polarised much more than the anode, which accounts for the fact that a small area of sacrificial anode will effectively provide protection to a relatively large cathodic area. The extent of polarisation will determine how effective any particular metal may be as a cathode.

Some metals, such as titanium, are not very efficient at reducing dissolved oxygen compared with copper alloys. So it is possible for a less noble metal to corrode more if coupled to a copper alloy than to titanium, despite titanium being much more electropositive.

3.3   Variable potential

Changes in the corrosion potential of individual metals and, therefore, in the polarity of a couple, from commonly encountered values can result from the presence of complexing ions, from changes in pH and temperature, and from intense aeration which enhances film formation on the (hitherto) anodic metal. Large differences in area ratio, especially with metals of nearly the same corrosion potential, can also influence the relative polarity of metals by causing intense polarisation. Tin is usually cathodic to iron in neutral salt solution, but in the presence of the complexing organic acids found, for instance, in fruit preservation, it is anodic and therefore an effective sacrificial coating for 'tin' cans. Lead, tin, and their solder alloys form soluble corrosion products in alkaline solutions and are anodic to iron, whereas in acid solutions they are usually cathodic to iron.

Non-oxidising acid solutions can cause breakdown of the natural oxide film on passive metals; for example, in oxalic acid, titanium can be anodic to stainless steel and in concentrated sulphuric acid it is anodic to aluminium.

Reversals of significant practical importance are encountered with zinc and aluminium, which are usually anodic to iron in natural waters. At temperatures above 60°C iron becomes anodic to zinc, which explains why problems are sometimes encountered in galvanised steel hot-water systems. In fresh waters, polarity reversal is enhanced by the presence of bicarbonate and decreased by sulphate and chloride. The aluminium/iron couple undergoes polarity reversal at elevated temperatures in fresh water and in sea water (about 95°C) and the aluminium/zinc couple exhibits polarity reversal in seawater at about 90°C.

3.4   Electrolyte

Electrolyte factors that have a major influence on bimetallic corrosion are composition, pH and, in particular, electrical conductivity, which affects both the intensity and distribution of corrosion.

The severity of corrosion often increases with increasing electrical conductivity of the electrolyte because, in practice, high conductivity is often caused by the presence of aggressive ions such as chloride, or by acid or alkali.

The electrical conductivity of electrolytes can vary widely: typical values are as follows:

Distilled water	0.5 - 2 μS/cm
After storage	2 - 4 μS/cm
Supply water	50 - 1,500 μS/cm
Saturated sodium chloride solution	250,000 μS/cm
Sulphuric acid	up to 8,000,000 μS/cm
Molten salts	20,000 - 107 μS/cm

Except for very critical items of equipment such as electronic components and where it is essential to suppress metal dissolution, bimetallic corrosion is seldom a problem in pure water.

In a solution of inherently low conductivity (or when the metals are covered with only a thin film of a highly conducting electrolyte), corrosion is confined to an area near the junction between the two metals and, while the total amount of corrosion may be low, it is likely to be relatively localised and therefore may also be intense. Corrosion will still be more intense at the metal junction than elsewhere in a highly conducting solution but it will also be more widespread. Intense corrosion is likely to arise even with nominally pure water under condensing conditions if the atmosphere is polluted with acid gases such as sulphur dioxide, or with salt, for example at industrial or sea-coat locations.

In common with local-cell corrosion, bimetallic corrosion is sensitive to the presence of constituents in the electrolyte that effect stability of the corroded-metal ions. Thus, with lead the presence of bicarbonate, silicate and sulphate in water enhances formation of insoluble and adherent corrosion products. In some cases insoluble corrosion products from the anodic metal can deposit upon, and induce crevice corrosion of, the cathodic metal of a couple; stainless steels are susceptible to this type of corrosion, especially when in contact with aluminium or mild steel. In some cases the composition of the environment can be modified by adding inhibitors to control both local-cell and bimetallic corrosion. This practice has proved effective in the treatment of waters in engine cooling systems and industrial cooling plants. Bicarbonate, cyanide and tartrate ions form soluble complexes with copper and zinc, and thus their presence increases the rate of corrosion.

The effect of pH is even more far-reaching and depends upon the composition of both metals forming the couple. In the case of magnesium and its alloys there is a possibility of a significant amount of hydrogen evolution at the cathode in neutral solutions. Enhancement of the corrosion rate starts as pH is decreased to about 4-5 for aluminium and ferrous alloys, and at about pH6 for zinc. At pH1, hydrogen evolution is the predominant reaction on the cathode of most coupled metals and bimetallic corrosion rates may be increased by two to three orders of magnitude compared with those in neutral solutions. In sulphuric acid, however, much smaller increases in corrosion rate are encountered with lead because of the formation of films of insoluble lead sulphate.

Hence, care is required if hydrogen evolution is occurring and the cathode material is susceptible to hydrogen embrittlement.

Low pHs can also occur between two tightly coupled metals when one undergoes crevice corrosion (e.g. 316 and super austenitic stainless steel in sea water). The pH can become so low (<1) that corrosion initiates on the cathode within the crevice.

3.5 Area ratio

The area ratio is very important in the consideration of the likelihood of bimetallic corrosion. The larger the cathode compared to the anode, the more oxygen reduction can occur and, hence, the greater the galvanic current and, therefore, corrosion (see Figure 3).
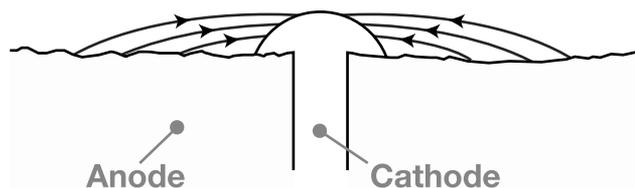
A) Large anode area, small cathode area showing relatively insignificant attack over a wide area of sheet.
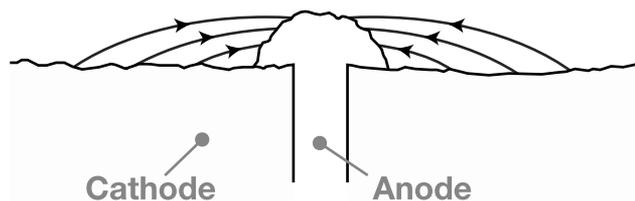
B) Large cathode area, small anode area showing relatively pronounced attack of the rivet head.

Figure 3. Effect of area ratios of bimetallic corrosion

Under static conditions, where the bimetallic corrosion current is often dependent upon the rate of diffusion of dissolved oxygen to the cathode, the amount of bimetallic corrosion is independent of the size of the anode and is proportional to the area of the cathodic metal surface. This is sometimes known as the catchment area principle, and has important implications in designing to minimise the risk of bimetallic corrosion. Thus, for a constant area of cathode metal the amount of corrosion of the anode metal is constant, but the intensity of corrosion is increased as the area of the anodic metal is decreased.

If the electrical conductance of the electrolyte bridging the bimetallic contact is low, either because the bulk conductivity is low or because the electrolyte is present only as a thin film, the effective areas taking part in bimetallic cell reactions are small and the total corrosion is relatively small, although it may be severe immediately adjacent to the metal junction.

Under immersed conditions in many supply waters, which have a relatively low electrical conductivity, adverse effects are uncommon if the contacting metals adjacent to the junction are of similar area. Thus, galvanised steel pipes can be used with brass or gunmetal connectors, but serious corrosion to the pipe end is likely to result if the contact is directly to a large area of copper, such as a tank or cylinder. Similarly, stainless steel and copper tubes can usually be joined without problems resulting, but accelerated corrosion of the copper tube is likely to occur if it is attached to a stainless steel tank (see Figure 4).

Figure 4. Accelerated corrosion of a copper tube attached to a stainless steel tank

Adverse area ratios are likely to occur with fasteners and at joints. Weld, braze or rivet metal should be of the same potential or, better still, cathodic to the base or parent metal. For example, the use of mild steel rivets to fasten nickel, copper or stainless steel plates should be avoided.

Under immersed conditions in a highly-conducting electrolyte, such as sea-water, effective areas will be greater, and severe corrosion may be encountered on small anodic areas of many metals.

Extremely small anodic areas exist at discontinuities such as cracks or pinholes in cathodic coatings such as magnetite (millscale) on iron and copper plating on steel. Where electrolyte conductivity is high it is necessary to apply protection or, in the case of metal coatings, to specify a thickness of adequate

integrity. Similar considerations apply to pores or defects in a paint coating if the metal is in contact with a more electropositive metal, i.e. the cathode to anode area ratio is dramatically increased compared with bare metal.

By correct selection of area ratio, dissimilar metals have frequently been used successfully together in sea water. One example is the use of 316 pump impellers in austenitic cast iron pump casings. Another is the use of high alloy trim (seats, stems etc.) such as alloy 625, alloy K-500 etc. with gun metal or aluminium bronze valve bodies. In both cases the large area of the anode compared to the cathode means that the increased corrosion is small and is well within the design limits for the unit.

3.6   Aeration and flow rate

The majority of practical situations involving bimetallic corrosion arise in aqueous solutions under conditions where the cathodic reaction is reduction of dissolved oxygen. As with single metal corrosion, bimetallic corrosion is therefore partly dependent upon the rate at which oxygen can diffuse to the surface from the bulk of the electrolyte.

The bimetallic corrosion rate of many copper-based and nickel-based alloys, and of stainless steels in sea-water, depends upon the flow rate of the water as well as on the area ratio. Copper and copper-nickel alloys tend to become less noble with increasing flow rate and to corrode more, while nickel alloys and stainless steels become more noble and corrode less. In well-aerated flowing solutions nickel alloys and stainless steels are also likely to become passive and corrode less.

Noble metals such as platinum, silver and copper, on which the naturally formed oxide films are very thin and are readily reduced to metal, act as efficient cathodes without polarising and therefore tend to promote bimetallic corrosion. However, aluminium, stainless steel and titanium have a stable oxide film and tend to polarise; in flowing, aerated electrolyte the oxide film is likely to thicken, thus diminishing bimetalic corrosion of the coupled metal even further.

In neutral electrolytes complete de-aeration will, in many instances, suppress single-metal and bimetallic corrosion. However, under such anaerobic conditions cathodic depolarisation and corrosion can occur if sulphate-reducing bacteria are present.

3.7 Metallurgical condition and composition

In some cases differences in corrosion potential can exist between coupled metals or alloys of nominally the same composition. Subjection to cold working often tends to make a metal/alloy more anodic. In some alloys heat treatment can produce galvanic differences; for example 2014 aluminium copper alloy in the artificially aged condition is anodic to the same alloy in the naturally aged condition. Such conditions account for this risk of bimetallic corrosion on contact between aluminium alloys as indicated in Figure 2.

Local changes in composition can also arise at joints made by welding, both in the weld bead and in the heat affected zone of the parent metal. Problems are usually avoided by selecting the appropriate filler metals and welding techniques, or in some cases, by painting the joints. Figure 5 shows preferential corrosion of the weld in a carbon steel pipe handling partially deaerated sea water ($O_2 \sim 0.1$ mg/L). The welding operation produced a weld bead which was ~50 mV electronegative to the parent metal, and the large area of the cathode resulted in rapid corrosion of the weld metal.

Figure 5. Preferential corrosion of a weld in a carbon steel pipe

Bimetallic corrosion can occur between alloys of similar type but somewhat different composition; thus 90/10 cupro-nickel can be anodic to 70/30 alloy, austenitic stainless steels are cathodic to the martensitic type, and austenitic cast iron is more cathodic than, and can induce corrosion of, other types of cast iron. Cast iron that has become graphitised will induce additional corrosion of non-graphitised alloy i.e. the surface of the cast iron is essentially just graphite which is strongly electropositive to most metals.

3.8 Stifling effects

In general the rate of corrosion of coupled and non-coupled metals decreases with time of exposure. This is partly due to the diminishing rate of diffusion of oxygen through the electrolyte and through films of corrosion product to cathodic regions and, partly owing to the protection afforded to anodic regions by the corrosion product. To some extent, therefore, the bimetallic corrosion rate is affected by the permeability of the corrosion product. In sea-water and, to a lesser extent, in hard supply waters, the alkaline conditions produced at he cathode result in the formation of calcareous deposits of calcium and magnesium carbonates and magnesium hydroxide which may decrease the rate of bimetallic corrosion. With steel, for example, corrosion is decreased by one order of magnitude after less than a year's exposure. Where corrosion products are water-permeable or hygroscopic, however, their presence can sometimes increase the rate of bimetallic corrosion, either because they are more aggressive than the bulk environment or because they maintain wet conditions at the metal surface.

4.0 Bimetallic corrosion without physical contact

Localised corrosion of a metal may give rise to soluble corrosion products which deposit by a displacement reaction onto a less noble metal exposed in the same solution and form local, intense bimetallic cells. This is particularly evident with the more electropositive metals such as copper, and problems have been encountered in water-heating systems as a result of copper dissolving from pipework and depositing onto steel radiators, aluminium alloy sinks and pump impellers, and galvanised tanks. Insulation of joints between dissimilar metal components is not necessarily a safeguard if cuprosolvent water flows or diffuses from copper to aluminium parts of the system. Similar problems can also be encountered with aluminium in the near vicinity of steel under conditions where the iron corrosion products flow over the aluminium and are deposited as strongly cathodic magnetite or where alkaline solution formed at the steel cathode flows onto the aluminium.

Copper can also cause corrosion of steel and galvanised steel, particularly in warm or hot water. Hence, it is usual to specify that copper and its alloys may be used downstream of galvanised steel but not vice versa.

In plant and equipment that involves recirculated electrolyte such as vehicle cooling systems, central heating systems and industrial heat exchangers, this type of problem can sometimes be avoided by removing oxygen from the system or by adding inhibitors.

Caution is also necessary when chloride-containing waters flow from lead to aluminium surfaces and pitting of an aluminium roofing sheet has been reported as a result of contact with lead salts leached from lead-containing paints.

5.0 Bimetallic corrosion in some common environments

5.1 Introduction

From an engineering point of view, it is helpful to consider bimetallic corrosion of some common engineering materials in frequently encountered service environments.

5.2 Sea water

Although the comments in this section refer to sea water they can be applied more or less across the board to all near neutral aerated waters with 3 g/L chloride or more.

In sea water the corrosion data show that the commonly used alloys can be collected into four groups, as shown in Table 3.

Table 3. Corrosion date of 4 groups

GROUP	TYPE	ALLOY
1	Noble; Passive	Ni/Cr/Mo alloys (Mo>7) Super Austenitic Stainless Steel Super Duplex Stainless Steel Titanium and its alloys
2	Corrosion Resistant; Susceptible to Crevice Corrosion	22 Cr Duplex Stainless Steel Alloy 825 Alloy 400 Alloy K-500 316
3	Moderate Corrosion Resistance	Copper alloys Austenitic Cast Iron
4	Poor Corrosion Resistance	Carbon Steel Cast Iron
		Aluminium Alloys

Group 1 are all passive alloys which adopt electropositive potentials in sea water. The nickel alloys include alloy 625 and C-276, while the super austenitic and super duplex stainless steels have PREN values, where PREN (the pitting resistance equivalent number) = % Cr + 3.3% Mo + 16%N, exceeding 40.

Group 2 includes alloys which have low corrosion rates but are susceptible to crevice corrosion in sea water. These alloys are only used when coupled to an alloy from group 3 or 4, where the anodic metal effectively protects the group 2 alloy from crevice corrosion. This assumes a suitably large ratio of anode area to cathode area.

Group 3 covers alloys with moderate corrosion resistance and essentially comprises the copper alloys, although austenitic cast iron can be included in this group. It includes single phase brasses (eg aluminium brass) but the inclusion of those containing beta phase, e.g. naval brass and manganese bronze, is debatable. This is because brasses containing beta phase will dezincify in sea water and this can be exacerbated when coupled to a more noble alloy from groups 1 or 2 or even when coupled to 70/30 copper nickel.

Group 4 includes alloys of low corrosion resistance. It has been subdivided to separate the aluminium alloys from the steels and cast irons because of the variable effects which can occur in couples depending upon alloy composition. The Al-Mg alloys (5000 series) generally form protective films in sea water and can be coupled to iron or steel if the area ratio is not too adverse. However, alloys such as the 7000 series can suffer pitting and stress corrosion cracking which can be exacerbated by a bimetallic couple. Hence couples between these two subdivisions of group 4 must be examined on a case by case basis. The rules for selecting alloy compatibility are, subject to the exceptions above;

1) **Alloys within each group can be coupled together with no significant problems.**

2) **When coupling an alloy to one from a higher group a high anode to cathode area ratio (e.g. valve trim) or a generous corrosion allowance is needed, unless measures are taken to avoid bimetallic corrosion (see next section).**

Two materials not included in Table 3 are zinc and magnesium. Both of these corrode rapidly in seawater and coupling to any more noble alloy will increase the dissolution rate. Zinc is sometimes used as a sacrificial anode to provide cathodic protection. Magnesium is not normally used in this application because its corrosion rate is very high and substantial quantities of hydrogen are evolved on the cathode, increasing the risk of embrittlement.

Another material not included in Table 3 is graphite, which can be a part of seals and gaskets. Both laboratory tests and service experience show that where the graphite is wetted, bimetallic corrosion of the adjacent metal is likely to occur, leading to leaks. Hence graphite-containing seals and gaskets should be avoided.

Spiral wound metal gaskets are often used with flanges and it is important not to use a gasket of a group 2 alloy in a piping system of a group 1 alloy. This has caused failure at some flanged joints on offshore oil and gas platforms.

When using alloys from groups 1 and 2 there is another factor to take into account, and this is the cathodic efficiency. In natural sea water at ambient temperature, a thin biofilm forms on these alloys which results in very electropositive potentials and, more importantly, a very efficient reduction of dissolved oxygen. Both affects promote bimetallic corrosion. In systems where the water has been heated to 25°C - 30°C above ambient the biofilm does not form and cathodic reduction of dissolved oxygen is 2 to 3 orders of magnitude less efficient. If chlorine is injected in small quantities (0.5 to 1.0 mg/L) to prevent bio-fouling, the potentials increase still further, but the cathodic reaction is now the reduction of hypochlorite to chloride. This is one to two orders of magnitude less efficient than the reduction of oxygen by the biofilm.

Hence, in hot sea water or chlorinated sea water, the reduced rate of the cathodic reaction means that the extent of bimetallic corrosion is substantially reduced compared with that in natural seawater.

An example of this is super duplex stainless steel coupled to nickel aluminium bronze. Figure 6a shows couples with a cathode/anode area ratio of 10:1 after 63 days immersion in natural seawater. The substantial galvanic corrosion of the
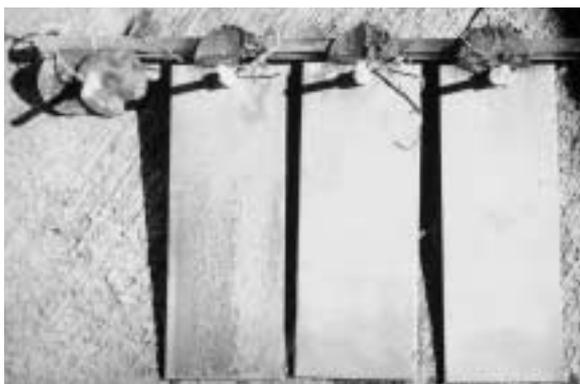

Figure 6a. Couples with cathode/anode area ratio of 10:1 after 63 days in natural seawater
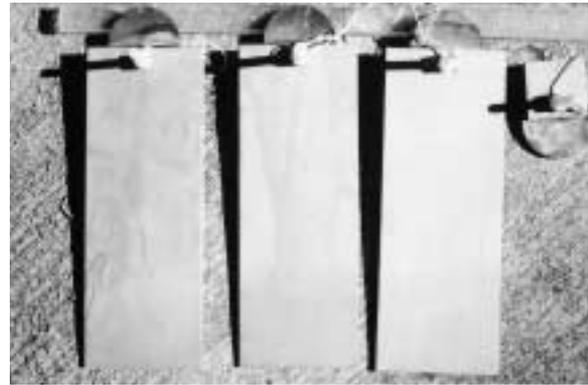

Figure 6b. Couples with cathode/anode area ratio of 10:1 after 63 days in chlorinated seawater

bronze adjacent to the joint is clearly visible. In contrast the samples exposed to chlorinated seawater (Figure 6b) show little or no attack. This clearly demonstrates the difference in the cathodic efficiency. Similar results have been produced for super austenitic stainless steel coupled to 90/10 copper nickel (2,3).

5.3   Atmospheric environments

Because an electrolyte is a necessity for corrosion it tends to occur where rainwater and/or condensation cannot run off or becomes trapped.

As with fully immersed conditions, the tendency for bimetallic corrosion to occur in atmospheric environments increases with increasing conductivity of the electrolyte bridging the coupled metals. However, corrosion is usually more localised at the metal junction than under immersed conditions.

The severity of the environment depends upon general and local climate conditions; it is low in dry or low-humidity regions, moderate in temperate and semi-arctic regions and in open rural locations; and greatest in tropical and marine locations of high humidity and in polluted industrial atmospheres.

With the exception of couples involving magnesium, aluminium, zinc and low-alloy or carbon steels, the additional corrosion in environments of low to moderate severity is often negligible unless contact is with carbon or a precious metal. Due consideration must be given to local conditions, however, as the electrical conductivity of rain water or condensation is increased by pollution with fuel-combustion products, fertilizers and road salt, which produces aggressive conditions in a nominally clean atmosphere.

Bimetallic corrosion at sea-coast locations is usually more severe than at industrial/urban locations, and the effect is similar to that experienced under fully-immersed conditions in a low-conductivity electrolyte with small, equal areas of dissimilar metals in contact.

The general behaviour of metals in bimetallic contact in rural, industrial/urban and marine environments is fully documented in PD 6484 (1). Information which is specific to electrical power equipment, but also summarises the service experience with a wide range of metallic and non-metallic protective coatings on aluminium, copper and steel under different climatic conditions, is contained in CP 1014 (4).

5.4   Buried and embedded metals

In general, the behaviour of metals in contact in soils is similar to that under immersed conditions in water. The quantitative effect depends upon a number of factors including moisture content, pH, salt content, permeability to oxygen, and electrical conductivity, of which the last is of major importance. Soils are regarded as aggressive if the electrical conductivity is greater than about 1000 μs/cm. Bacterial activity can be a significant factor in poorly-aerated, waterlogged soils and the presence of sulphate can sustain a cathodic reaction by sulphate reducing bacteria.

Other microbial systems can have corrosive effects by producing sulphuric and organic acids, or organic and inorganic sulphides, or by oxidising and removing nitrogen-containing inhibitors, thus increasing the corrosiveness of the environment and the amount of bimetallic corrosion. Behaviour of coupled and uncoupled metals varies widely in soil because of the wide range of environmental conditions encountered. Satisfactory performance may be encountered with apparently incompatible metals because of passivation or stifling resulting from the precipitation of insoluble salts by local alkalinity.

However, severe corrosion has been encountered - and, in general, protective measures are necessary to avoid problems - where ground water has a high conductivity, for example with lead/copper and copper/iron pipe junctions. From a consideration of area ratio effects it is evident that failure of bolts is likely to precede that of structures to which they are attached unless they are made of materials which are cathodic to the larger area of metal.

Soil analysis is not a completely reliable guide to the likely

behaviour of coupled metals, and specialised advice based upon service experience should be sought.

Corrosion of metals embedded in concrete is often not significantly affected by contact with a second embedded metal; aluminium for example, tends to form a surface film when coupled to steel in the alkaline environment of concrete, plaster and mortar. Behaviour will depend upon the permeability to water and air and the salt content of the concrete, and corrosion is more likely to occur where the concrete is damaged. Special care is necessary when attaching inserts to reinforced concrete to avoid making direct contact with steel reinforcing bars.

5.5   Acids and alkalis

Alkalis are used in a range of industrial processes, for example from 4 wt% to 70 wt% caustic soda at temperatures up to 250°C. There are no published data on galvanic corrosion in alkalis but, because of the risk of caustic cracking under coupled conditions with many metals, it is advisable to carry out testing or seek previous experiences with such couples.

In most acids, particularly the mineral acids, corrosion rates can be high and the tendency is to select high alloy materials which resist corrosion. However, couples between different alloys can produce a variety of effects which are not seen in other electrolytes. A galvanic series has been produced for some acids (5) but it is of limited value for the following reason. The corrosion resistant alloys used in acids are usually in their passive region, but at lower potentials these can move into the active region where general dissolution occurs (Figure 7). An example of this was a super duplex stainless steel basket in 20% sulphuric acid at 50°C in a plant producing
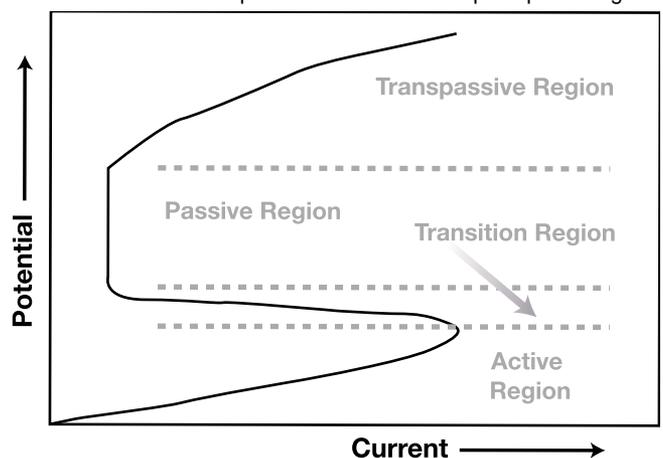

Figure 7. Location of passive, transpassive, transition and active region.

titanium dioxide from ilmenite ore. Scrap steel cubes were tossed into the basket to keep the acid reducing throughout the process but this resulted in corrosion of the basket from the inside. This was because the potential of the stainless steel adjacent to the carbon steel was depressed into the region where active dissolution occurs. There was no simple alloy change to cure the problem and it was solved by using a thick polypropylene basket inside the stainless steel to prevent contact with the steel.

Another possibility may arise on coupling two corrosion resistant alloys, the anodic one having its uncoupled potential in the active region. When coupled the corrosion rate of the anodic alloy can be reduced if its potential is being moved into the transition region (Figure 7). The electropositive member of the couple may suffer no corrosion if it remains in its passive zone, but corrosion could occur if its potential is moved into the transition zone or active zone. This would create a siutation where the corrosion on the anode decreased and the corrosion on the cathode increased (6).

As the performance of metals in acids can change dramatically with acid concentration, temperature, and the presence of small quantities of other chemicals, it is imperative that alloy performance be evaluated under conditions as close to the expected service conditions as possible.

5.6 Oil and gas process fluids

Concern about environmental cracking in oil and gas environments means that alloys for new developments are chosen carefully and galvanic corrosion in the process fluids is not usually a major problem.

This is an area which is not well researched, but the increasing development of marginal fields, with more corrosive process fluids, and tie-ins to old field lines designed for mildly corrosive fluids, opens the possibility for galvanic corrosion at these junctions.

A number of laboratory studies (7,8,9) have looked at galvanic corrosion, mostly in sweet brines. Wilhelm (7), however, also carried out tests in a sour brine i.e. one contaminated by hydrogen sulphite, a packer fluid and a simulated acidising fluid.

All the workers concluded that, in process fluids (sweet and sour), the greatest corrosion occurred when both metals were active. Coupling passive to active alloys also caused increases

in corrosion of the active alloy. The increase was no more than doubling of the corrosion rate, with equal area ratios, or up to three times the corrosion rate at a 4:1 area ratio of passive to active alloy. This suggests that cathodic reactions under these conditions are not very efficient compared to the reduction of dissolved oxygen in sea water. Coupling of two passive alloys together produced no additional corrosion when both alloys remained passive.

The problems at dissimilar metal joints can mostly be solved by increased corrosion allowances or by the use of inhibitors.

One significant risk is downhole when a corrosion resistant alloy (CRA) is in contact with carbon steel e.g. the well casing on production tubing. Although the CRA is the cathode in such a couple, evolution of hydrogen is the cathodic reaction and hydrogen embrittlement can occur. Embrittlement under such conditions has been reported for duplex stainless steel tubulars and alloy K500 drill collars.

5.7 Non-Aqueous environments

Behaviour in molten salts and anhydrous non-aqueous fluids such as liquid ammonia, liquid sulphur dioxide and conducting organic compounds can sometimes differ significantly from that in aqueous environments. Unfortunately, very little information on this subject has been published and it is usually necessary to search the relevant specialised literature and deduce likely behaviour from data on non-coupled metals and electrode potentials.

As with aqueous systems, the severity and extent of bimetallic corrosion will depend partly upon electrical conductivity, which for molten salts can be very high.

6.0 Prevention

The extent to which bimetallic corrosion is likely to occur and the selection of counter-measures should be considered at the design stage. Ideally, metals should be selected that are close to each other in the galvanic series, but engineering requirements for different material properties in various parts of equipment or an installation often necessitate the use of several different metals.

A major consideration, however, is to identify the composition and conductivity of the environment, since these will play a

significant role in defining the extent and severity of any corrosion. Other objectives are to maximise the area of the anodic metal and minimise that of the cathodic metal. Experience in similar situations should be sought where possible because it is not uncommon for dissimilar metals to be coupled without adverse effect, especially when the electrical conductivity or oxygen content of the electrolyte is low.

Under immersed conditions in static or slowly moving aerated electrolyte, the catchment area principle (see Section 3.5) can be usefully applied to assess whether intense corrosion will arise, but it becomes less influential as the electrical conductivity of the electrolyte diminishes, because the effective area of the cathode is then less than its geometric area. The catchment area principle does not often apply in atmospheric environments, and design considerations are then more important to effect good drainage and thus minimise accumulation of condensation and rain-water at joints and in hollow sections (Figure 8).
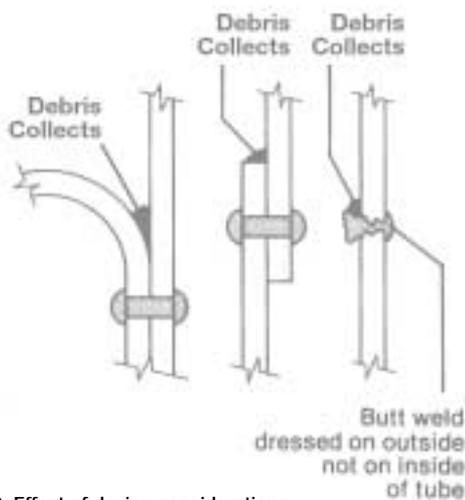

Figure 8. Effect of design considerations

Methods of preventing or minimising bimetallic corrosion are based upon breaking the electrical path in the metallic or electrolyte parts of the system, by excluding oxygen from the electrolyte, by adding inhibitors to the electrolyte, and by sacrificial corrosion.

Electrical insulation can be achieved by the use of plastic bushes and washers such as nylon or PTFE or impervious plastic or rubber gaskets (Figure 9). Plastic pipework and fittings are now commonly used in chemical plant and supply-water installations. Bimetallic contact is not a problem in structures in the atmosphere if insulating washers are applied to break the conducting path through the water layer; joint
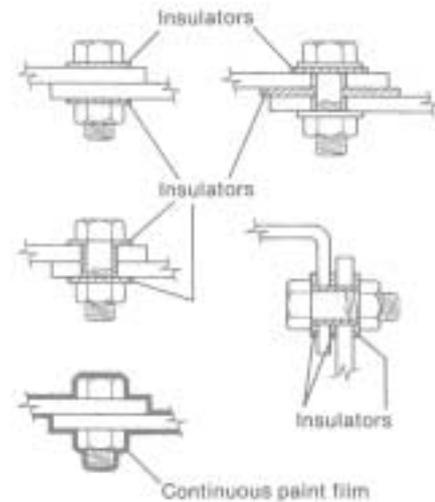

Figure 9. Methods of electrical insulation

overlays that extend the path are also effective if the conductivity of the water is low. Despite confidence based on design considerations that bimetallic corrosion will not arise, electrical insulation should be confirmed when equipment is brought into service. It is not unknown for subsequent modifications to a system or in its vicinity to result in electrical connections between nominally insulated components. Be aware that it is often a safety requirement for all equipment to be earthed. This is common in chemical plant and on offshore platforms and completely negates any attempt at insulation. An example is the separation of dissimilar metal pipes with an insulated flange coupling. Both sides of the flange can still be connected if both are connected to earth. The use of coated spool pieces and other methods of separating dissimilar metal pipes are discussed in detail by Francis (10).

Similar considerations also apply to verifying the conductivity of the electrolyte. For instance, flux residues can promote bimetallic corrosion in otherwise non-aggressive electrolytes, and joints should be thoroughly cleaned after assembly.

Jointing compounds applied to the contacting surfaces of fasteners and lap joints do not normally provide electrical insulation. They are very useful, however, in excluding water from the joint and thereby preventing bimetallic (and crevice) corrosion within the joint, and the exuded flexible fillet will prevent cracking of subsequently applied paint along the line of the joint.

A wide range of paint and taping systems are available for protecting metals; paints can contain inhibitors or sacrificial

metals such as zinc. Ideally both members of a bimetallic couple should be painted, but where this is impracticable the cathodic member should be coated in preference; treating only the anodic metal increases the risk of severe localised bimetallic corrosion at any defect in the coating. Metal coatings can be applied by electroplating, dipping or spraying to give close identity with the second metal; an example is the aluminium coating of steel in contact with aluminium. Alternatively compatibility between two metals can be obtained by coating one of them with a third metal such as zinc or cadmium. In some cases it is preferable to coat both metals with a third metal. In industrially polluted atmospheres zinc coatings on steel are superior to those of cadmium, while the latter are preferred where high humidity and condensation occur.

Apart from their use in jointing compounds, the application of inhibitors is generally limited to certain recirculating water systems. An exception to this is in the oil and gas industry with carbon steel piping containing wet gas or wet process brines. Inhibitors are often injected to reduce corrosion of the carbon steel and this will also minimise corrosion at bimetallic junctions. Galvanic action in systems containing copper can sometimes be controlled by a specific inhibitor such as benzotriazole.

In the case of microbial corrosion, materials can be protected by coating with resistant synthetic polymers or inhibited paints, by dosing with biocides or by designing to avoid conditions that favour microbial growth.

7.0 Checklist

In situations where contact between dissimilar metals cannot be avoided the following steps should be considered:

Select metals that are close together in the galvanic series for the particular environment.

Avoid relatively small areas of the less noble metal and large areas of the more noble metal.

Insulate the metals from each other or separate them with internally coated spool pieces.

Exclude electrolyte from around the bimetallic junction, for example, by painting or taping.

Paint both metals where possible; where impractical, paint the more electropositive metal (cathode).

Make extra allowance for corrosion by increasing the thickness of the electronegative metal.

Apply compatible metal or sacrificial metal coatings.

In equipment containing dissimilar metals that are not in contact, ensure that localised corrosion does not result from deposited noble metals such as copper, by inhibiting the electrolyte or by coating susceptible surfaces.

If electrical insulation is adopted, check that it is effective after installation of equipment is complete.

With critical items of plant and equipment, include electrical insulation checking in routine inspection schedules.

8.0 References

1) **PD6484: 1979 Commentary on Corrosion at Bimetallic Contacts and Its Alleviation, British Standards Institution.**

2) **E. Bardal, R. Johnsen and P.O. Gartland Corrosion 40 (1984) 12.**

3) **R. Johnsen and S. Olsen Paper 397, Corrosion '92; Nashville, USA, April 1992, NACE.**

4) **CP1014: 1963 Protection of Electrical Power Equipment Against Climatic Conditions. British Standards Institutions.**

5) **J.R. Crum, 'Development of a Galvanic Series in Various Acid and Water Environments'. Int. Conf. Corros. of Nickel Base Alloys, ASM, Ohio, 1984.**

6) **G.O. Davis, J. Kolts and S. Sridhar, Corrosion 42, 6 (1986) 329.**

7) **M. Wilhelm, Paper 480; Corrosion '92 Nashville, USA, April 1992, NACE.**

8) **T. Hara, H. Asahi and H. Kaneta, Paper 63; Corrosion í96; Denver, USA, March 1996, NACE.**

9) **T. Hara, H. Asahi and H. Kaneta, Paper 118; Corrosion '98; San Diego, USA, March 1998, NACE.**

10) **R. Francis, Brit. Corr. J. 29, 1 (1994) 53.**

9.0 Sources of advice

Advice on design and choice for a given use can be obtained from the corrosion advisory centres and consultancy services listed in the Corrosion Handbook (published by MPI, 1998).

The same organisations can investigate failures and make recommendations for avoiding them in future. Reputable equipment manufacturers can also offer advice, based on their experiences.

10.0 Further information

For sources of general information on corrosion and data on the compatibilities of metal and fluids, see Guide No. 1 in this series.

General information is available from the following organisations:

National Corrosion Service
National Physical Laboratory
Teddington
Middlesex
TW11 0LW
Tel: 020 8943 6142
Fax: 020 8943 7107

Institute of Corrosion
4 Leck House
Lake Street
Leighton buzzard
Bedfordshire
LU7 8TQ
Tel: 01525 851771
Fax: 01525 376690

Materials Information Service
Institute of Materials
1 Carlton House Terrace
London
SW1Y 5DB
Tel: 020 7451 7350
Tel: 020 7451 7354
Fax: 020 7839 5513

Information on materials is available from the following organisations:

1. **Copper and copper alloys.**
   CDA
   Verulam Industrial Estate
   224 London Road
   St Albans
   Herts AL1 1AQ
   Tel: 01727 731200
   Fax: 01727 731216

2. **Nickel and nickel-containing alloys.**
   NiDI
   The Holloway
   Alvechurch
   Birmingham B48 7QB
   Tel: 01527 584 777
   Fax: 01527 585 562

3. **Titanium and titanium alloys.**
   Titanium Information Group
   c/o Timet UK Ltd
   Kynoch Works
   Witton Road, Witton
   Birmingham B6 7UR
   Tel: 0121 356 1155
   Fax: 0121 356 5413

4. **Aluminium and its alloys.**
   Aluminium Federation Ltd
   Broadway House
   Calthorpe Road
   Birmingham B15 1TN
   Tel: 0121 456 1103
   Fax: 0121 456 2274

5. **Zinc and its alloys.**
   Zinc Development Association
   42-46 Weymouth Street
   London W1N 3LQ
   Tel: 020 7499 6636

6. **Magnesium and its alloys.**
   International Magnesium Institute
   17, Avenue Hoche
   75008 Paris
   France
   Tel: +33 145630634
   Fax: +33 142894292

The National Corrosion Service

The National Corrosion Service (NCS) is operated by NPL on behalf of the DTI to provide a gateway to corrosion expertise for UK users. By acting as a focal point for corrosion enquiries, the NCS can make the UK's entire base of experts available to solve problems or can, using in-house expertise or teams, carry out consultancy. The NCS also helps raise awareness of corrosion problems and methods of control.

For more information on NCS services and products please contact us at:
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National Physical Laboratory, Queens Road, Teddington, Middlesex TW11 0LW

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