

Corrosion

Corrosion for Science and Engineering
Trethewey and Chamberlain
2ed Longman

What is Corrosion?

- Derived from Latin corrodere to gnaw to pieces
- Dictionary definition; to eat or wear away gradually
- Corrosion/rust/degradation
- Formation of a metal oxide
- Not just restricted to metal; glass, concrete, wood and plastics are all subject to environmental corrosion
- Electrochemical reaction

Causes

- External factors
- Water
- Acids
- Bases
- Salts
- Oils
- Solid and liquid chemicals
- Gases – acid vapours, ammonia gas, sulphur gas

Electrochemical reaction

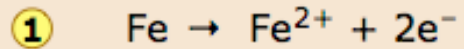
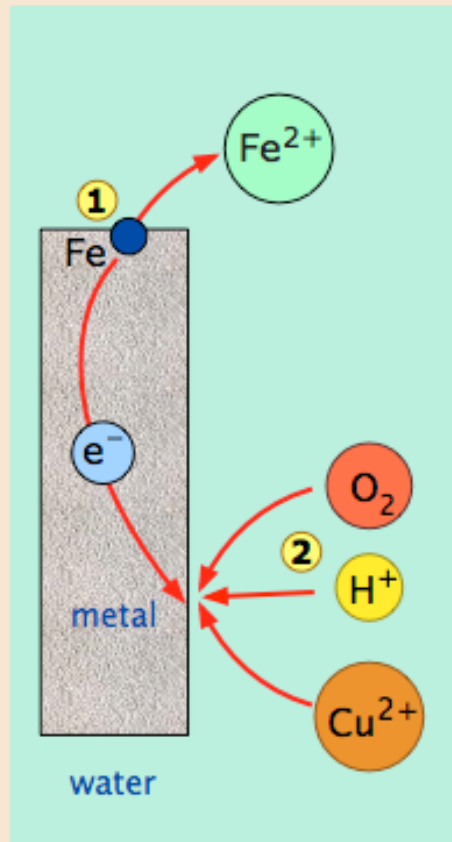
- Anodic reaction: Metal atoms + water – give up electrons to oxygen molecules and form positive metal ions
- $M \rightarrow M^+ + e^-$
- $Fe(s) \rightarrow Fe^{2+}(aq) + 2 e^-$
- Cathodic Reaction: consumes electrons
- $M^{2+} + 2 e^- \rightarrow M(s)$ *or*
- $H^+ + e^- \rightarrow \frac{1}{2} H_2(g)$
- $O_2 + 2 H_2O + 4e^- \rightarrow 4 OH^-$ (hydroxide ions)

Electrochemical corrosion of iron

- Corrosion often begins at a location
- **(1)** where the metal is under stress (at a bend or weld)
- or is isolated from the air (where two pieces of metal are joined or under a loosely-adhering paint film.)
- The metal ions dissolve in the moisture film and the electrons migrate to another location **(2)** where they are taken up by a ***depolarizer***.
- Oxygen is the most common depolarizer; the resulting hydroxide ions react with the Fe^{2+} to form the mixture of hydrous iron oxides known as ***rust***.

Electrochemical corrosion of iron

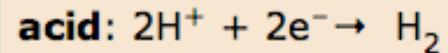
Corrosion is a two-step process



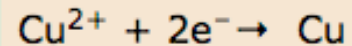
Fe atom at metal surface dissolves into moisture film, leaving negative charge in metal.

- ② Corrosion continues as a *depolarizer* removes electrons from metal.
Common depolarizers are:

oxygen:



cation of more-noble metal:



Noble metals

- Noble metals resist oxidation and corrosion in moist air. They are the opposite of base metals which more readily oxidize and corrode.
- ruthenium
- rhodium
- palladium
- silver
- osmium
- iridium
- platinum
- gold

Noble metals in the periodic table

H																	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo	
* La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu																		
** Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr																		

Refractory metals

Platinum group

Other precious metals

Non-precious unreactive metals

Radioactive unreactive metals

Base Metals

- A base metal is any metal other than the noble metals or precious metals (gold, silver, platinum, etc.). Base metals typically tarnish or corrode easily.
- Common examples of base metals are copper, lead, tin, aluminum, nickel, and zinc. Alloys of these elemental metals are also base metals, such as brass and bronze.
- iron, steel, aluminium, molybdenum, tungsten

Why do we care?

PERIODIC TABLE OF THE ELEMENTS

<http://www.ktf-split.hr/periodni/en/>

PERIOD

GROUP	1	2	13	14	15	16	17	18	1	2	13	14	15	16	17	18		
1	IA									IIA						VIIA		
1	1 1.0079 H HYDROGEN									2 4.0026 He HELIUM								
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM																
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM																
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.933 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRNIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUBIUM		114 (289) Uuq UNUNQUADIUM				

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)

Relative atomic mass is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivardhan@netline.com)

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM
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ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MEDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM
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For more information and downloads please visit - - - > <http://www.periodni.com/en/download.html>

Corrosion is Expensive

- 4.2% GNP
- lost production
- high potential maintenance costs
- environmental impact
- impact on health
- contamination of materials with corrosion products
- leaky pipes and possible failures
- cost of replacements

Industrial implications

- Nuclear power
- Aerospace
- Electrical and electronics
- Marine and offshore
- Automotive
- Construction
- Chemicals
- Defence

The cost of corrosion

- Annual cost of corrosion worldwide is >3% of the world's GDP
- =£1.4 trillion
- - George Hays, Director General of World Corrosion Organisation
- The Hoar report – 25% annual cost of corrosion saved by using existing knowledge
- Average return on investment in corrosion projects 50:1

- Infrastructure, including building structures (onshore and offshore), transportation (roads, bridges, and tunnels), water distribution mains, energy distribution (electricity, gas, and oil), and communication systems and devices.
- Transport methods, including railways, automotive (materials technology, coating technology, clean exhaust technology by catalysts or filters), aerospace, and ships (diesel engines).
- Energy production and storage, including fossil fuels, nuclear fuels, biomass fuels, alternative energy sources, and hydrogen technology.
- Raw materials, including mining, metallurgy, recycling, and oil & gas for non-energy use.
- Production technologies in refineries, petro-chemistry, chemistry, pulp & paper, and electronics.
- Food, including agriculture, food production technologies, and water cleanliness and availability.
- Health, including implant materials and technologies.
- Safety and social integrity.

- A simple example demonstrates the impact of corrosion in everyday life on human health.
- This example was contributed by Prof. Lucien Bonou from Burkina Faso, Africa, at the WCO workshop during the 17th International Corrosion Congress⁷ in September 2008.
- metal composition of cooking pots produced in his country from recycled aluminium alloys. He found that the material consisted of 32% iron and 10% copper. In addition, considerable amounts of other heavy metals were present (10% zinc, 2.5% lead, and 0.12% cadmium).

Cost to human health

Using aluminium-containing scrap from parts of cars, drinking cans, tins, tubes, etc, causes the pot metal to easily corrode from a reaction with the cooked food.

As a result, heavy metal ions are released into the food and impair the health of the humans who consume it.

Important to bring this problem into the public domain and take measures that only corrosion-resistant purer aluminium alloys be used for cooking pot manufacturing.



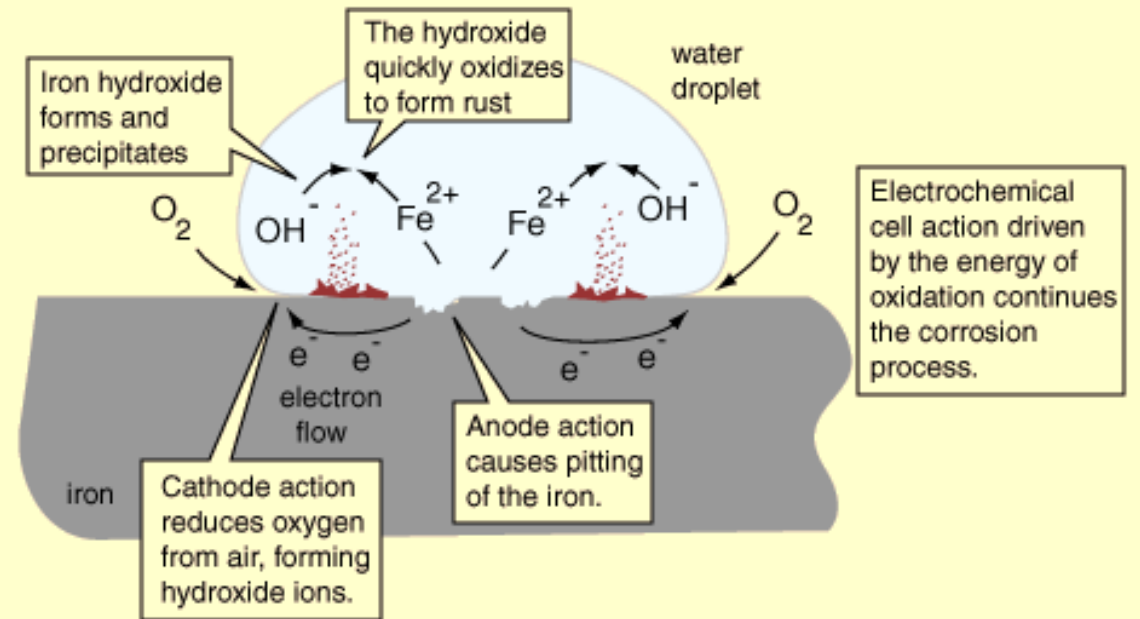
Lessons of History

- Historically and currently corrosion is a huge problem that affects the use of metals
- Cars made of steel rust! Or do they?
- Corrosion can occur in some truly bizarre ways!
- Royal Navy 1763, 1962, 1982

Rust

hydrated iron (III) oxide $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$

Or iron (III) oxide-hydroxide ($\text{FeO}(\text{OH})$, $\text{Fe}(\text{OH})_3$).



Schematic diagram of corrosion cells on iron [\[link\]](#)

Types of corrosion – group 1

Group I: identifiable by visual inspection



Uniform Corrosion



Pitting



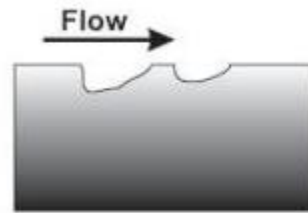
Crevice Corrosion



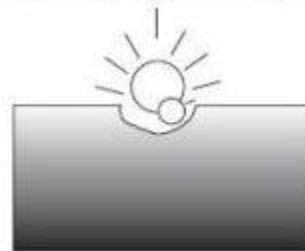
Galvanic Corrosion

Types of corrosion – group 2

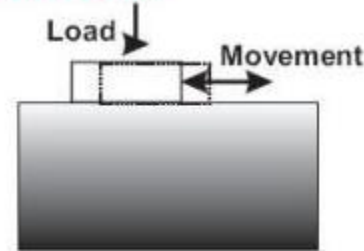
Group II: identifiable with special inspection tools



Erosion



Cavitation



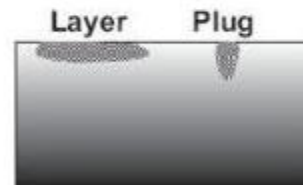
Fretting



Intergranular



Exfoliation



De-Alloying

Types of corrosion group 3

Group III: identifiable by microscopic examination

Cracking



Stress Corrosion
Cracking



Corrosion Fatigue

High Temperature Attack



Scaling



Internal Attack

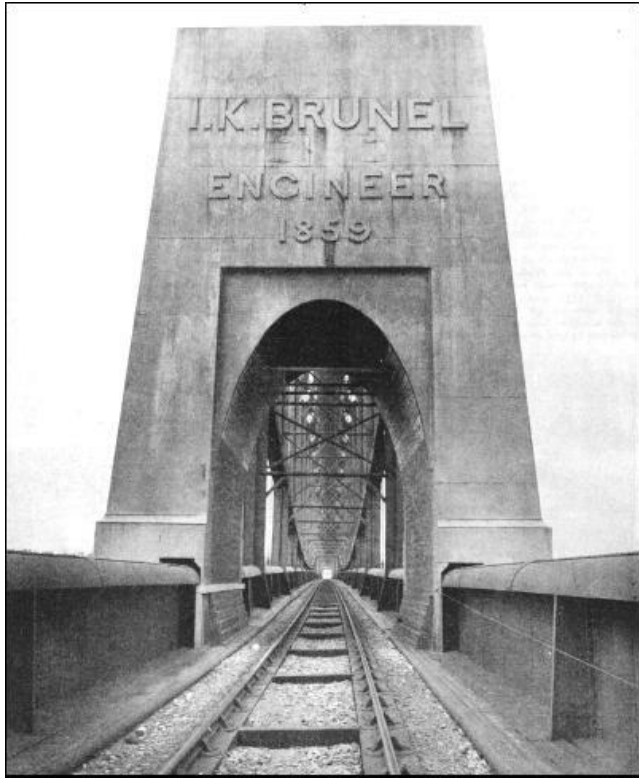
Corrosion in armour and art

- Knights in shining (or not) armour
- Metal oxide corrosion products can be used for decorative effects
- Bluining and anodising protect iron and aluminium respectively
- Rusty sculptures
- Roman philosophers

Corrosion in armour and art



Saltash Rail Bridge - wrought iron 1859 - Brunel



Iron Bridge – Thomas Pritchard 1781 made of cast iron.
Still in use today and no real corrosion damage

Environmental Considerations

- Acid rain enhances corrosion
- Corrosion can damage the environment -Tanker failure 2009
- Water treatment to remove corrosion products
- Materials used to prevent corrosion can harm the environment (chromate)



The Search for Chromate Free Pigments



Coffee break and research

Group 1: Uniform corrosion

Group 2: Pitting corrosion

Group 3: Crevice corrosion

Group 4: Galvanic corrosion

What happened to:

1763; H.M.S. Alarm?

1962 Navy submarine

1982 The Falklands

What type of corrosion
caused it?

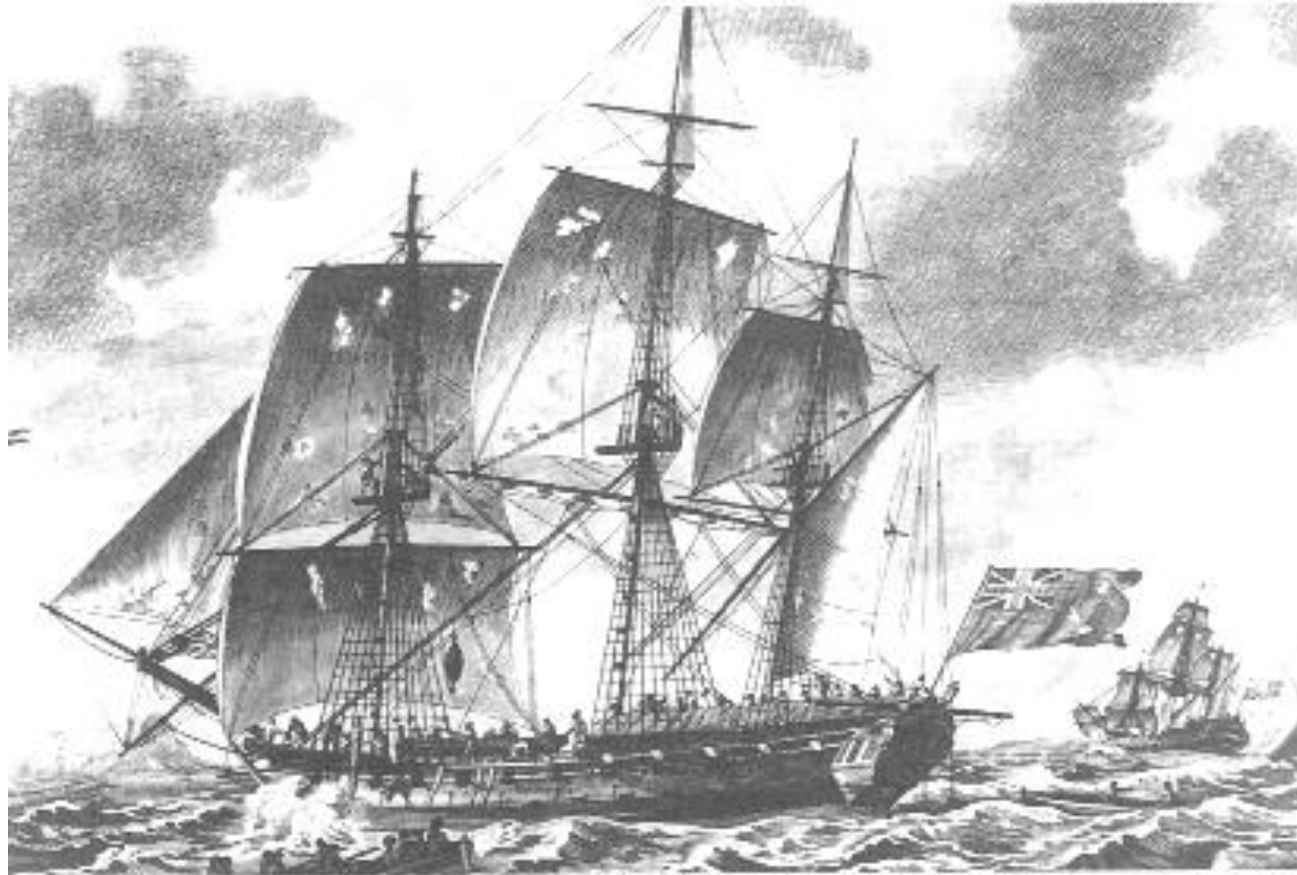


"Notice all the computations, theoretical scribbles, and lab equipment, Norm. ... Yes, curiosity killed these cats."

QUIZ

- What happened to:
- 1763 H.M.S. Alarm?
- 1962 Navy submarine
- 1982 The Falklands

1763; H.M.S. Alarm



nails failed at copper bottom of the boat;
dissimilar metal corrosion (Dolphin?)

1962; Navy Submarine



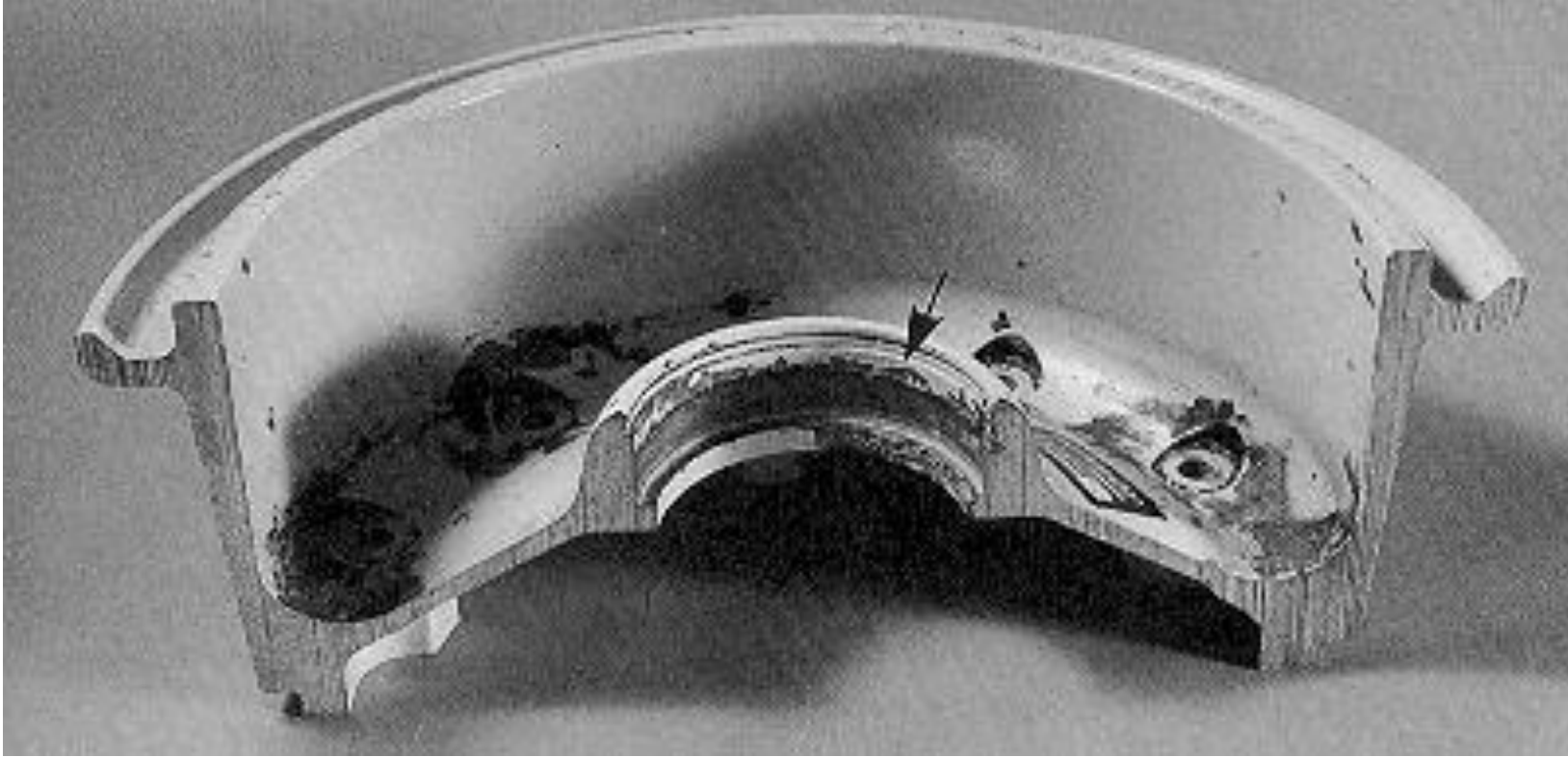
steel bolts corroded when holding on a copper alloy end plate on a submarine sea water evaporator;
Dissimilar metals corrosion

1982; The Falklands



Bizarre failure of front under carriage

Why did the wheels fail?



dissimilar metal corrosion at magnesium
alloy iron boundary

Learning the lessons of Corrosion

- All three examples over 200 years had the same basic problem of *dissimilar metal corrosion*
- By more careful design and materials selection we can overcome the problems.

Chemical Aspects of Corrosion

Aargh the tedium!

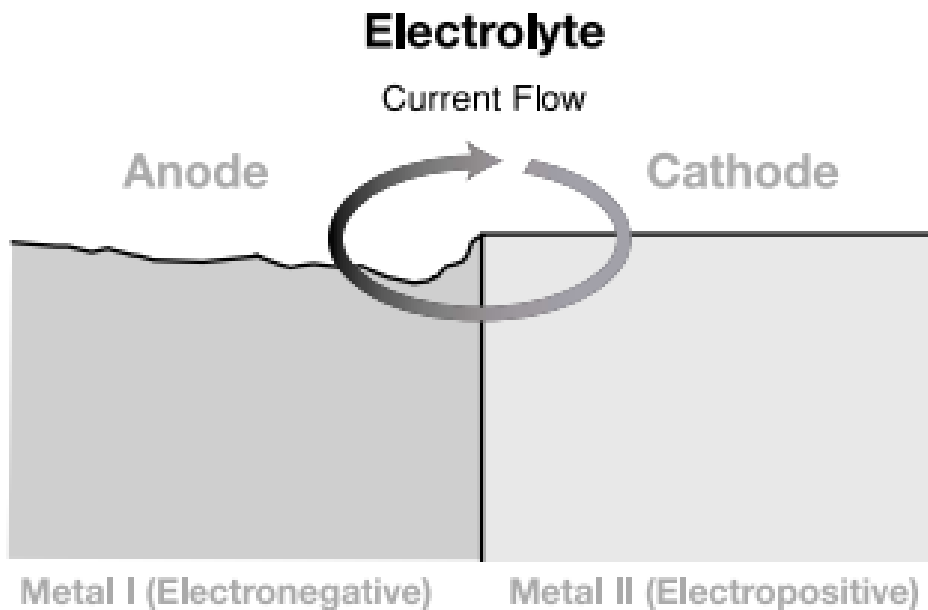
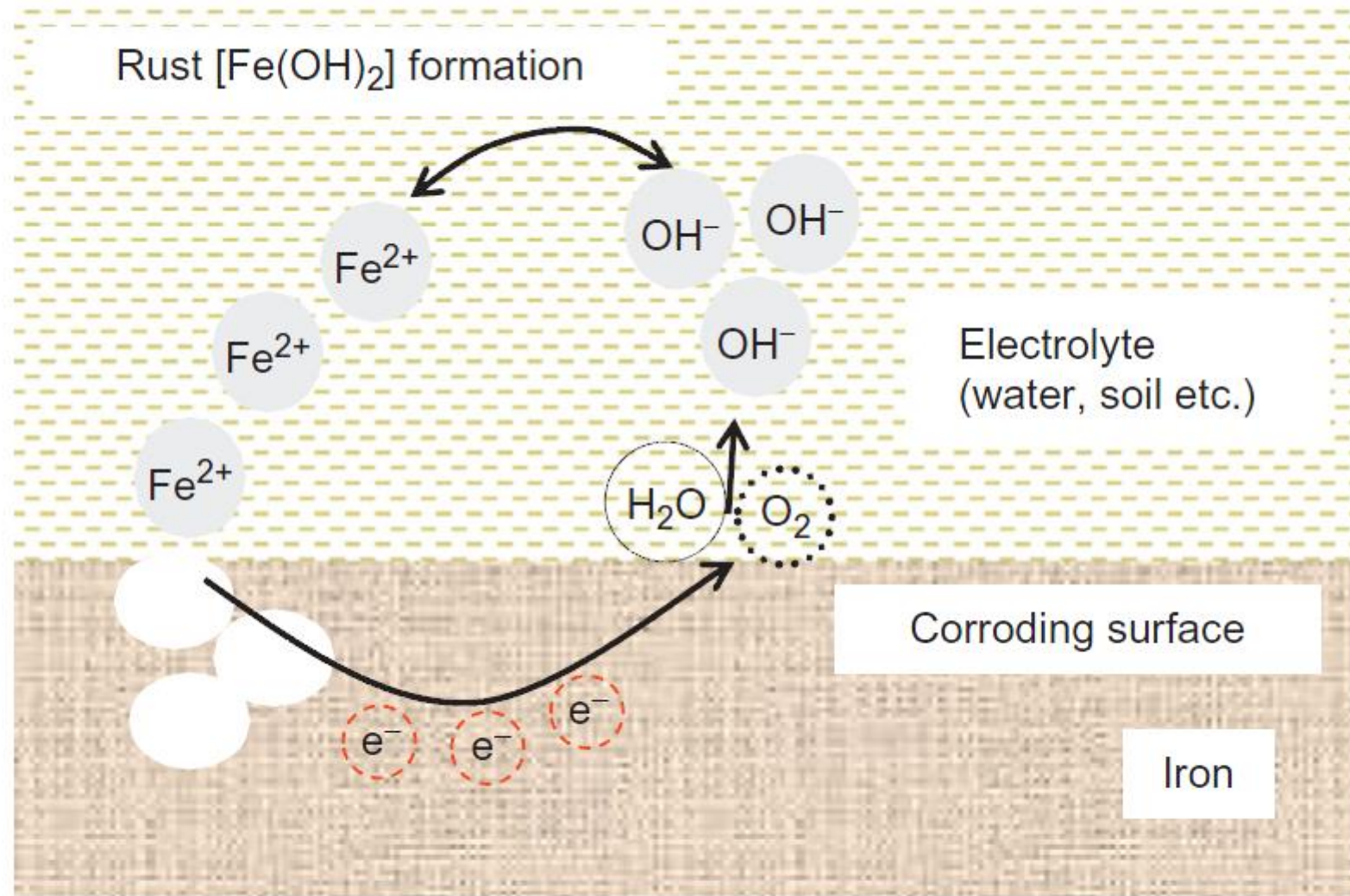


Figure 1. Method of bimetallic corrosion

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 increase the corrosion on the anode.

- 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

- When a metal is corroding two processes occur. One is the
- dissolution of metal at the anode (e.g. iron):
- $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}$
- 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:
- $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e} \rightarrow 4\text{OH}$
- In acid liquids the cathodic reaction is often the reduction of
- hydrogen ions to hydrogen gas:
- $2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2$



Corrosion cell formed as a result of rusting of iron.

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 this is the consumption of dissolved oxygen.

Basic Principles of Corrosion

- Dissolution of a metal and simultaneous formation of a metal oxide.
- Can occur via a number of mechanisms.
- Corrosion prevention method depends on mechanism of corrosion.

What is Corrosion?

- Formation of a metal oxide from a metal
- Degradation of a metal by an *electrochemical* reaction with its environment
- Chemical reaction – elements added or removed from a chemical species – no change in valence precipitation of iron hydroxide
 - $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$
- Electrochemical reaction - elements added or removed from a chemical species – at least one species changes number of valence electrons
 - oxidation of metallic iron $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
-
- Engineering materials dissolve mostly by electrochemical reactions

Electrochemical Thermodynamics and Corrosion

Table 1 Partial List of Standard
Electrochemical Potentials

Reaction	Standard Potential (V vs. NHE)
$\text{Au}^{3+} + 3\text{e}^{-} = \text{Au}$	1.42
$\text{Cl}_2 + 2\text{e}^{-} = 2\text{Cl}^{-}$	1.36
$\text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} = 2\text{H}_2\text{O}$	1.229
$\text{Cu}^{2+} + 2\text{e}^{-} = \text{Cu}$	0.34
$2\text{H}^{+} + 2\text{e}^{-} = \text{H}_2$	0.000
$\text{Ni}^{2+} + 2\text{e}^{-} = \text{Ni}$	-0.23
$\text{Fe}^{2+} + 2\text{e}^{-} = \text{Fe}$	-0.44
$\text{Zn}^{2+} + 2\text{e}^{-} = \text{Zn}$	-0.763
$\text{Al}^{3+} + 3\text{e}^{-} = \text{Al}$	-1.706
$\text{Mg}^{2+} + 2\text{e}^{-} = \text{Mg}$	-2.375
$\text{Na}^{+} + \text{e}^{-} = \text{Na}$	-2.712

Standard conditions are 298K and all reactants and products are at unity activity

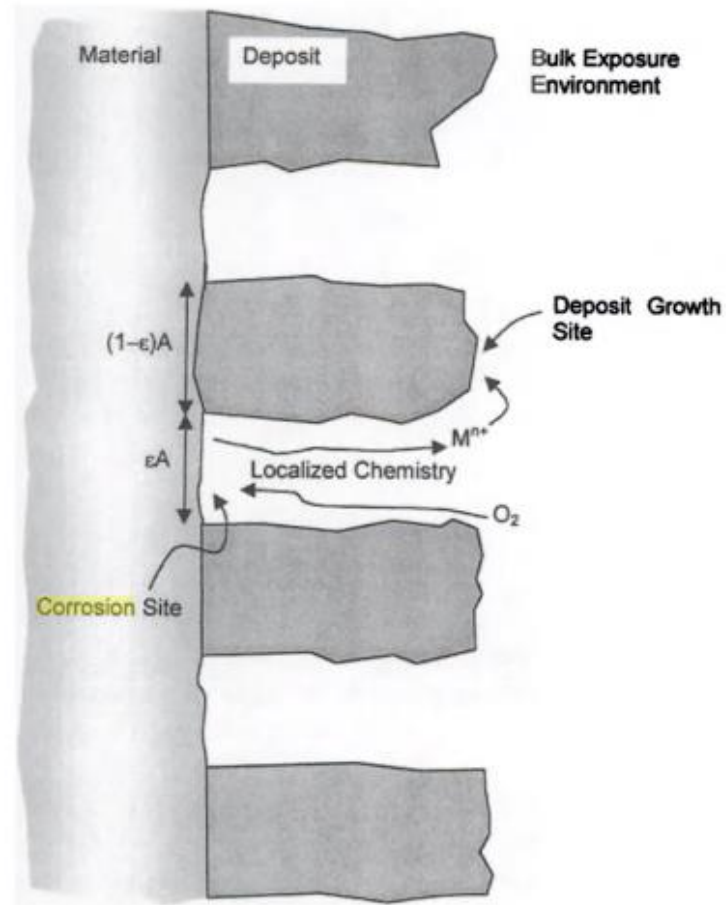
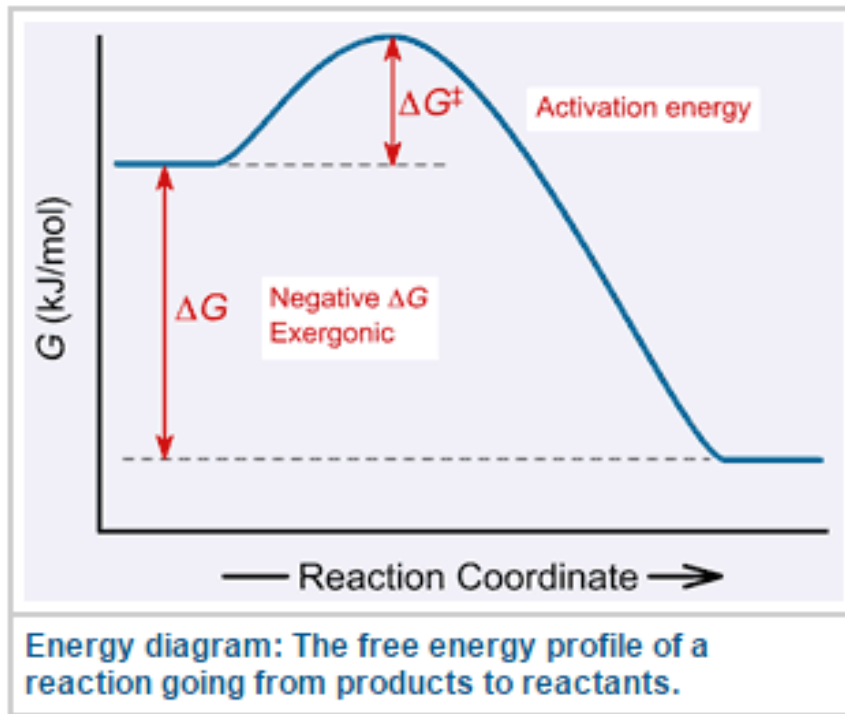


Figure 17 Schematic of an idealized corrosion product deposit on a corroding surface; l is the pore length, ϵA the fraction of the surface area exposed to the corrosion environment; $(1 - \epsilon A)$ is the fraction of the surface blocked by corrosion product deposit.

Gibbs Free Energy



$$\Delta G^{\circ} = \sum \Delta G_f^{\circ}(\text{products}) - \Delta G_f^{\circ}(\text{reactants})$$

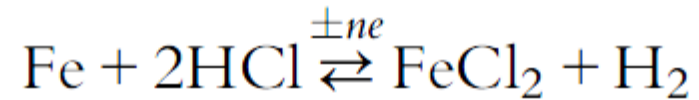
$$\Delta G^{\circ} = \sum v_i G_i^{\circ}$$

$$\Delta G^{\circ} = -nFE^{\circ}$$

Maximum potential usable energy of a system, $\Delta G = (\text{energy of products}) - (\text{energy of reactants})$
If ΔG is negative the reaction is thermodynamically favourable

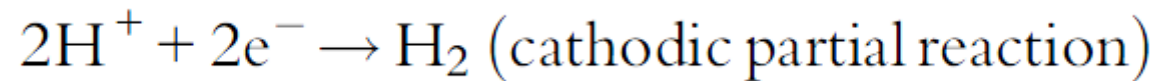
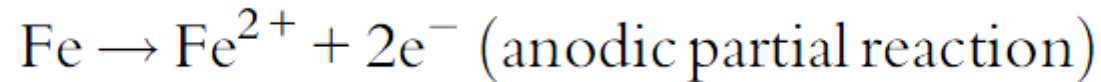
Thermodynamics

- The corrosion of iron in an acid environment occurs according to the following reaction:



n = number of elementary charges $e=4.803 \times 10^{-10}$

The dissolution of iron in an acidic solution releases hydrogen without the formation of any oxide barrier films on the surface.



- The quantity of electricity produced as a result of the chemical reaction is equal to the product of nFE , where E is the electromotive force measured in the case of reversible reactions.
- The quantity F is the Faraday constant, which can be estimated
- from the product, $F = N_A e$ where $N_A = 6.02 \times 10^{23}$ (Avogadro's number) and “ e ” is the elementary charge. The absolute value of the Faraday constant equals 96,485 C (coulomb).
- n = number of elementary charges $e = 1.602 \times 10^{-19}$ (1.602 X 10⁻¹⁹ coulombs)

- The corrosion reaction at constant pressure decreases Gibbs free energy (G)
- The change in the Gibbs free-energy represents the maximum useful work for an isothermal and isobaric conversion for the corrosion reaction. $G=H+TS$

- **Definition:** Cell potential is the potential difference between the cathode and anode of an electrochemical cell.
- The anode and cathode are defined by the flow of current. Current flows in the same direction as positive charge carriers, for example, when positive ions or protons carry the charge.
- Current flows opposite the direction of negative charge carriers, such as electrons in metals.

- **Cathode**

- The cathode is the negatively charged electrode.
- The cathode attracts cations or positive charge.
- The cathode is the source of electrons or an electron donor. It may accept positive charge.

- **Anode**

- The anode is the positively charged electrode.
- The anode attracts electrons or [anions](#).
- The anode may be a source of positive charge or an electron acceptor.
- Remember the **cathode** attracts **cations** or the **cathode** attracts **+** charge. The **anode** attracts **anions** or **negative** charge.
- Anode: positively charged terminal - oxidation reaction.
Cathode: negatively charged terminal - reduction reaction
- Oxidation is Loss Reduction is Gain (of electrons) OILRIG

- **Definition:** An electrochemical cell is a device that generates a [potential difference](#) between [electrodes](#) using [chemical reactions](#).
- **Examples:** [Galvanic cells](#) and [electrolytic cells](#) are examples of electrochemical cells.
- Galvanic cells are electrochemical cells which use the transfer of electrons in redox reactions to supply an electric current. [This example problem](#) illustrates how to form a [galvanic cell](#) from two [reduction reactions](#) and calculate [the cell EMF](#).

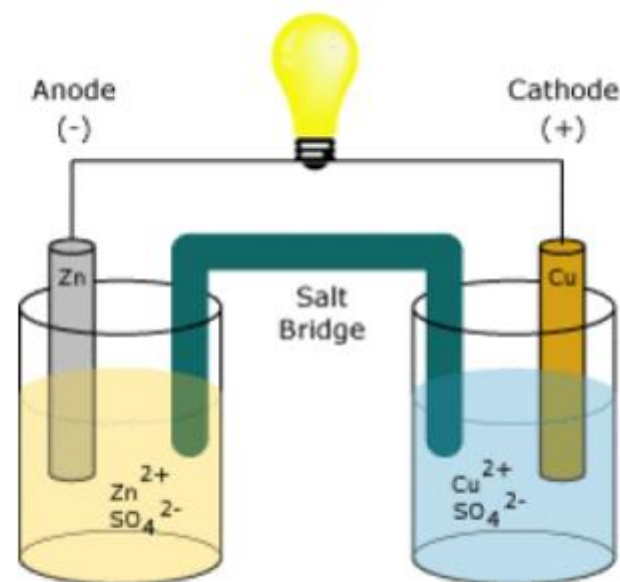
Galvanic cell/ Daniell cell/ Voltaic cell

Electrodes & Charge

The anode of an electrolytic cell is positive (cathode is negative), since the anode attracts anions from the solution. However, the anode of a galvanic cell is negatively charged, since the spontaneous oxidation at the anode is the *source* of the cell's electrons or negative charge. The cathode of a galvanic cell is its positive terminal. In both galvanic and electrolytic cells, oxidation takes place at the anode and electrons flow from the anode to the cathode.

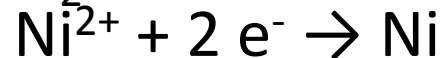
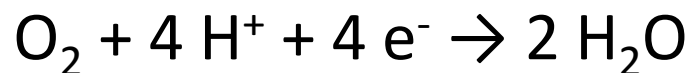
Galvanic or Voltaic Cells

The redox reaction in a galvanic cell is a spontaneous reaction. For this reason, galvanic cells are commonly used as batteries. Galvanic cell reactions supply energy which is used to perform work. The energy is harnessed by situating the oxidation and reduction reactions in separate containers, joined by an apparatus that allows electrons to flow. A common galvanic cell is the Daniell cell.



- **Problem:**

Given the following reduction half-reactions:



Construct a galvanic cell using these reactions. Find:

- a) Which half-reaction is the cathode.
- b) Which half-reaction is the anode.
- c) Write and balance the total cell redox reaction.
- d) Calculate E^0_{cell} of the galvanic cell.

- **Solution:**

To be galvanic, the [electrochemical cell](#) must have a total $E^0_{\text{cell}} > 0$.

From the [Table of Common Standard Reduction Potentials](#):



To construct a cell, one of the half-reactions must be [an oxidation reaction](#). To make a reduction half-reaction into an oxidation half-reaction, the half-reaction is reversed. The cell will be galvanic if the nickel half-reaction is reversed.

The *Nernst Equation* enables the determination of cell potential under non-standard conditions. It relates the measured cell potential to the [reaction quotient](#) and allows the accurate determination of equilibrium constants (including solubility constants).

Introduction

The *Nernst Equation* is derived from the Gibbs free energy **under standard conditions**.

$$E^o = E_{reduction}^o - E_{oxidation}^o$$

ΔG is also related to E under general conditions (standard or not) via

$$\Delta G = -nFE$$

with

- n is the number of electrons transferred in the reaction (from balanced reaction),
- F is the Faraday constant (96,500 C/mol), and
- E is potential difference.

Under standard conditions, equation 2 is then

$$\Delta G^o = -nFE^o.$$

Hence, when E^o is positive, the reaction is spontaneous and when E^o is negative, the reaction is non-spontaneous. From thermodynamics, the Gibbs energy change under non-standard conditions can be related to the Gibbs energy change under standard equations via

$$\Delta G = \Delta G^o + RT \ln Q \tag{4}$$

Substituting $\Delta G = -nFE$ and $\Delta G^o = -nFE^o$ into equation 4, we have:

$$-nFE = -nFE^o + RT \ln Q \tag{5}$$

Divide both sides of the equation above by $-nF$, we have

$$E = E^o - \frac{RT}{nF} \ln Q \tag{6}$$

Standard cell potentials are calculated in [standard conditions](#).

The temperature and pressure are at [standard temperature and pressure](#) and the concentrations are all 1 M [aqueous solutions](#).

In non-standard conditions, the Nernst equation is used to calculate cell potentials.

It modifies the standard cell potential to account for temperature and concentrations of the reaction participants.

[This example problem](#) shows how to use the [Nernst equation](#) to calculate a cell potential.

Problem 1:

Find the cell potential [of a galvanic cell](#) based on the following reduction half-reactions at 25 °C



where $[\text{Cd}^{2+}] = 0.020 \text{ M}$ and $[\text{Pb}^{2+}] = 0.200 \text{ M}$.

How to convert Celsius to Kelvin

0 degrees Celsius is equal to 273.15 degrees Kelvin:

$$0\text{ }^{\circ}\text{C} = 273.15\text{ K}$$

The temperature T in Kelvin (K) is equal to the temperature T in degrees Celsius ($^{\circ}\text{C}$) plus 273.15:

$$T_{(\text{K})} = T_{(^{\circ}\text{C})} + 273.15$$

Solution:

The first step is to determine the cell reaction and total cell potential.

In order for the cell to be galvanic, $E^0_{\text{cell}} > 0$.

For this reaction to be galvanic, the cadmium reaction must be the oxidation reaction.

The [Nernst equation](#) is:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/nF) \times \log_{10} Q$$

where

E_{cell} is the cell potential

E°_{cell} refers to standard cell potential

R is the [gas constant](#) (8.3145 J/mol·K)

T is the [absolute temperature](#)

n is the number of moles of electrons transferred by the cell's reaction

F is [Faraday's constant](#) (96484.56 C/mol)

Q is the [reaction quotient](#)

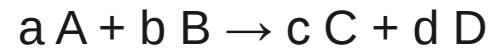
[At equilibrium the reaction quotient Q is the equilibrium constant K](#)

[So](#)

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/nF) \times \log_{10} K$$

$$Q = [C]^c \cdot [D]^d / [A]^a \cdot [B]^b$$

where A, B, C, and D are chemical species; and a, b, c, and d are coefficients in the balanced equation:



In this example, the temperature is 25 °C or 300 K and [2 moles](#) of electrons were transferred in the reaction.

$$RT/nF = (8.3145 \text{ J/mol}\cdot\text{K})(300 \text{ K})/(2)(96485.337 \text{ C/mol})$$

$$RT/nF = 0.013 \text{ J/C} = 0.013 \text{ V}$$

The only thing remaining is to find [the reaction quotient](#), Q.

$$Q = [\text{products}]/[\text{reactants}]$$

****For reaction quotient calculations, pure liquid and pure solid reactants or products are omitted.****

$$Q = [\text{Cd}^{2+}]/[\text{Pb}^{2+}]$$

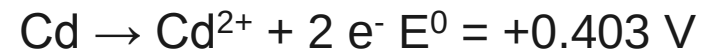
$$Q = 0.020 \text{ M} / 0.200 \text{ M}$$

$$Q = 0.100$$

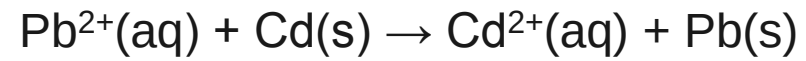
$$\begin{aligned}E_{\text{cell}} &= E_{\text{cell}}^0 - (RT/nF) \times \ln Q \\E_{\text{cell}} &= 0.277 \text{ V} - 0.013 \text{ V} \times \ln(0.100) \\E_{\text{cell}} &= 0.277 \text{ V} - 0.013 \text{ V} \times -2.303 \\E_{\text{cell}} &= 0.277 \text{ V} + 0.023 \text{ V} \\E_{\text{cell}} &= 0.300 \text{ V}\end{aligned}$$

Answer:

The cell potential for the two reactions at 25 °C and $[\text{Cd}^{2+}] = 0.020 \text{ M}$ and $[\text{Pb}^{2+}] = 0.200 \text{ M}$ is 0.300 volts.



The total cell reaction is:

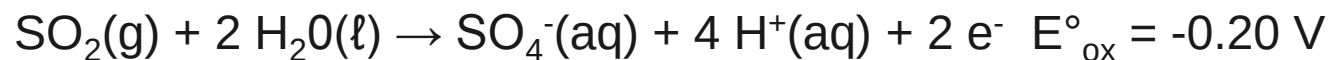


$$\text{and } E^0_{\text{cell}} = 0.403 \text{ V} + -0.126 \text{ V} = 0.277 \text{ V}$$

Problem 2:

The following two half-reactions are used to form an [electrochemical cell](#):

Oxidation:



Reduction:

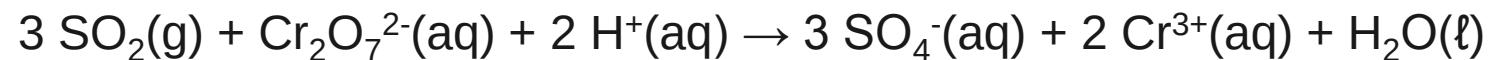
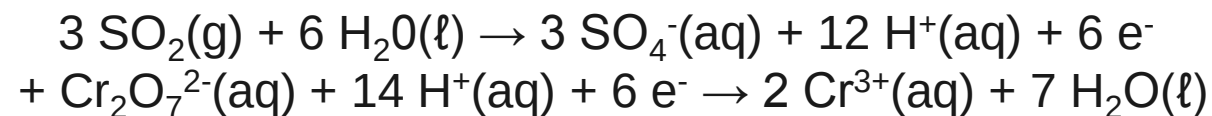


What is the equilibrium constant K of the combined cell reaction at 25 °C?

Step 1 Balance the two half reactions equation

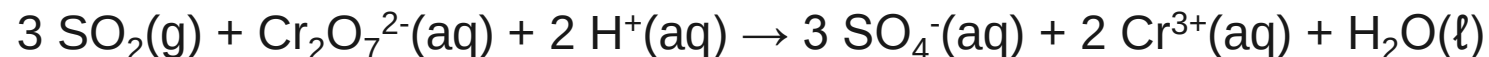
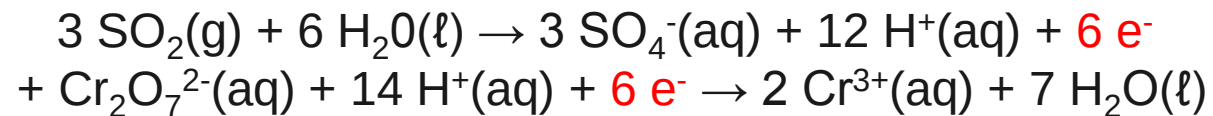
- The oxidation half-reaction produces 2 electrons and the reduction half-reaction needs 6 electrons.

To balance the charge, [the oxidation reaction](#) must be multiplied by a factor of 3.



What is the total number of electrons exchanged in the reaction?

To balance the charge, [the oxidation reaction](#) must be multiplied by a factor of 3.



What is the total number of electrons exchanged in the reaction? 6

Step 2 Calculate the cell potential

- $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}}$

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- $E^\circ_{\text{cell}} = E^\circ_{\text{ox}} + E^\circ_{\text{red}}$
 $E^\circ_{\text{cell}} = -0.20 \text{ V} + 1.33 \text{ V}$

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 $E^\circ_{\text{cell}} = -0.20 \text{ V} + 1.33 \text{ V}$
 $E^\circ_{\text{cell}} = +1.13 \text{ V}$

Step 3: Find the equilibrium constant, K .

When a reaction is at equilibrium, the change in free energy is equal to zero.

The change in free energy of an electrochemical cell is related to the cell potential by the equation:

$$\Delta G = -nFE_{\text{cell}}$$

where

ΔG is the free energy of the reaction

n is [the number of moles](#) of electrons exchanged in the reaction

F is Faraday's constant (96484.56 C/mol)

E is the cell potential.

If $\Delta G = 0$:, solve for E_{cell}

$$0 = -nFE_{\text{cell}}$$

If $\Delta G = 0$:, solve for E_{cell}

$$0 = -nFE_{\text{cell}}$$

$$E_{\text{cell}} = 0 \text{ V}$$

This means, at equilibrium, the potential of the cell is zero. The reaction progresses forward and backwards at the same rate meaning there is no net electron flow. With no electron flow, there is no current and the potential is equal to zero.

Time for the Nernst equation

- $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/nF) \times \log_{10} Q$

where

E_{cell} is the cell potential

E°_{cell} refers to standard cell potential

R is the [gas constant](#) (8.3145 J/mol·K)

T is the [absolute temperature](#)

n is the number of moles of electrons transferred by the cell's reaction

F is [Faraday's constant](#) (96484.56 C/mol)

Q is the [reaction quotient](#)

- At equilibrium, the reaction quotient Q is the equilibrium constant, K . This makes the equation:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/nF) \times \log_{10} K$$

From above, we know the following:

$$E_{\text{cell}} = 0 \text{ V}$$

$$E^{\circ}_{\text{cell}} = +1.13 \text{ V}$$

$$R = 8.3145 \text{ J/mol}\cdot\text{K}$$

$$T = 25 \text{ }^{\circ}\text{C} = 298.15 \text{ K}$$

$$F = 96484.56 \text{ C/mol}$$

$$n = 6 \text{ (six electrons are transferred in the reaction)}$$

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$$F = 96484.56 \text{ C/mol}$$

$$n = 6 \text{ (six electrons are transferred in the reaction)}$$

- Solve for K

- $0 = 1.13 \text{ V} - [(8.3145 \text{ J/mol}\cdot\text{K} \times 298.15 \text{ K}) / (6 \times 96484.56 \text{ C/mol})] \log_{10} K$
 $-1.13 \text{ V} = - (0.004 \text{ V}) \log_{10} K$
 $\log_{10} K = 282.5$

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 $K = 10^{282.5}$

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$$-1.13 \text{ V} = - (0.004 \text{ V}) \log_{10} K$$

$$\log_{10} K = 282.5$$

$$K = 10^{282.5}$$

$$K = 10^{282.5} = 10^{0.5} \times 10^{282}$$

$$K = 3.16 \times 10^{282}$$

Answer:

The equilibrium constant of the cell's redox reaction is 3.16×10^{282} .

- <http://chemistry.about.com/od/workedchemistryproblems/a/Equilibrium-Constant-Of-An-Electrochemical-Cell-Reaction-Example-Problem.htm>

How are potentials determined?

The zero value of the hydrogen reference electrode has been adopted by IUPAC as suggested by Nernst for convenience, in order for the standard hydrogen electrode (SHE) to serve as a reference potential

A half-cell potential of any redox corrosion reaction is measured when the half-cell is coupled with the SHE

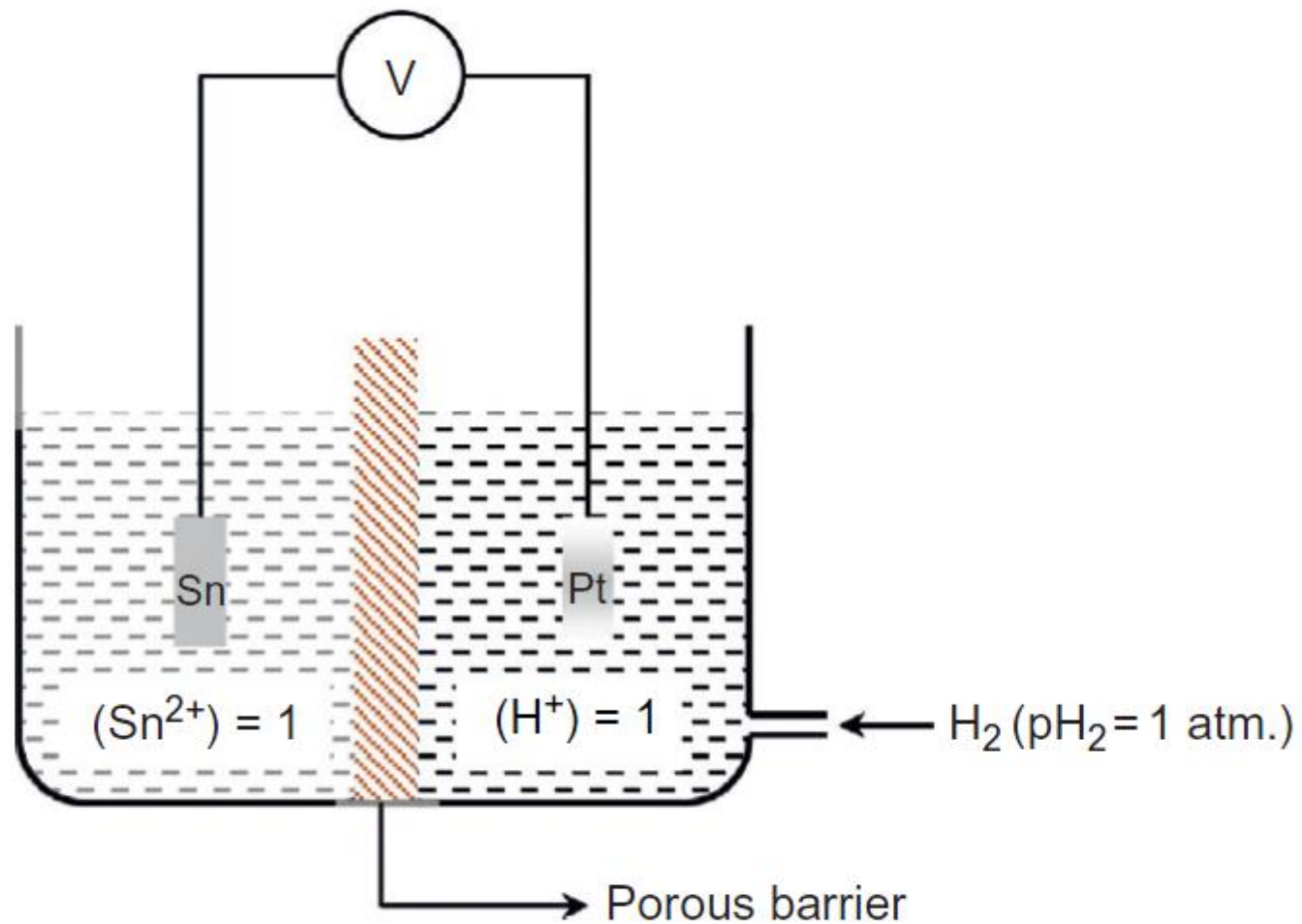
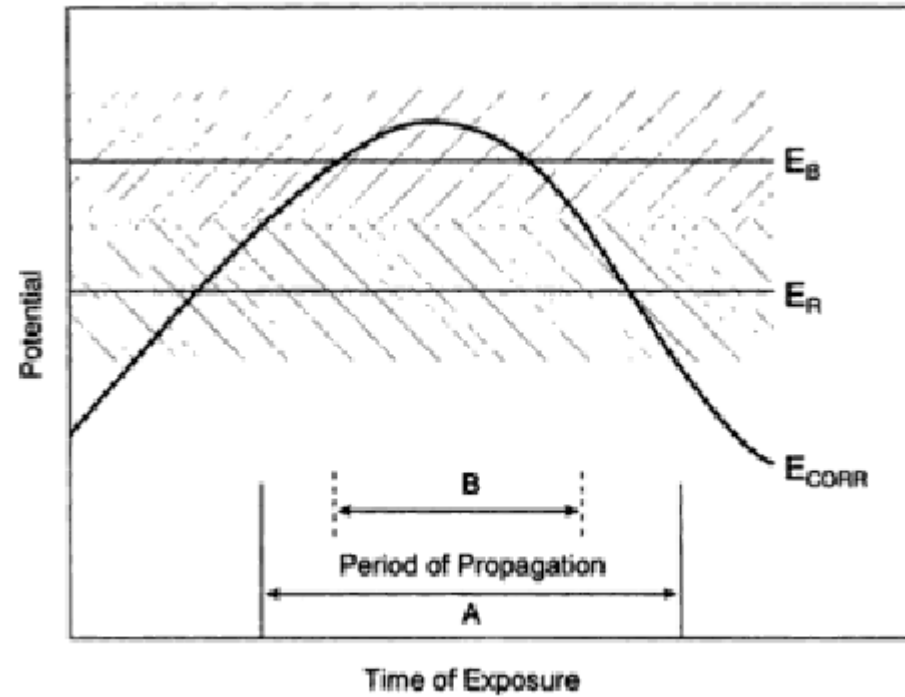


Fig. 2.2 Schematic of electrochemical cell showing the measurement of cell potential.

Pitting Corrosion



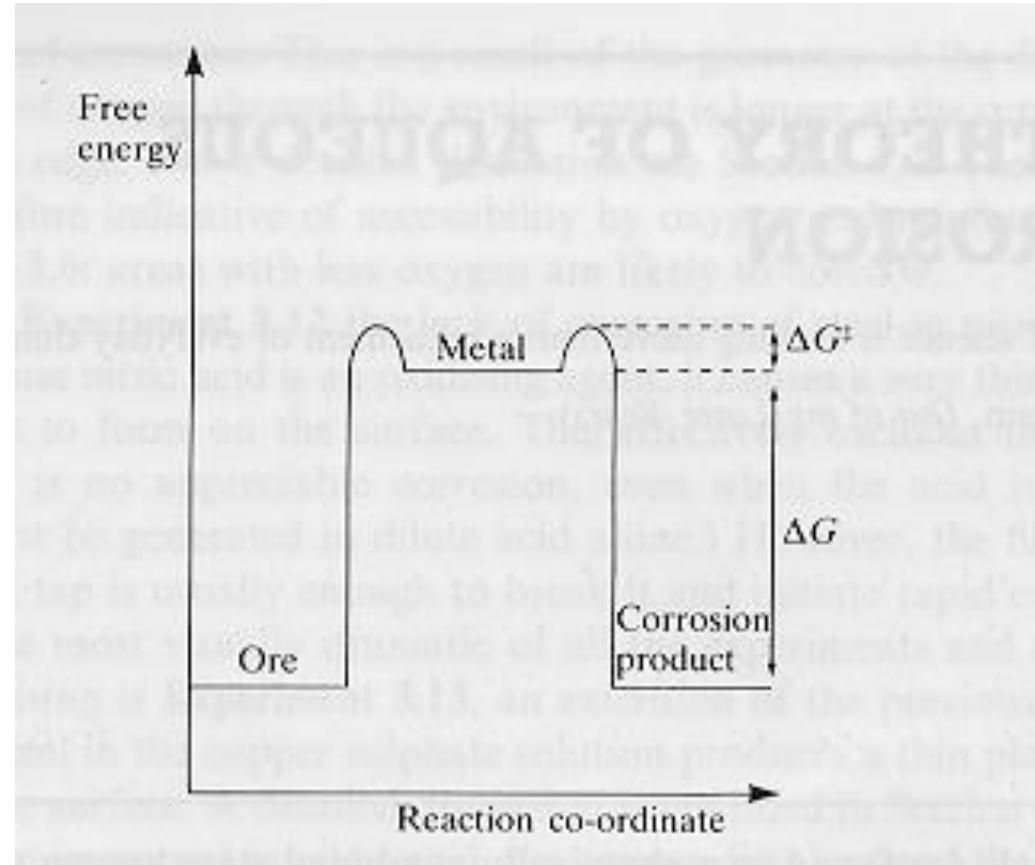
Dry and Wet Corrosion

- Dry corrosion occurs when the metal is heated in air without moisture
- Firmly bound oxide film can be protective
- Wet corrosion is the most damaging form which we will study
- It is an electrochemical process

Why do metals corrode?

- Metals are thermodynamically unstable with respect to corrosion products
- Negative Gibbs Free Energy change
- Corrosion is inevitable
- Activation energy barrier ΔG^* can keep metals stable

Thermodynamic instability of metals



Corrosion Nature's Recycling

- Most metals are extracted from their ores by reducing a metal oxide
- i.e. basically $2MO = 2M + O_2$
- This process usually requires large energy input
- Nature prefers the metal oxide form and so tries to reform it by oxidising (corroding) the metal

Types of Wet Corrosion

- Single metals
- Dissimilar metals
- Selective attack
- Crevice and pitting corrosion
- *Flow induced corrosion*
- Stress induced corrosion
- Corrosion results in failure of materials

Electrochemical process

- Corrosion involves transfer of electrons
- The metal loses electrons and is oxidised
- Other species gain electrons and are reduced
- OIL RIG!!!
- Plating of metals is a simple model we can use to look at electrochemical processes very similar to corrosion

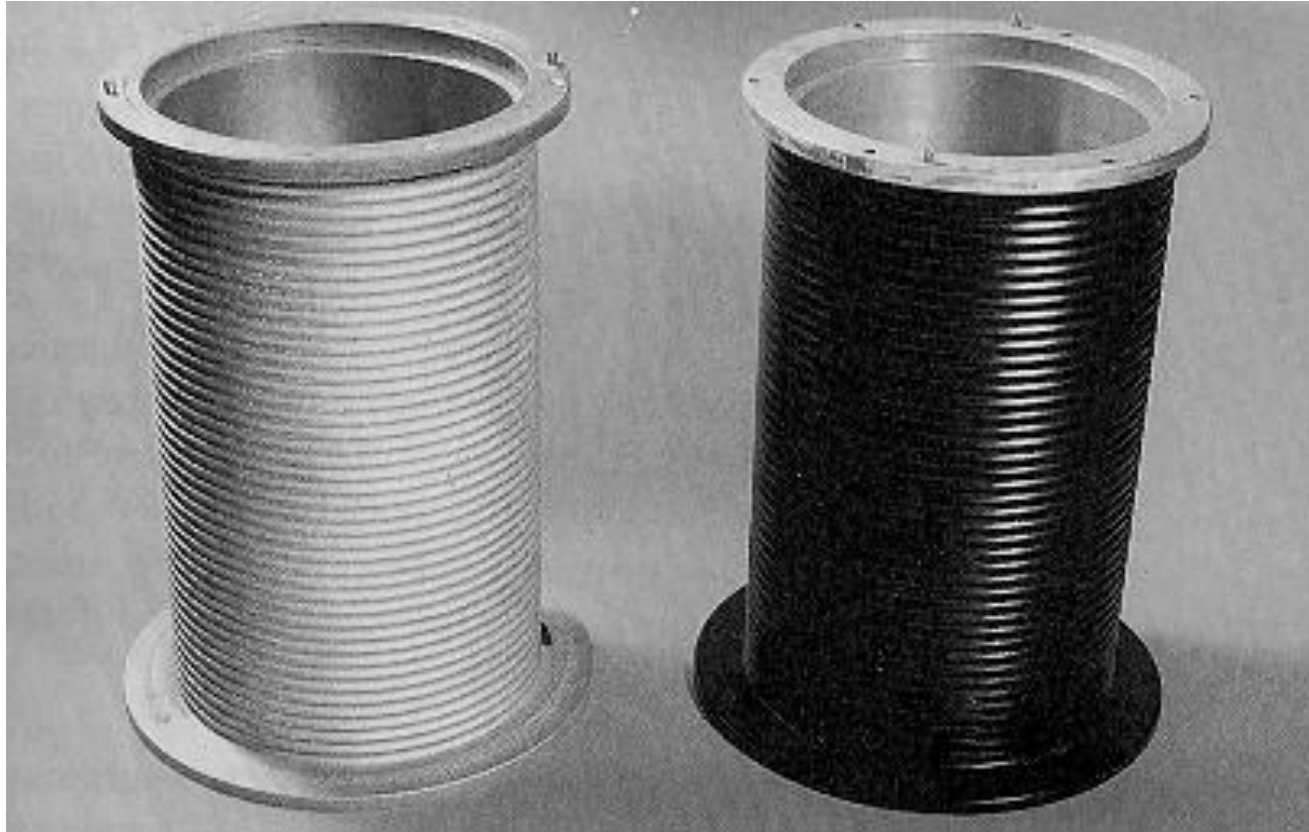
Reasons and Solutions

- Brass screw less corrodible than steel
- Brass becomes the cathode and steel the anode
- Corrosion occurs under paint
- Use non brass fastener
- Insulate the brass screw using a plastic expansion grommet

Other Automotive Dissimilar Metal Corrosion

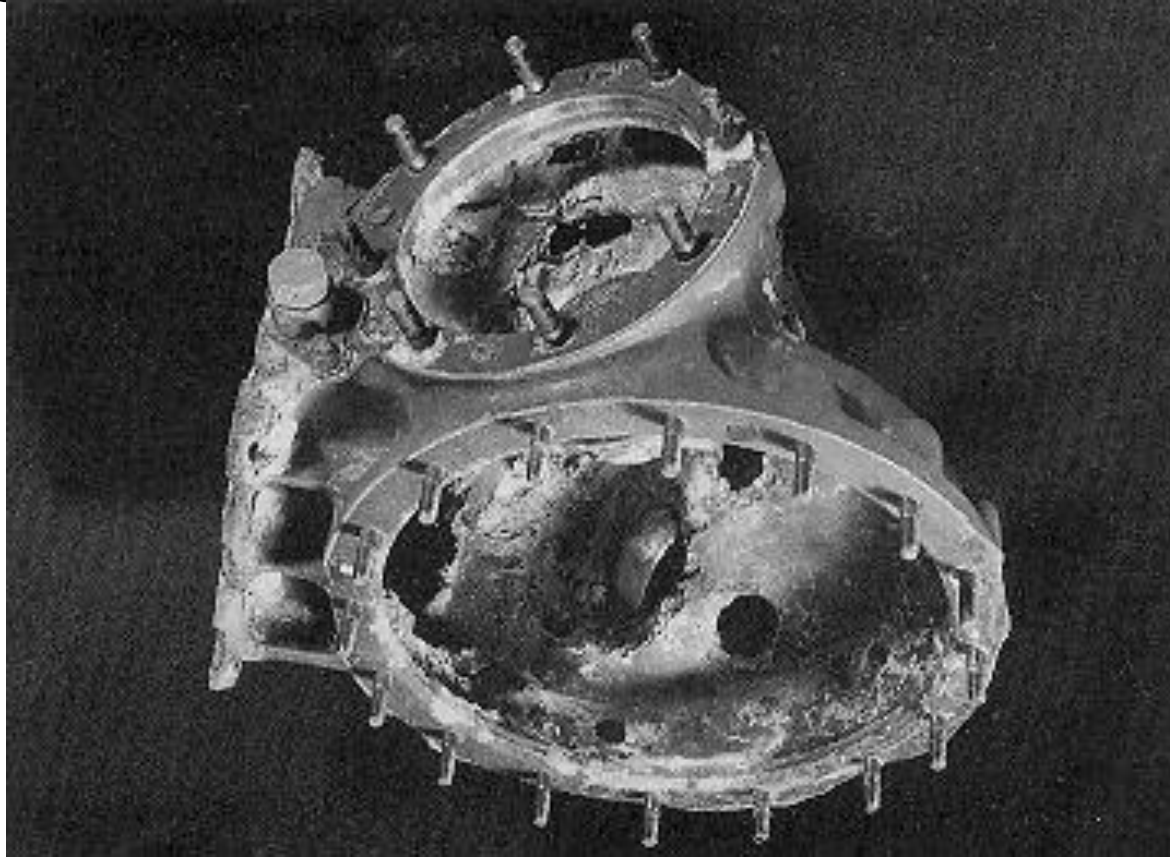
- Alloy Wheels; attached to steel wheel hubs with steel nuts prone to corrosion in areas where there is lacquer damage
- All alloy engines; older versions used copper cored radiators with disastrous consequences!

Helicopter Winch



Corrosion of alloy winch drum in contact with less reactive steel wound wire

Other Aircraft Parts



corrosion of aluminium based alloys where steel fixing studs have been used

Reasons and solutions

- Magnesium and aluminium are more reactive metals than iron
- Steel is the oxygen reduction cathode and alloy material is corroded
- Insulate the two metals by applying a coating or setting steel parts in an insulating resin or sheath

Time for Trevor (Again!)



This time our man has decided to fit a stainless steel exhaust
The car is rare so he modifies an off the shelf exhaust by
welding on new brackets.

The stainless steel rapidly corroded in the area of the weld.

Welding Stainless Steels

- Welding Stainless can be dangerous
- Heating to 600-850 C will precipitate out chromium carbide locally
- The stainless is now *SENSITISED*
- Severe pitting corrosion in the heat treated area
- *Handy tip;* Never clean the weld area with an oil based cleaner as it will precipitate out more carbon

Ways of Preventing Intergranular Corrosion in Stainless Steels

- Use of a low carbon stainless steel with $<0.03\%$ C
- Heat treatment will re-dissolve the carbides; rapid quenching will prevent precipitation
- Addition of titanium or niobium at levels *ca* 10 fold the carbon content; these preferentially form carbides (eg type 321 stainless)

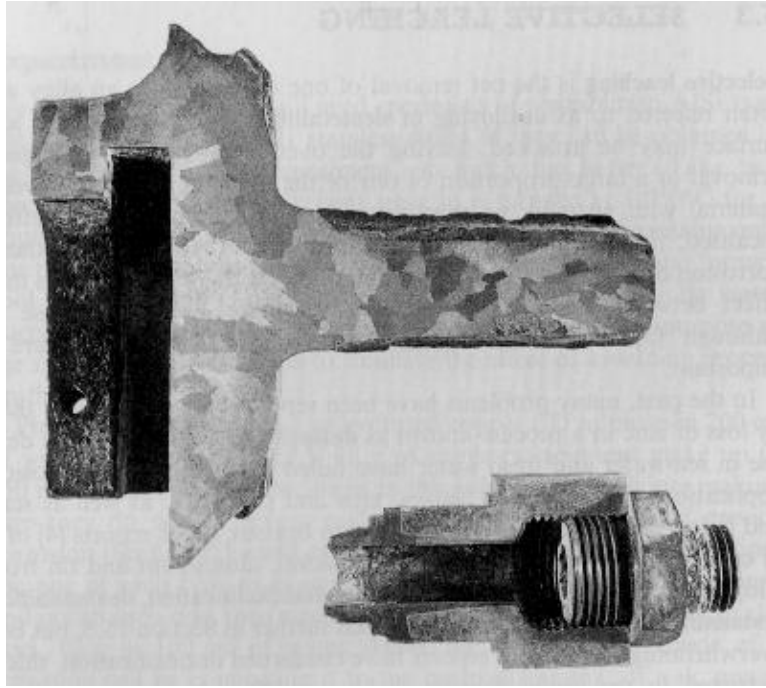
3. Selective Leaching

- Selective leaching can occur when elements that have very different electrode potentials are alloyed and come in to contact with corrosive media
- The more reactive (most negative electrode potential) metal is selectively leached from the structure
- Cathodic activity (oxygen reduction or hydrogen evolution) occurs on the other metal

Selective Leaching in Brasses

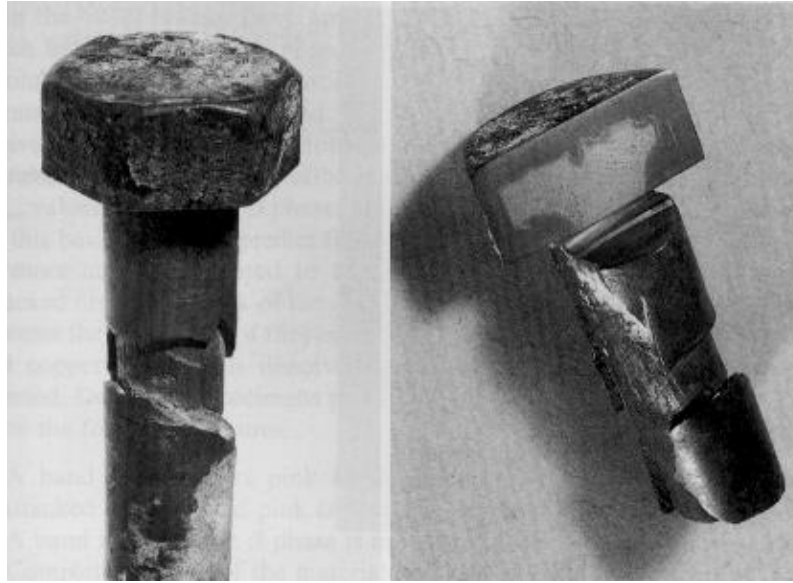
- Brass is an alloy of Copper and Zinc
- 70/30 and 60/40 brasses are most common
- Zinc has a more negative electrode potential
- Zinc is more easily corroded than copper
- Zinc becomes anodic and copper cathodic
- Zinc dissolves from the structure
- Structure loses strength and fails

Failure of Brass Castings



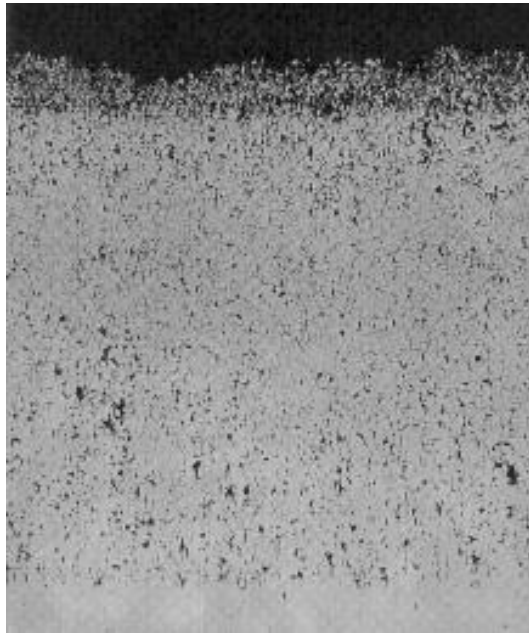
Both these are 60/40 cast brass marine valves
Both suffered severe *dezincification*
Both subsequently failed

Failure of Leaded Brass Bolts



Lead added to 60/40 brass to improve machining
These 12mm bolts severely corroded after a short time
Lead increased rate of zinc removal by lowering activity
of the other metals

What is happening during dezincification?



60/40 brass has two phases α and β with β phase having more zinc and so preferentially corroded.

Upper layer complete wastage, then β removed and partial α attack then β only attack

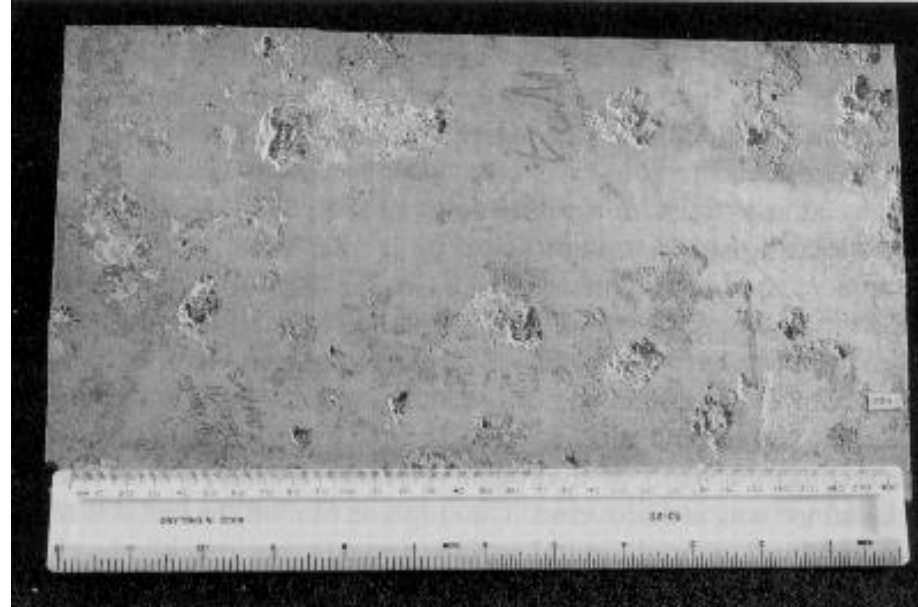
Prevention of Dezincification

- Arsenic addition (0.05%) to 70/30 brass prevents this damaging corrosion
- This is Admiralty Brass

4 Microbiologically Induced Corrosion MIC

- The fouling of the undersides of boats with organic matter is well known
- Biofouling can also induce corrosion
- Microbes can live in the contamination and incite corrosion
- MIC costing the US \$400million annually
- Can be fungi, algae or bacteria

Fungal Growth



Badly pitted panel from an RAF Comet Transporter
Corrosion due to a fungal growth in the fuel tank

Fungal Growth (cont.)

- Many fungi thrive on the combination of hydrocarbons oxygen and water
- Aircraft fuel tanks became matted in fungi
- Fungal mat released organic acid resulting in severe localised corrosion of the aluminium
- Fungal mat caused most problems when sucked into fuel lines!!!

Sulphate Reducing Bacteria SRB

- Very bad for iron and steel
- Corrosion of up to 2 inches per year
- Reduce sulphates in water to sulphides and hydrogen sulphides that are highly corrosive
- Protect themselves with a polymer film
- Very common in industrial pipework with low oxygen concentrations

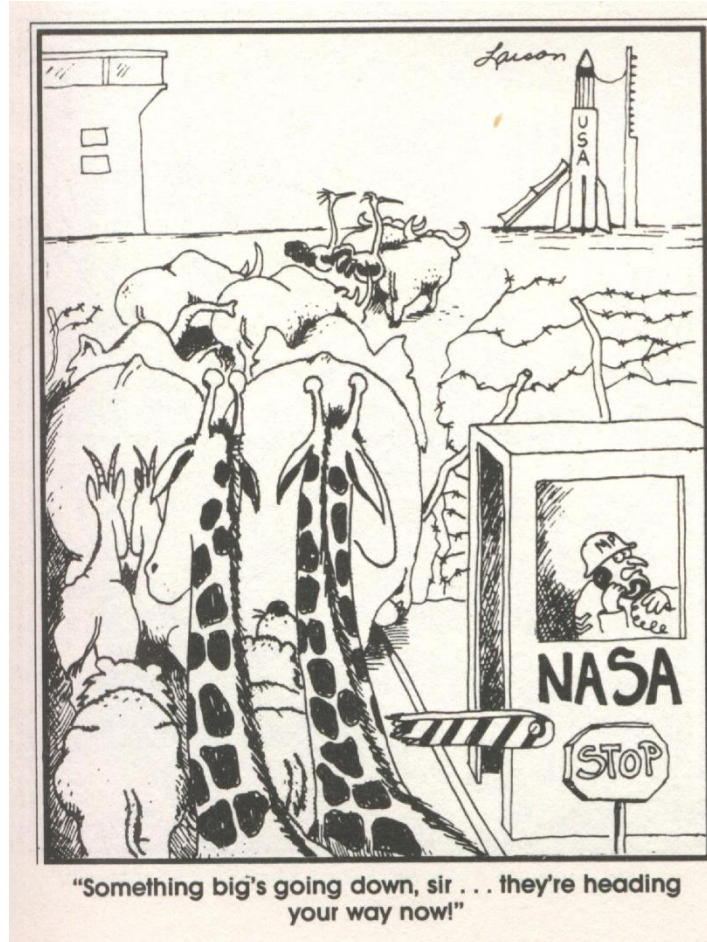
MIC in Stainless Steels

- *Gallionella* is an anaerobic bacteria that attacks stainless
- Forms in the slime on the bottom of pipework
- Low oxygen concentrations beneath the film aggravated by corrosive salts cause rapid pitting corrosion.

Prevention of MIC

- Redesign the component to prevent biofouling
- Apply a polymer coating
- Switch to a polymeric material
- Use of biocides to destroy biological contaminants

Tea?



Crevice, Pitting and Differential Aeration Corrosion

Corrosion due to concentration cells

Summary of Corrosion Methods

- Dissimilar Metal Corrosion
metals of different activity connected
- Selective attack
Grain boundary corrosion
Intergranular corrosion
selective leaching
- All have four electrolytic components; anode, cathode, electrolyte and direct electrical connection

Other Forms of Selective Attack

- Selective attack can be based on attack at certain areas of the metal due to heterogeneities in the metal structure
- Corrosion can also be induced by variations in the composition of the electrolyte over a metal surface

Concentration Cells

- What happens when the electrolyte composition becomes heterogeneous?
- If the oxygen or corrosive ion level at one area of a metal is different to another a concentration cell is set up in which local areas become anodes and cathodes
- In low oxygen concentration area anodic (corrosion) reactions are likely to dominate

Types of Concentration Cell Corrosion

- Crevice Corrosion
- Pitting Corrosion
- Differential Aeration Corrosion
- All related to each other and to some of the selective attack mechanisms mentioned last time.

Stainless Steels

- Believed to be corrosion proof
- Not so as we saw last time
- Severe localised corrosion around grain boundaries if chromium carbides are allowed to precipitate
- Can also suffer from pitting, crevice and differential aeration corrosion

Consider the MIC of Stainless Pipework

- Stainless Steel Pipework in MIC
- Slime covers the bottom of the pipe and oxygen concentration drops
- Bottom of pipe becomes anodic
- Top and sides of pipe are cathodic
- Bottom of pipe suffers rapid pitting corrosion induced by the *differential aeration cell*

Stainless Steel Thermometer Pocket



Stainless used in a sea water cooled condenser; Failure where there was an area of stagnant water
This is an example of pitting corrosion

Universal Joints



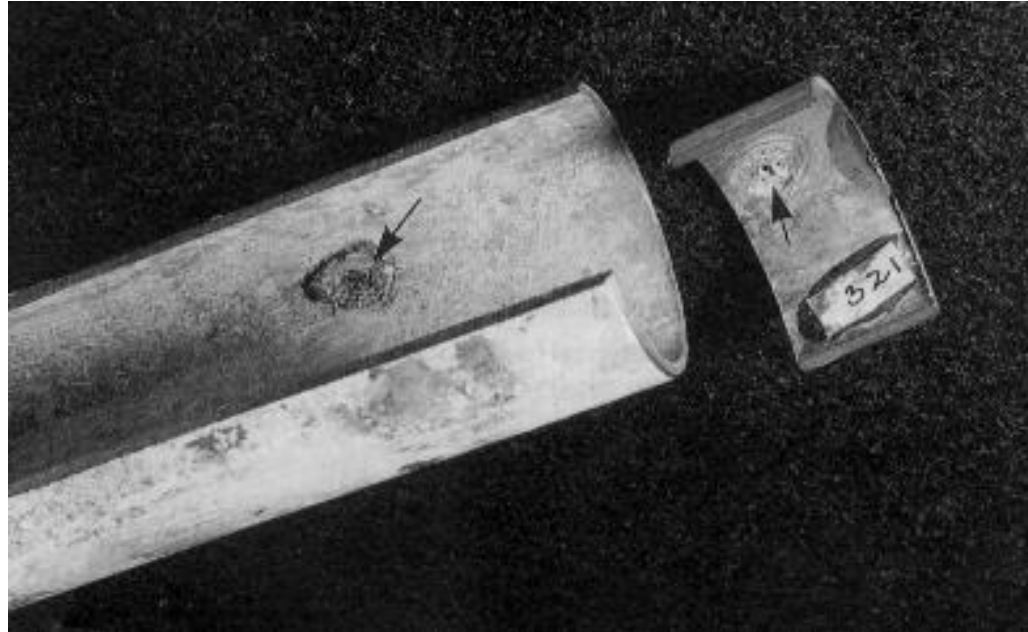
Stainless steel universal joint badly pitted where it was covered with a rubber grommet.

This is an example of crevice corrosion

Decorative Cladding

- Stainless with small holes punched in it
- OK in conditions of severe weather
- Poor performance in sheltered sites
- Water trapped in holes sets up a differential aeration cell

Copper Pipe Failure



During preparation an oil film was wiped on the pipe
Annealing this laid a carbon film down which was
cathodic to the metal;
The development of corrosion product on the metal
leads to corrosion via a crevice mechanism

1 Crevice Corrosion

- Crevice corrosion is attack which occurs because part of the metal is in a restricted or shielded environment to the rest of the metal.
- A Crevice is typically 25-100 μm wide
- Crevices arise during fabrication (welds, seams, joints, threads etc)
- Crevices arise due to surface contamination (dirt, corrosion products etc)

Mechanisms of Crevice Corrosion

- When the geometry of a sample is such that a crevice is present and electrolyte composition becomes non uniform Crevice corrosion occurs
- Electrolyte can have different ion or oxygen concentrations within it
- A basic mechanism is the Fontana Greene mechanism for stainless steel

Fontana Greene Mechanism

- Initial attack is even all over the surface
- Electrons flow through metal and ions through solution
- Oxygen used up in crevice and less easily replaced
 - differential aeration corrosion
 - negative ions diffuse in to balance positive charge

Consequences of Ion Transport into Crevice

- Negative ions often chloride diffuse into crevice
- These are aggressively corrosive
- Can generate acid which further attacks metal
- *Autocatalytic* self perpetuating process
- Once it has started it is difficult to stop!!!

Consequences of Crevice Corrosion

- Rapid self sustaining corrosion mechanism
- Corrosion focussed in crevice area
- Rapid failure of component in this area
- Huge problem that affects joining of metals

The Car Industry



Simplified Galvanic Series in Sea Water

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

Crevice Corrosion in the Car Industry

- Door skins
- Seams
- Box sections
- Fitting of accessories
- Major cause of corrosive failure in cars
- Results in inside to outside corrosion

Graphite Grease

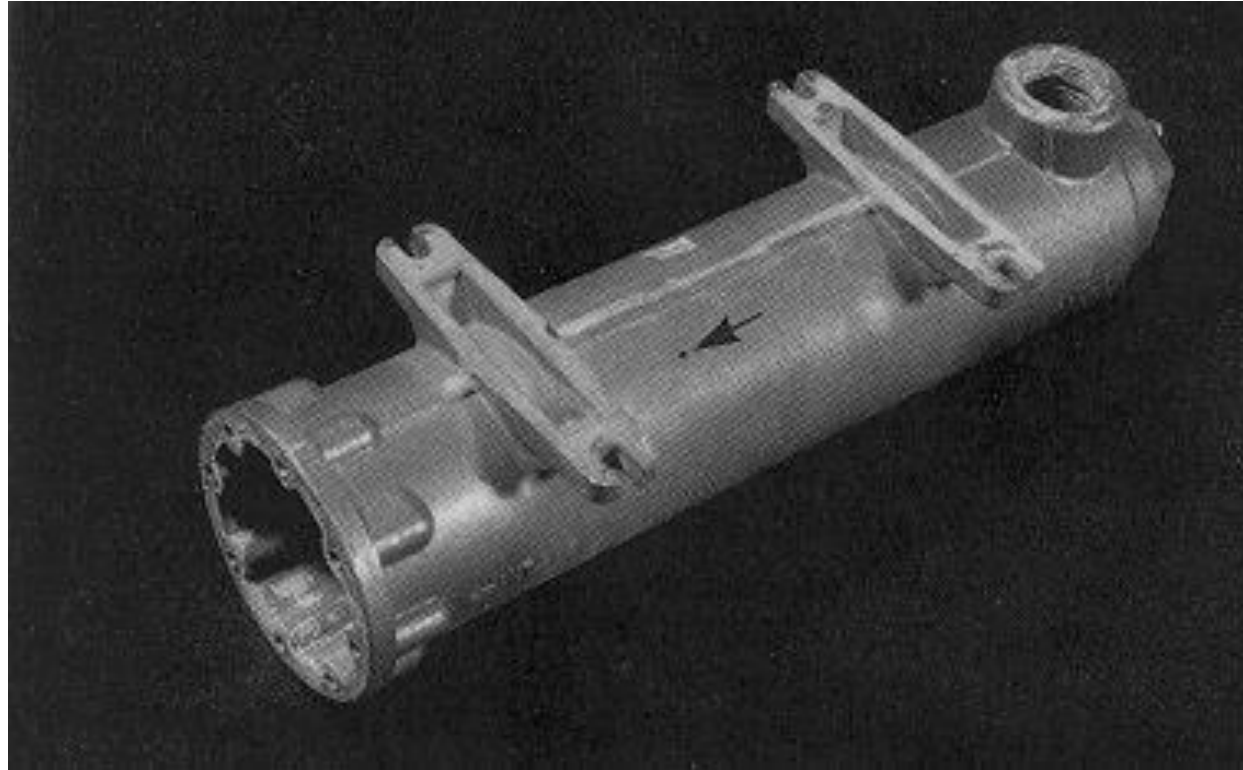


aircraft fitters having difficulty with an aluminium alloy fuel connector applied graphited grease to the joint with the steel pipe. This was fine until it rained when the joint seized.

Reasons and Solution

- Graphite conducts electricity
- Grease acted like a wire forming an excellent electrical contact between the metals
- Rapid corrosion and seizing!
- Use an alternative grease with no conducting material in it

Aluminium Heater Housing



Copper heating element in an aluminium cast shroud;
Rapid corrosion leading to rupture of the housing

Pipework

- Iron and copper frequently used in combination
- Copper very ductile and good thermal properties
- Iron and aluminium relatively cheap easily worked and cast
- Central heating, automotive and industrial applications
- Corrosion Inhibitors

Solutions to Pipework Corrosion

- Use of insulators between different types of metal pipe
- Use of sacrificial sections in pipework which are maintained more anodic and can be routinely inspected and replaced
- Site anodic metals upstream of cathodic metals to avoid replating

Lessons of Dissimilar Metal Corrosion

- Many more examples of dissimilar metal corrosion
- Think carefully when you are going to use metals of different types
- Try and electrically isolate different metals (especially copper and aluminium)

Electrochemical and Galvanic Series

- Electrode potentials act as a guide to activity but are precise values measured under certain conditions for pure metals
- Galvanic series more realistic based in sea water and includes metal alloys
- Metals to far right most likely to be anodic
- Metals far apart will corrode worst by dissimilar metal mechanism

Tea



Selective Attack Corrosion

Who fancies a snooze?

Dissimilar Metal Corrosion

- Metals have different electrode potentials
- Metals with more negative reduction electrode potential more likely to corrode
- Dissimilar metal corrosion when metals with different electrode potentials used together
- Metal with most negative E^0 is the anode and dissolves
- Other metal is the cathode

Alloys

- Alloys utilize combinations of metal atoms to produce superior performance materials
- Brass; Copper and zinc
- Aircraft alloys; aluminium, copper and magnesium
- Stainless Steel
- The combination of these different metals can be dangerous and give rise to *Selective Attack Corrosion*

Defects in Metals

- Metallic structures are rarely uniform
- Wide variety of defects such as dislocations, voids and grain boundaries
- The defective nature is important in determining metal properties
- Localised corrosion can occur at defects
- This is another form of *Selective Attack*
- Can also be very dangerous

Thermodynamics of Metal Defects

- Any atom or collection of atoms at a defect site will have a higher energy than an atom in the perfect lattice.
- Defect site atoms will be more prone to corrosion as a result of this
- Since corrosion is more likely at defect site surface will become pitted and is more likely to fail catastrophically

Types of Selective Attack Corrosion

- Grain boundary corrosion
- Intergranular corrosion
- Selective leaching of metals
- *Microbiologically induced corrosion*
- Any form of corrosion that attacks certain parts of a metal preferentially

1 Grain Boundary Corrosion

- At a grain boundary there is a mismatch in crystal structures
- Atoms at the boundary have *higher thermodynamic energy*
- Atoms at the boundary are more likely to be corroded
- Vital in microstructural investigations

Mild Steel Micrograph



Mild Steel polished and *Etched* by 2% nitric acid;
Grey is solid solution ferrite phase; stripy dark area
is a pearlite mixed ferrite and iron carbide. Specs
are a magnesium sulphide inclusions.

2 Intergranular Corrosion

- Intergranular corrosion occurs when a grain boundary is attacked by the presence of precipitates.
- Precipitates can be
 - Intermetallics* (mixed metal species)
 - Compounds* (metal/non-metal species)
- Precipitation occurs at grain boundaries and can be *cathodic* or *anodic* sites in damaging localised corrosion

Aluminium Aircraft Alloys

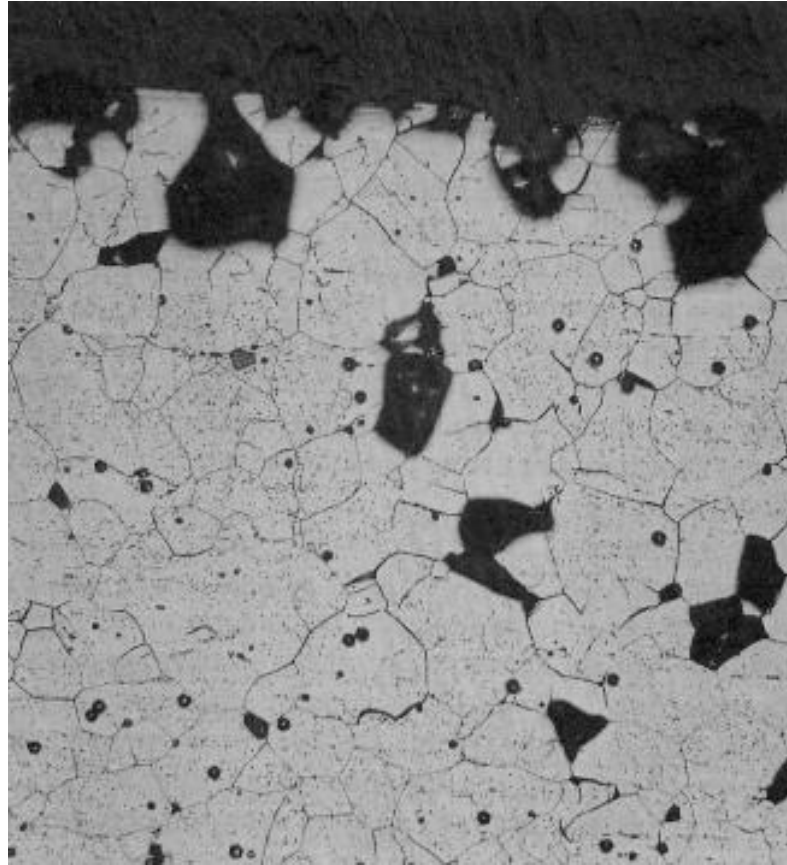


The alloys for aircraft are very often made from a potentially corrosively dangerous combination of aluminium, copper and magnesium.

Corrosion in Aluminium Alloys

- *Intermetallics* can precipitate out
CuAl₂ and FeAl₃ are cathodic
Mg₅Al₈ and MgZn₃ are anodic
- If an electrolyte is present then anodic intermetallics dissolve leaving a porous surface and cathodic intermetallics encourage corrosion in the surrounding airframe
- Potentially catastrophic failure
- Highlights importance of metal preparation and microstructural investigation

Stainless Steel



Severe pitting corrosion in a sample of type 304 stainless steel (18%Cr 8% Ni)

What is type 304 Stainless Steel?

- Chromium is added to inhibit the corrosion of iron by deposition of an inert oxide film
- When carbon content is $< 0.03\%$ only one phase. Above 0.03% C and two phases exist (a γ phase and a mixed material known as chromium carbide $(\text{FeCr})_{23}\text{C}_6$)
- Chromium carbide precipitates out at grain boundaries.
- Precipitation prevented if rapidly quenched

Why does type 304 suffer intergranular corrosion?

- Carbides precipitate at the grain boundary
- Chromium depletion around the grain boundary
- Loss of corrosion resistance around the grain boundary
- Localised and highly damaging corrosive attack

Replating Reactions

- Take a piece of iron and place it in a solution of copper ions
- Iron coats with copper and iron ions go into solution (corrodes)
- Cu^{2+} reduced Fe oxidised REDOX
- Made up of two half reactions
- Electrons travel through the metal

What if we have an iron and a copper electrode?

- Iron anode dissolves (corrodes)
- Copper cathode builds up
- HMS Alarm and dissimilar metal corrosion

Electrochemical terms

- Anode; anodic reactions (oxidation)
- Cathode; cathodic reactions (reduction)
- Electrode
- Half reaction
- Electronic current -current produced by the movement of negatively charged electrons. This is usually the case in metals
- Ionic current – current carried by positively charged ions

Why does the plating reaction occur?

- Overall negative Gibbs Free Energy change
- Easier to reduce copper than iron
 ΔG_1 $\text{Fe}^{2+} + 2\text{e} = \text{Fe}$ ΔG_2 $\text{Cu}^{2+} + 2\text{e} = \text{Cu}$
- ΔG_1 more negative than ΔG_2
- Driving force is the more favourable reduction reaction of copper

Electron transfer and electrode potentials

- Electrons flow from the anode to the cathode
- The electrodes must have a potential difference
- The potential difference drives the reaction
- Electrodes have a potential which must relate to Gibbs Free Energy

Relating Gibbs Free Energy to potential

- Faradays Law
- $\Delta G_1 = -nFE_1$
- For the copper plating reaction
negative than ΔG_{Fe} E_{Cu} more positive than E_{Fe} ΔG_{Cu} more
- Metals of different types will have different potentials

Metals have different potentials

- Electrode potential is a measure of ease of extraction and likelihood of corrosion
- Large positive E metal stable
- Large negative E metal corrodes
- Electrochemical series

Measuring Electrode potentials

- Potential must be measured relative to a standard value
- $2\text{H}^+ + 2\text{e}^- = \text{H}_2$ set as zero
- Standard hydrogen electrode
- Gases 1 atmosphere
- solutions at 1 mol dm^{-3}
- Temperature 298K

What does an Electrode potential mean?

- Likelihood of reaction in thermodynamic terms
- $\Delta G = -nFE$
- Large positive E stable metal
- Large negative E metal readily corrodes

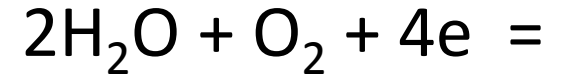
The effects of concentration

- Most likely that concentrations will not be unity
- Nernst equation

- Galvanic Series? $E = E^0 - \frac{RT}{nF} \ln \frac{[\text{products}]}{[\text{reactants}]}$

Practical Wet Corrosion

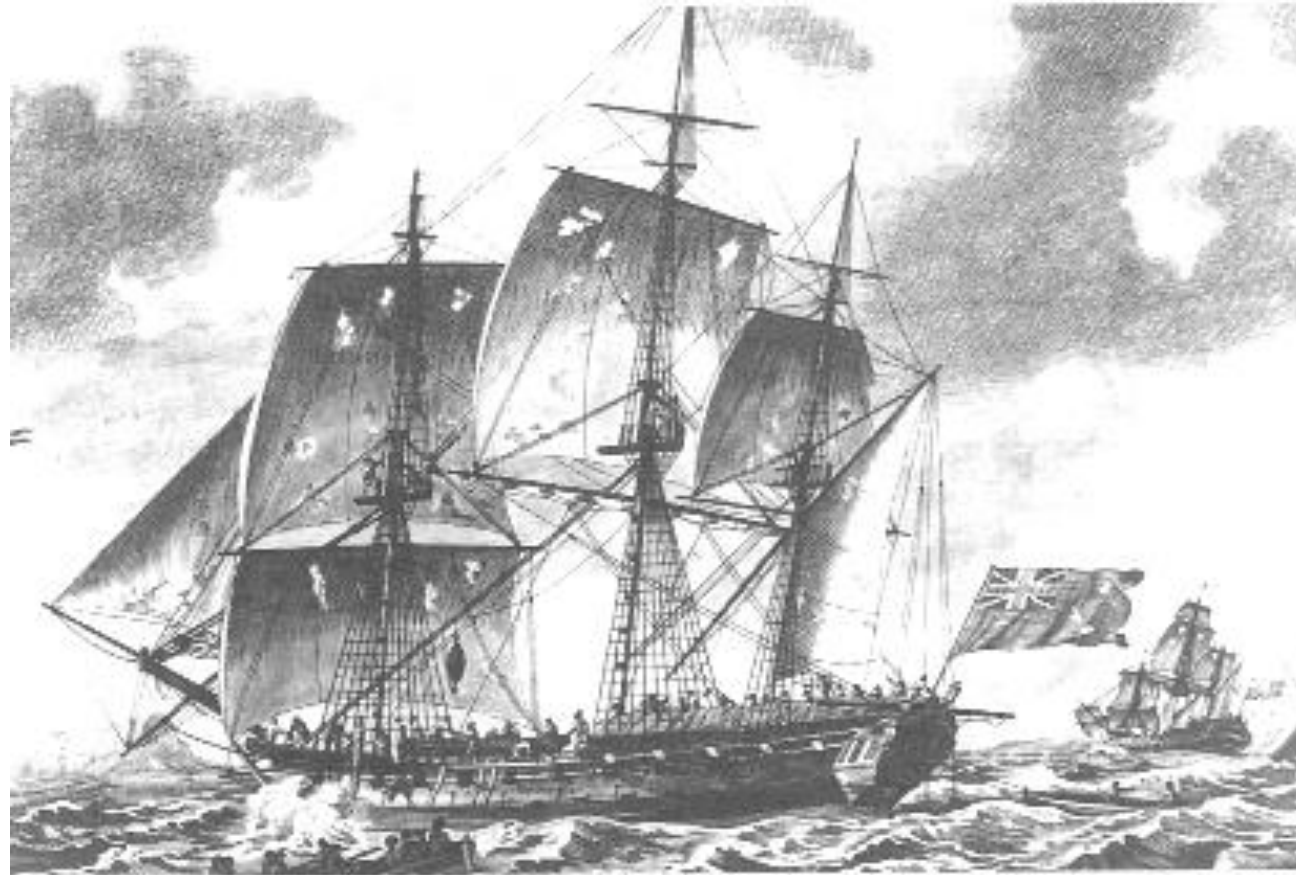
- Anodic Reaction is metal dissolution
- Cathodic reaction depends on the pH
- Low pH hydrogen evolution
- Normal pH oxygen reduction
 $4\text{OH}^- \quad E = +0.4\text{V}$



Preventing Wet Corrosion

- Wet corrosion cell comprises 4 basic parts
- anodic and cathodic activity, electron flow through the metal, ionic flow through the electrolyte
- First law of corrosion prevention; stop any one of the four and you will prevent corrosion

HMS Alarm; 1793



Copper base attached to the hull with
iron nails, which rusted

Why did the nails corrode?

- Copper acts as a huge cathode for oxygen reduction
- Thermodynamically easier to oxidise iron
- Electrons for oxygen taken from iron
- iron dissolves in preference to copper
- Prevention involves electrical isolation of the nails

Sea Harrier 1982



Magnesium wheel hubs collapsed

Why?

- This time magnesium is easier to oxidise than iron
- Iron is the cathode and anodic reaction is dissolution of the wheel hub
- Prevention by electrical insulation

Anodes and cathodes on a single surface

- When a metal corrodes in isolation of other metals the anodes and cathodes exist on the same surface
- Electrons flow from anodes to cathodes
- Precipitation Hardened Aluminium

Metals Have Different Potentials

- Electrode potential indicates thermodynamic driving force for corrosion
- Large negative electrode potential; metal more likely to corrode
- Problem if we have a system where two metals of different potential are connected
- Sets up a battery!!

Roman Boat Builders

- Romans recognised the benefit of copper plating wooden boats
- Use of iron nails failed as iron was rapidly corroded
- Switch to copper nails in 3 BC

Dissimilar Metal Corrosion

- The presence of two metals with different E^0 values that are connected and have an electrolyte present leads to corrosion
- The metal most easily oxidised (most negative E) corrodes
- The other metal becomes the oxygen reduction cathode
- Iron and copper; H.M.S. Alarm, Copper and steel pipes (central heating systems)

Dissimilar Metal Corrosion to Protect a Metal

- Galvanised steel; dissimilar metal corrosion occurs.
- Zinc anodic and dissolves protecting iron which is cathodic; sacrificial anode
- Zinc corrosion products protect damaged area
- In aggressive media use sacrificial anode blocks

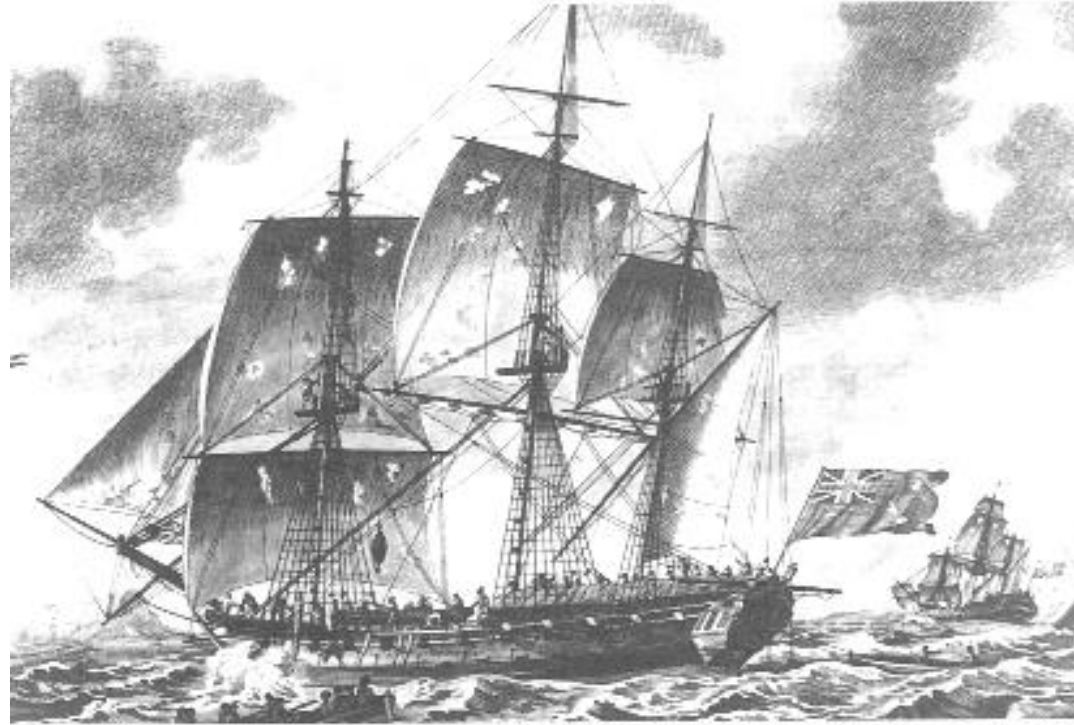
Dissimilar Metal Corrosion Illustration by Example

- Many examples of dissimilar metal corrosion from many industries
- In each case corrosion due to thermodynamic differences between connected metals
- Can usually be easy to solve

Marine and Navy

- Marine environment very hostile to metals
- Loads of examples from earliest times where use of different metals has caused problems

H.M.S. Alarm 1792

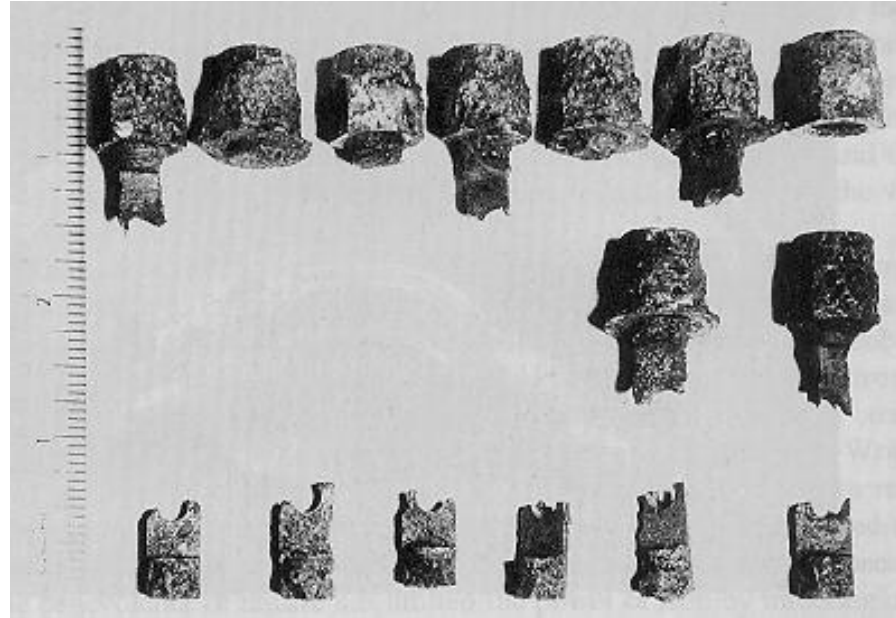


Copper sheeting attached to the boats hull with
iron nails that rapidly corroded
Copper acts as a cathode iron as an anode

Corrosion Prevention Through Electrical Isolation of the Metals

- Waxed paper that wrapped the sheeting insulated the metals and the iron did not corrode as fast
- First law of dissimilar metal corrosion prevention; stop your metals touching and having direct electrical contact

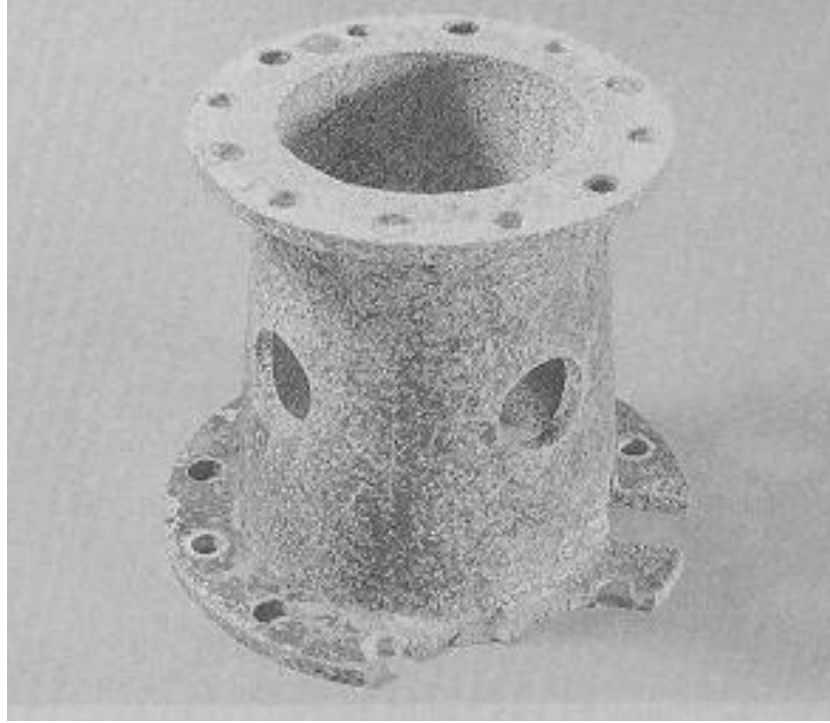
Submarine 1962



Copper evaporator plate in a boiler held on with iron nuts and bolts; rapid corrosion.

Insulate the nuts and bolts using plastic sleeves and washers

Aluminium Aerial Support



In order to get better reception aerial moved to a position just behind the funnel. Fumes stripped off paint and soot built up leading to corrosive failure

Reasons for Corrosion

- Soot is made of carbon
- Carbon conducts electricity
- Carbon is a good cathode material
- Soot acts as a cathode site inducing anodic corrosion of the more active aluminium
- Move aerial to in front of stack
- Ensure regular coating maintenance

Statue of Liberty

- Copper skin supported on a network of iron ribs
- Tar insulation between the skin and the iron
- Not permanently fixed to allow for expansion and contraction
- Tar failed and iron rusted causing rivets to fail
- Use of more modern sealers

Lightning Conductor and Smoke Stack

- A copper lightning conductor was placed over 6m from a aluminium roof on a chimney
- The aluminium roof rapidly failed after only a short time

Reasons for Corrosion

- Small amounts of copper dissolved in the rain
- Copper plated out on the aluminium
- Copper islands acted as cathodes in bimetallic corrosion with the more reactive aluminium dissolving
- Move the conductor to the other side of the chimney or use different roofing material

Designing against Crevice Corrosion

- If potential crevice site can be avoided during manufacture this is best.
- Some seams are inevitable and must be sealed
- Ensure that plastic and rubber fittings onto metal shafts are water tight

2 Pitting Corrosion

- Very similar in many ways to Crevice corrosion
- Difference is in the initiation phase
- Crevices initiate through heterogeneous electrolyte composition
- Pitting initiates at a metallurgical defect

Potential Pitting Sites

- A scratch on a barrier coated smooth metal surface
- An emerging dislocation or slip step
- A compositional defect such as an inclusion or precipitate (eg intermetallics in aluminium alloys or precipitate sites in stainless steels)

Pitting Corrosion Mechanisms

- Pit must protect itself to survive
- Many pits initiate and die; *unstable* pitting
- Pits that survive nucleation are *metastable* and can go either way
- If a pit can form a corrosion product cover over itself it can survive; this is *stable pitting*
- Stable pitting is dangerous and proceeds via a very similar mechanism to crevice corrosion

Prevention of Pitting Corrosion

- Stainless steels and aluminium particularly prone to this corrosion
- Polarise at an alternating potential
- Treat chemically
- Electrolyte flow
- Mechanisms of corrosion prevention not well understood
- Most likely the growth of protective oxide layers

3 Differential Aeration Corrosion

- Both crevice and pitting corrosion are due at least in part to differential aeration
- Here there are different oxygen levels at different parts of the metal
- Where oxygen levels are lowest anodic metal dissolution dominates
- Where oxygen levels are highest cathodic oxygen reduction predominates

Corrosion under a rain drop

- Initial anodic and cathodic activity everywhere
- Cathodic reactions use up oxygen
- Easily replenished at the edge of the drop more difficult at the middle
- Centre of drop becomes focal anode and edge cathode
- Corrosion product forms as a ring around a pit in the metal

Designing Against Differential Aeration

- Avoid Debris Traps
- Avoid water absorbent materials
- Ensure adequate drainage and ventilation
- Avoid sharp edges
- Care with metal tanks and pipes

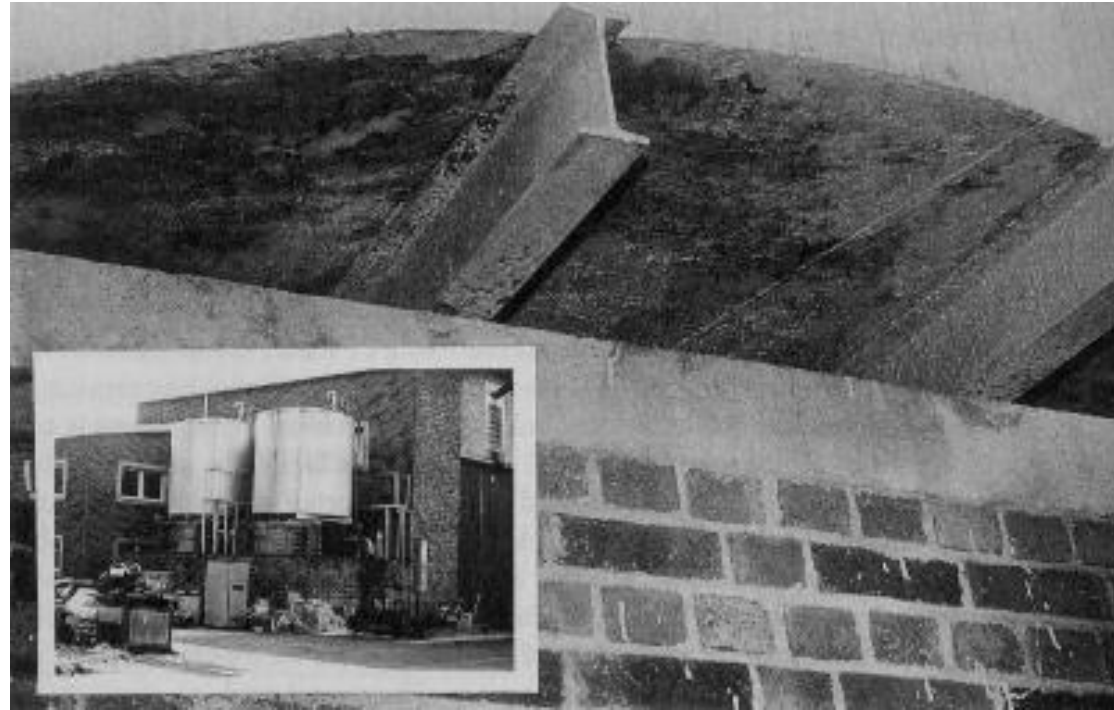
Debris Traps

- Road debris can be a particular problem in car corrosion
- Debris can be mud, loose corrosion products, leaves, sealing foams.
- Debris allows differential aeration corrosion to start
- Make curved and easily cleaned panel work

Sound and thermal insulation foam

- Sound proofing and thermal insulation can absorb water
- Water trapped against metal in absence of oxygen rapidly corrodes the metal
- Car doors and industrial pipe-work particularly affected

Inadequate Ventilation and Poor Drainage



Bottoms of tanks often badly corroded. poor ventilation means tank always wet and differential aeration corrosion can start

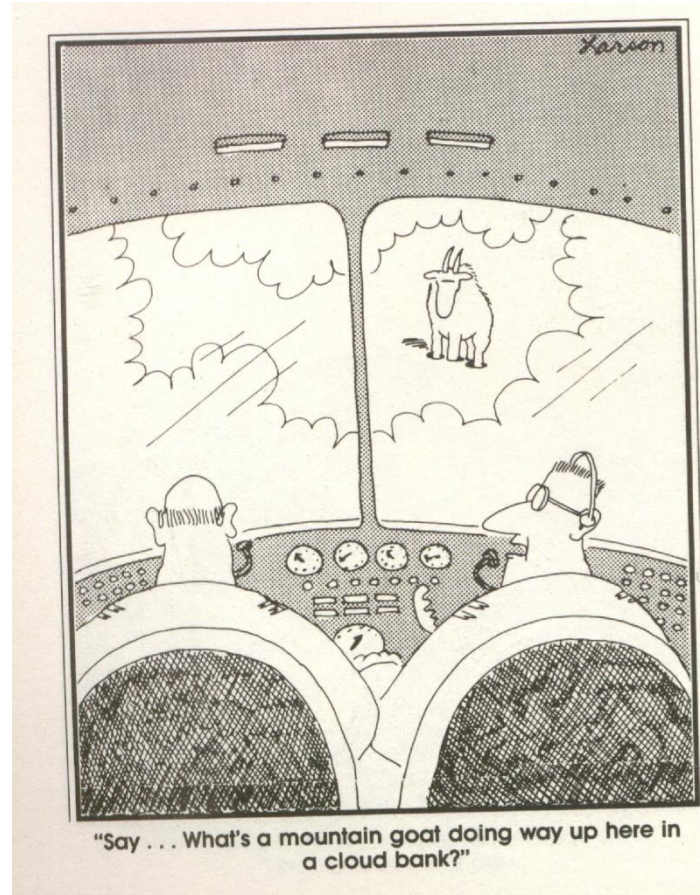
Improving Drainage on Girders

- Prevent pooling of stagnant water
- Provide good drainage
- Care when sealing box sections

Problems of Tank Drainage

- Do not allow stagnant water to sit in the tank
- Ensure free and complete drainage of the tank by improved design

Tea?



Flow Induced Corrosion

Stress Induced Corrosion

Corrosion in Fluids

- Differential aeration corrosion is a problem in static waters
- Many examples where the fluid is anything but static; propellers, turbines, pipes
- Although electrochemical corrosion can be a problem failure is often through mechanical abrasion
- This is Erosion Corrosion

Erosion Corrosion

- Damage to metal surfaces due to physical abrasion
- **NOT an Electrochemical Mechanism**
- Softer metals generally worse affected (Copper, brasses, aluminium)

Fluid flow types inducing erosion corrosion

- Laminar Flow
- Turbulent Flow
- Impingement
- Cavitation

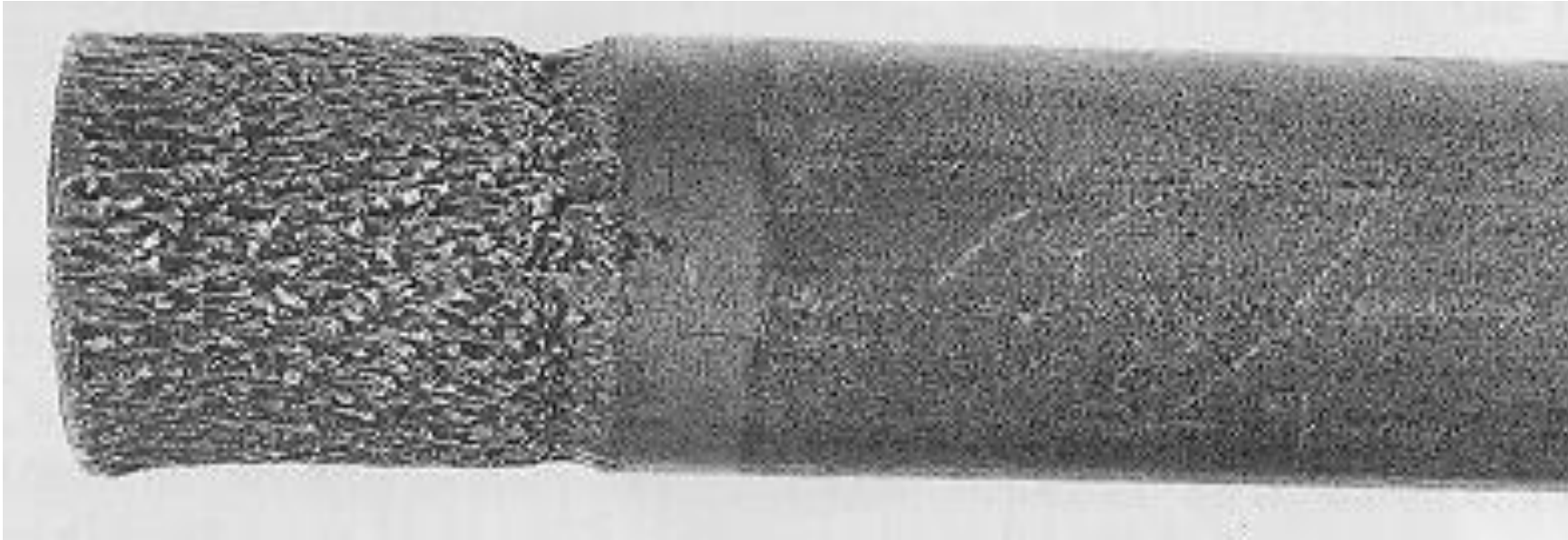
Laminar flow

- slow flow; liquid moves in layers
- layers closest to metal move slower due to friction and surface roughness
- Oxygen replenished
replenished
be scoured
May prevent silting
Ions
Protective layer may
- Complex problem!

Turbulent flow

- When flow rate increases such that frictional forces between layers cause flow in more than one direction
- Generally much more damaging
- Often characterised by samples looking as if they have been sculpted!

Heat Exchanger Tube

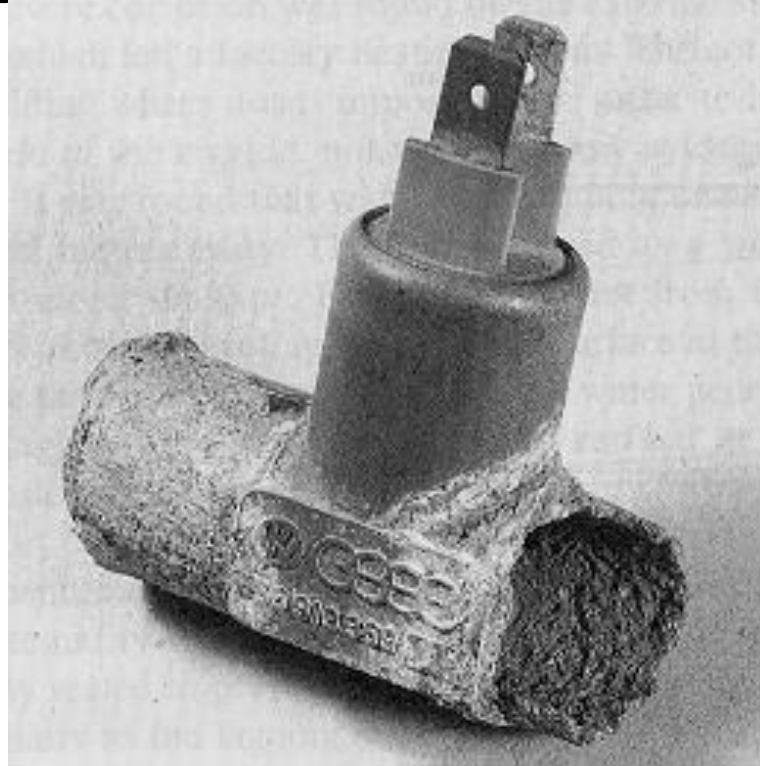


Admiralty brass heat exchanger tube took steam into a restricted condenser pocket. Very turbulent flow and subsequent erosion corrosion. Serious tip roughening

Turbulent flow as a result of surface geometry

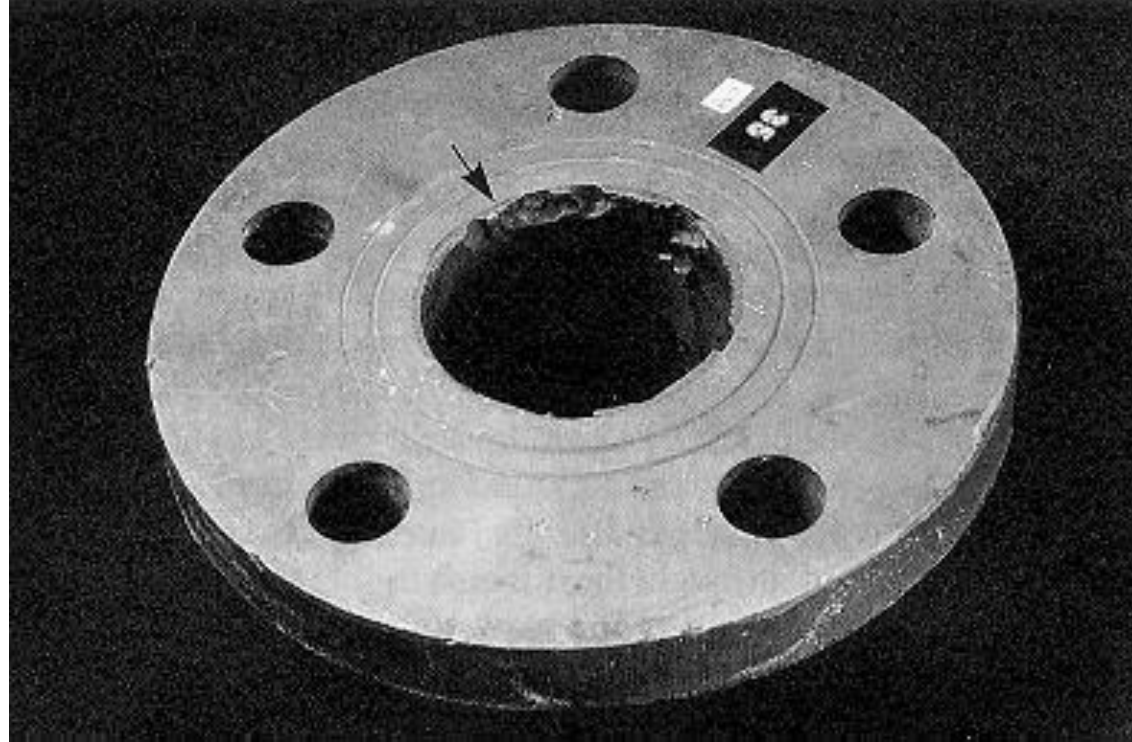
- The metal shape can induce turbulent flow
- Sudden Changes in pipe bore or direction
- Obstructions to electrolyte flow
- Crevices allowing fluid escape
- Debris and corrosion product build up

Temperature Sender Housing



Alloy Temperature Sender housing connected with wider bore rubber tubes. Sudden bore change results in turbulence and rapid erosion corrosion failure.

Badly Fitting Gasket



Gasket obstructed fluid path causing turbulence.
Erosion corrosion failure of copper alloy flange

Valves



Valve not closing properly allowed escape of fluid under pressure. Crevice erosion corrosion. Potential problems in cars.

3. Damage by Impingement

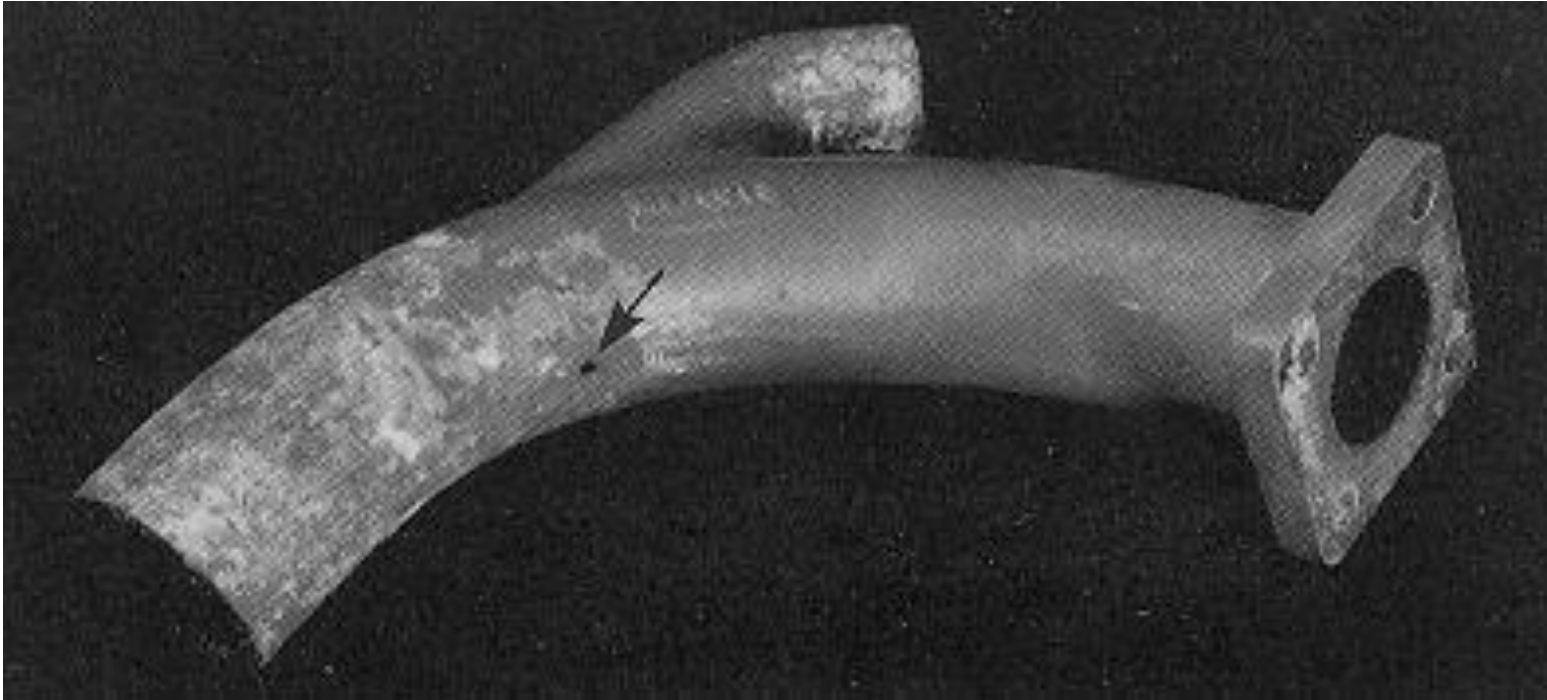
- Extreme form of turbulence
- Fluid molecules impinge directly on metal
- Perpendicular component to flow
- Potentially very damaging in Aircraft
- Highly localized wearing in impingement areas

Aircraft damage



Very careful design required due to water vapour and rain impingement on the metal. Early Supersonic aircraft were particularly affected.

Exhaust Manifold

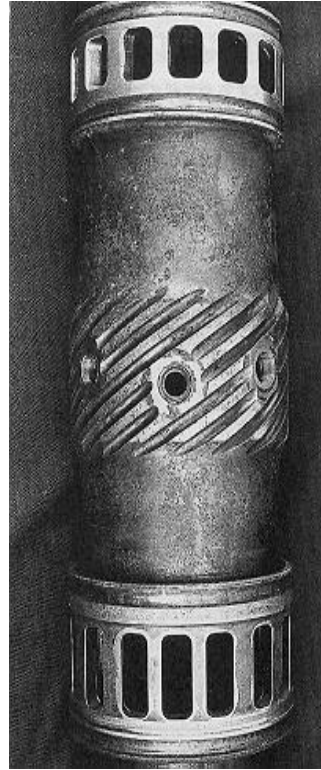


Marine Diesel Engine exhaust; exhaust gases down manifold and cooling water through a side tube.

Cavitation

- Affects objects moving rapidly in a fluid
- Propellers, turbines etc
- The hydrodynamic pressure on the back face of the turbine induces bubble formation
- Bubbles collapse violently directing a jet of fluid at the metal
- Causes pitting through mechanical impact
- Pitted surface better for bubble formation

Diesel Engine Wet Liner



Wet liner contains engine piston. Coolant flows around outside. Intense vibration from explosions induces cavitation and erosion corrosion despite smooth design

Design Against Flow Induced Corrosion

- Avoid turbulent flow
- Ensure smooth fluid paths
- Minimise obstructions
- Minimise debris in fluid
- Minimise cavitation and where possible chose a hard metal

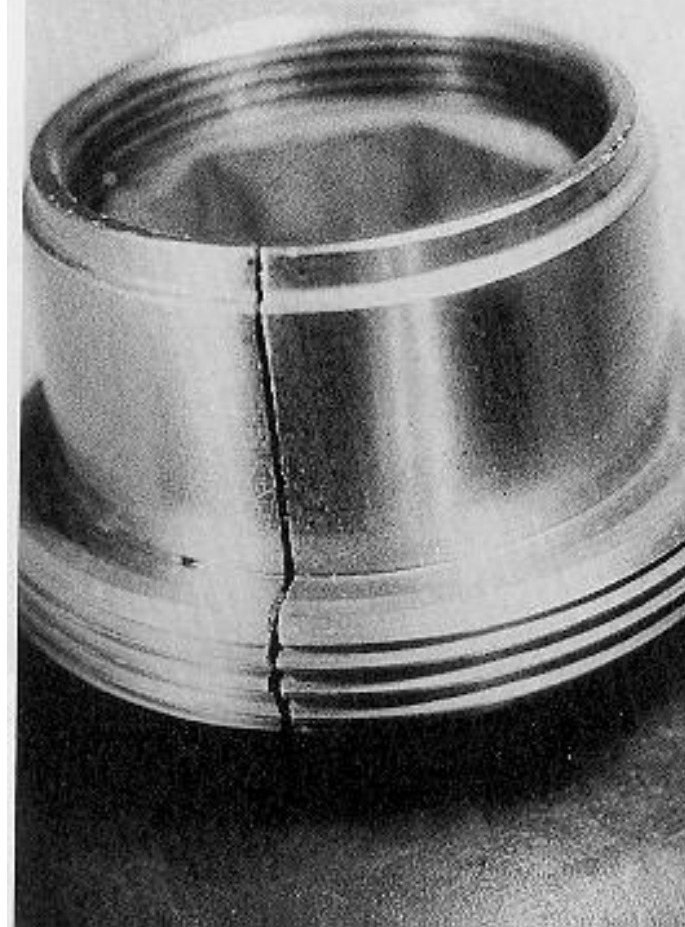
Environment Sensitive Cracking

- Ammunitions in 19th century India
- 70/30 brass cartridges failed after storage in stables during monsoon season
- Common failure of pressurised steam boilers at riveted joints
- Residual stresses induced corrosion

What is Stress Corrosion Cracking SCC

- Intergranular or transgranular corrosion induced in a metal by a combination of a static stress and a specific chemical environment
- Highly costly
- Very damaging affecting stressed objects from boiler, to pipes, turbines and welds.
- Seems to be worst in normally stable alloys

Stressed Brasses



This brass fitting for a pressurised gas bottle. Highly stressed during manufacture, failed by SCC in storage.

Pipework

- Stainless steels particularly affected
- In presence of trace chloride ions rapid failure in stressed areas
- Affects electricity generators and chemical industry to name a few

PWR reactor piping



Hand holds welded on. This introduced residual stresses in the metal and it failed

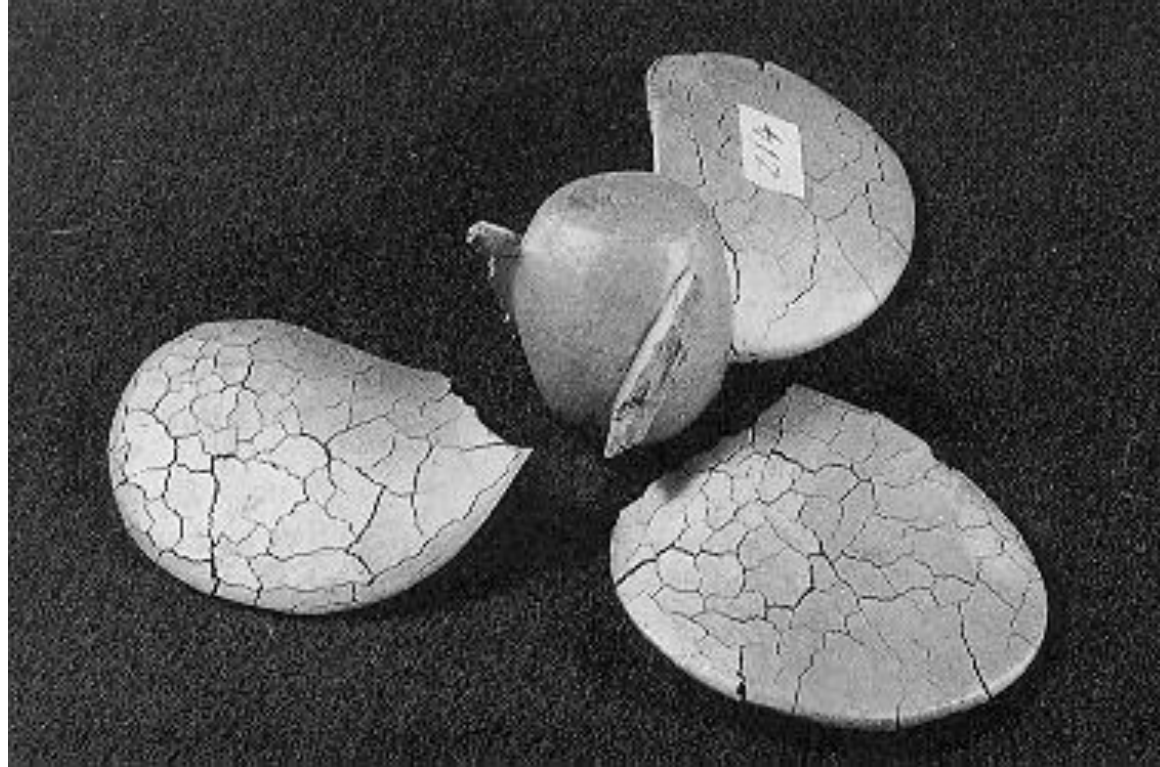
Turbine Blades

- Aberthaw;
- Failure of blades due to contamination of ultra-pure steam water with sea water coolant.
- Rapid corrosion in stressed area

Failure Below Fracture Stresses

- Residual Stresses in Objects can result in SCC
- Can be highly unpredictable

Al/Si Alloys



Particularly susceptible to this form of corrosion
High residual stresses resulted in failure of a normally stable alloy.

How does SCC Occur

- There is no one distinct mechanism and despite much research the details of the corrosion mechanism are as yet not well understood
- Comprises two stages
 - Initiation phase
 - Propagation Phase

Initiation before elastic limit

- In any structure there are defects which can act as pitting corrosion sites
- dislocations, grain boundaries, intermetallics and precipitates
- Can occur due to increases in surface atom thermodynamic energy due to applied stress

Initiation After Elastic Limit

- In forming objects metals are deformed plastically
- Deformation due to movement of dislocations
- Dislocations concentrate at grain boundaries
- Slip steps come through to surface
- Defects act as initiation sites and form a pitting corrosion cell

Propagation

- Pre-existing paths
- Strain generated active paths
- Adsorption related mechanisms

Pre-existing Pathways

- In a formed object very many dislocations at grain boundaries.
- Dissolution of these atoms is favourable
- Dissolution along the lines of grain boundaries by intergranular corrosion
- (intermetallics and precipitates a problem)

Strain Generated Active Path Mechanisms

- If a stress is applied and rupture a protective oxide film then corrosion will occur
- A pit will form and initiate cracking.
- Continued application of stress cracks any passivation at the crack tip
- fast and slow passivating metals are OK
- Intermediate passivation a real problem

Adsorption Related Mechanisms

- Aggressive electrolyte ions
- Hydrogen embrittlement

Aggressive Ion Adsorption

- Chloride ions in stainless will form complexes with metal atoms
- Breaks metal metal bond
- Increases crack depth

Hydrogen Embrittlement

- pH as low as 2 in crack
- hydrogen evolution is the cathodic reaction $\text{H}^+ + \text{e} = \text{H}$
- H atoms can diffuse into metal
- H atoms disrupt bonding, form hydrides, and hydrogen gas in metal voids
- Hydrogen embrittlement further weakens structure and encourages failure

Designing Against SCC

- Prevent residual stresses by careful annealing
- Take care when welding
- Eliminate possible sources of aggressive ion contamination in high stress applications such as turbines

Prepare for DOOOM



Day 2

Thermodynamics and Kinetics of
Corrosion and Corrosion Inhibitors

AAAARGH NO !!!!

Electrode Potential and Corrosion

- The electrode potentials of half cells drive the corrosion reaction
- Electrode potentials measured under standard conditions against SHE
- Expressed as reductions
- More negative E^0 the more easily corroded
- Conditions are rarely standard

Complex Electrochemical Corrosion

- Electrochemical corrosion is complex
- Electrode potential and pH are important in determining corrosion activity
- Usually a very wide range of potential chemical reactions
- From a knowledge of the important equations and the Nernst Equation we can predict materials performance.

Corrosion Reactions of Zinc

- Zinc is an important sacrificial anode material
- Five major corrosion reactions
- Some involve electron transfer, some protons and some involve both!
- Very complex but fortunately summarised by Mr Pourbaix into one figure!!

Pourbaix Definition of States of Corrosion

- Metal corroding when the concentration of its ions reaches $10^{-6} \text{ mol dm}^{-3}$
- Below this concentration the metal is immune
- If the metal becomes protected by an insoluble layer (eg zinc hydroxide) the metal is said to be passive
- Beyond passivity more activity known as trans-passive behaviour may result

Origin of Pourbaix Lines

- Complex; detailed on sheet for anyone with no life! All calculated with Nernst equation
- Horizontal lines involve only electron transfer ($\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$)
- Vertical lines only involve protons
$$\text{Zn}(\text{OH})_2 = \text{ZnO}_2^{2-} + 2\text{H}^+$$
- Sloping lines involve electron transfer and protons
- Corrosion when $[\text{Zn}^{2+}] = 10^{-6} \text{ mol dm}^{-3}$

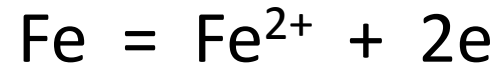
What does the Pourbaix Diagram Tell us?

- Shows at a glance the regions over which metals will be immune, corroding, passive and transpassive.
- Metals can easily and quickly be compared when uses in different chemical environments are needed.

Kinetics of Corrosion

- Electrode potential gives a measure of thermodynamic possibility of corrosion

- Oxidation and reduction involve electron transfer



- Rate of reaction will be given by a current i $\quad \quad \quad \text{dM/dt} = (i/nF)$

Gibbs Free Energy Changes and Corrosion Rate

- Gibbs Free Energy is thermodynamic driving force
- Gibbs Activation energy controls rate
- $k = A \exp(-G^*/RT)$
- Current exponentially related to Gibbs Activation energy

Gibbs Free Energy and Electrode Potentials

- $G = -nFE$
- Gibbs activation energy directly related to the electrode potential
- Current and potential must be exponentially linked

Relation of Cell Potentials to Corrosion Rates

- Corrosion rate given by current i
- Potential and current are exponentially related
- Need to develop a relationship that describes effect of potential on the current
- Need to consider Anode and Cathode reactions separately

Anode Reactions

- Oxidation and reduction of metal possible $M = M^{n+} + e$
 $M^{n+} + e = M$
- Oxidation has an anodic current i_a
- Reduction has a cathodic current i_c
- At equilibrium potential when E_{eq} given by Nernst
exchange current $i_a = i_c = i_0$

Corroding Anode

- Cell potential not given by Nernst due to non equilibrium
- Electrode is polarised w.r.t. equilibrium potential E_{eq}
- overpotential $\eta = E - E_{eq}$
- E is polarised potential and E_{eq} is the equilibrium value
- As η (E) varies anodic and cathodic currents will alter

Anodic and Cathodic Current Relationships at the Anode

- η variation induces variation in the current i
- Tafel equations
- α is a Tafel constant for a particular anode
- make η more positive increase in anodic current and decrease cathodic current
- make η more negative then cathodic current increases and anodic current decreases

Tafel Equations

- Overpotential and current exponentially linked
- Plot of $\log i$ vs η (or E) will linearise data
- i_a increases with increase in η
- i_c decreases with increase in η
- intersection where $E = E_{eq}$
- intersection current is exchange current i_0

Cathode Reaction Kinetics

- Identical Tafel type equations
- E_{eq} is more positive since material is an oxidising agent
- Intersection of lines gives E_{eq} for the cathodic reaction

Evans Diagram

- Combined anode and cathode reactions
- Ignore lines except for i_c for oxygen reduction and i_a for metal dissolution
- Point of intersection gives i_{corr} corrosion rate and E_{corr} the potential adopted by the metal as it corrodes
- From Tafel parameters corrosion rate and potential can be calculated

Passivation and the Anode Reaction Kinetics

- Pourbaix tells us that a metal may passivate
- This affects the Tafel plot for the anodic (metal dissolution)
- Initial Tafel region
- Passivation potential; stable
- Critical pitting potential removes passive layer
- Transpassive pitting corrosion has different Tafel parameters

Corrosion Control by Inhibition

- Many coatings contain chemical species that inhibit the rate of one of the half reactions
- Anodic Inhibitors
- Cathodic Inhibitors
- Adsorption Inhibitors

Anodic inhibition by Precipitation

- Species form an insoluble precipitate by reaction with metal ions produced from corrosion
- phosphates, chromates, molybdates
- Inhibitor plugs anodic site
- Lowers i_a , and increases electrode polarisation
- Lower i_{corr} but higher E_{corr}

Anodic Inhibition by Cathodic Depolarisers

- Oxidising agent (chromate) increases rate of oxygen reduction and increases i_c
- Increase in E_{corr} to passive region slows down overall corrosion rate
- Can also be a problem!

Advantages and disadvantages of anodic inhibitors

- Small amounts can have a large effect
- Included in paint pigments
- If passive layer incomplete aggressive attack
- E_{corr} pushed higher can be dangerous
- Increased cathodic activity can drive overall corrosion
- Aggressive ions might remove passive layer
- Environmental hazard of inhibitors

Cathodic Inhibitors

- Precipitation; inhibitors react with hydroxide ions produced from oxygen reduction
- Calcium and strontium compounds as well as zirconates and titanates
- Cathodic Poisoning; suitable for metal in acid environments
- Arsenic Bismuth and antimony compounds prevent hydrogen gas formation

Advantages and Disadvantages of Cathodic Inhibitors

- Safer since they do not increase E_{corr}
- Can be inefficient
- Potential for hydrogen embrittlement
- Problems of metal leaching from coatings if heavy metals used

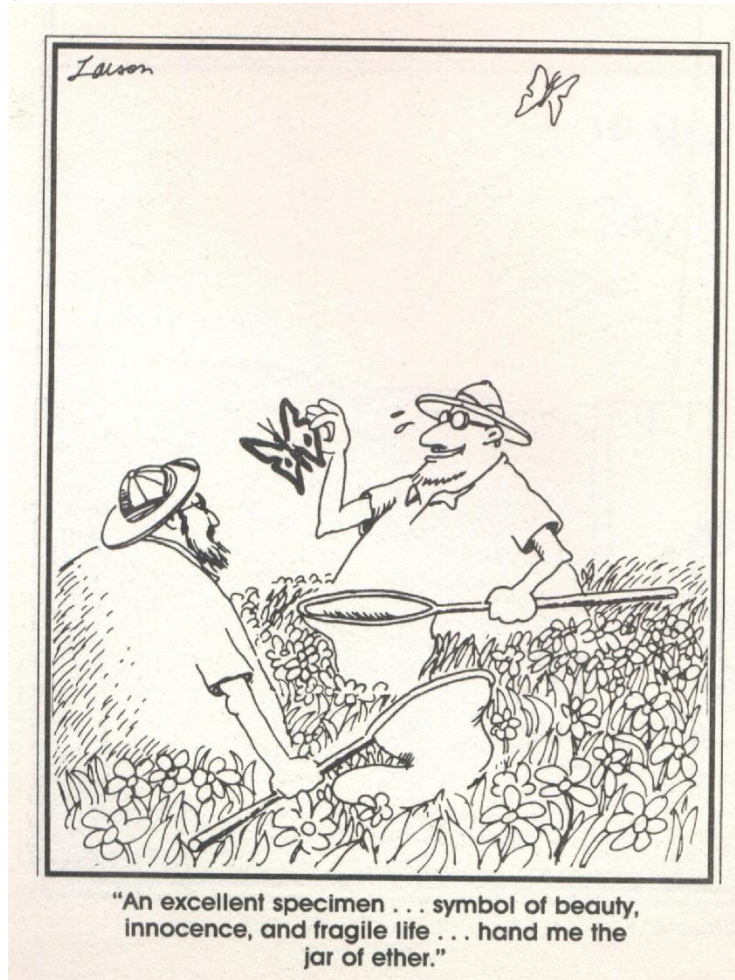
Mixed Inhibitor Systems

- Strontium chromate is often used
- Strontium for cathodic inhibition
- Chromate for anodic inhibition
- Synergistic affect

Other Inhibitors

- Adsorption inhibitors
- Long bulky organic group functionalised by adding a reactive end group
- Phosphonates, amines and mercaptans
- Active end bonds to metal
- Large bulky group prevents oxygen penetration and aids coating adhesion

Enough Already!!!!



Cathodic and Anodic Protection

Corrosion Control by Potential Control

- Alternative to inhibitors better suited to bulk applications
- Potential of the metal is altered so it becomes immune or passive
- *Cathodic Protection*;

sacrificial anodes

impressed current protection
- *Anodic Protection*

Pourbaix Diagram for Iron

- Free corrosion potential E_{corr} for iron ca -600 to -700mV vs SSC (from Evans diag)
- The metal is corroding in this range
- In sea water no passivation below pH 5
- Sea water pH is ca 8.2 - 8.5
- E_{corr} remains similar in sea water
- Potential aggressive corrosion

Possible Methods of Corrosion Prevention

- Increase the pH; not feasible!!
- Apply a more negative potential; If we lower E_{corr} then metal can become immune This is *Cathodic Protection*
- Make the potential more positive; If we raise E_{corr} then metal can become passive This is *Anodic Protection*

Sacrificial Anode Cathodic Protection

- Make a wet corrosion cell in which the steel is the cathode and another metal is the anode
- Chose a dissimilar metal with a more negative E^0 for the anode
- Set up a dissimilar metal corrosion cell
- Care when choosing a suitable metal
- Anode size depends on the structure size

Effects of Connecting Dissimilar Metals

- Consider the Evans diagram for two connected metals
- E_{corr} for system is more negative than E_{corr} steel and more positive than E_{corr} zinc
- Zinc is the anode (Metal dissolution)
- Steel is the cathode (oxygen reduction)

Metal Corrosion Protection

- Steel will be protected as long as E_{corr} for system remains $< -800\text{mV}$ vs SSC
- This is defined as the protection potential E_p
- As zinc is used up E_{corr} may start to rise and there is some danger of iron corrosion
- Important to replace anodes regularly maintaining desired anode to cathode area ratio

Sacrificial Anode Materials

- Zinc based alloys
- Aluminium alloys
- Magnesium

Zinc Alloys

- $\text{Zn}^{2+} + 2\text{e} = \text{Zn}$ $E^0 = -0.76\text{V}$
- Alloys used since zinc will passivate
- Zinc contains trace iron which above 0.0014% forms islands
- Iron islands act as cathodes
- Zinc hydroxide precipitation raises E_{corr}
- Aluminium added to remove this effect
- Cadmium added to lower effect of lead

C-Sentry Zinc



Zinc anodes; 0.1-0.5% Al 0.025-0.15% Cd
Widely used Marine Sacrificial Anode Materials
360 mm long; weight ca 4kg

Aluminium

- $\text{Al}^{3+} + 3\text{e} = \text{Al} \quad E^0 = -1.67\text{V}$
- Typically suffers pitting corrosion in sea water due to inert oxide layer and intermetallic precipitates
- Zinc, mercury and indium added prevent the oxide layer forming
- Very efficient anode since three electrons transferred and anode material is very light weight

Magnesium

- $\text{Mg}^{2+} + 2\text{e} = \text{Mg}$ $E^0 = -2.34\text{V}$
- Efficient anode for application in non sea water environment
- In sea water rapidly dissolves
- Care must be taken in potential combustible environment
- Often used for underground pipes

Combined Coating and Cathodic Protection

- For many applications the cathode size is reduced by painting
- Minimises anode usage and saves money on painting
- As coating is worn and removed sacrificial anode will cathodically protect the structural metal

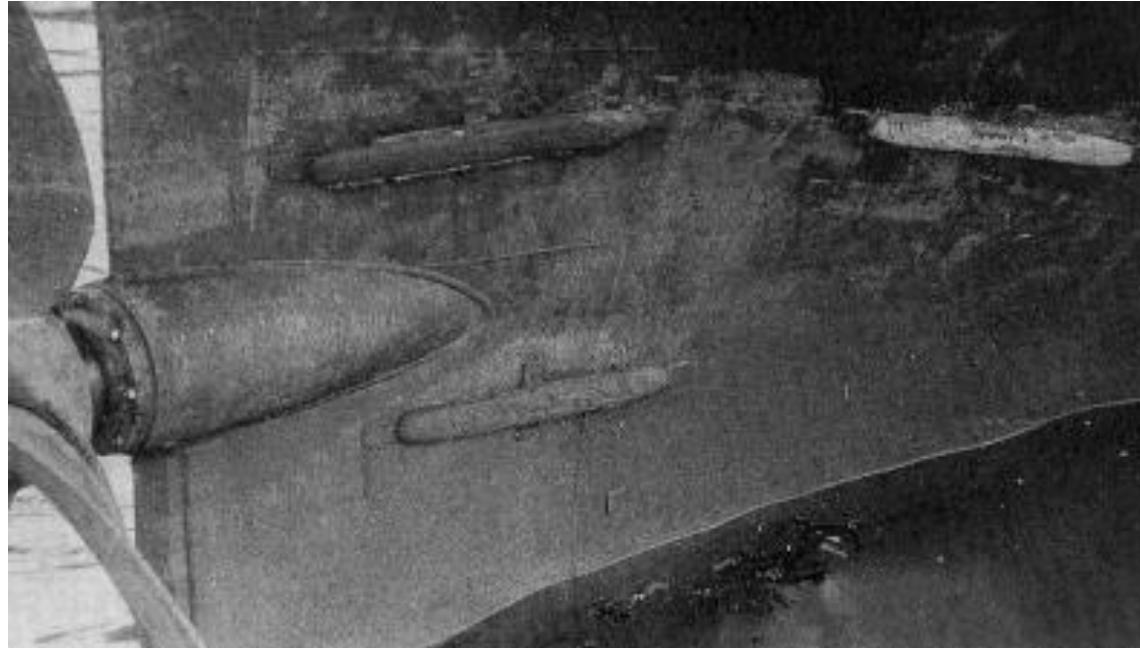
Possible Problems with Coatings

- Cathodic reduction reaction produces hydroxide ions
$$O_2 + 2H_2O + 4e^- = 4OH^-$$
- Hydroxide ions can delaminate paint
- If potential too low then the reduction reaction can become hydrogen evolution
- This can occur if anode to cathode area ratio too high
- Potential hydrogen embrittlement problems

Sacrificial Anodes Applications

- Ships
- Offshore Rigs
- Subterranean Pipelines
- Subsea pipelines

Ships



Sacrificial anodes placed in direct contact with the hull
Often placed in propeller area to prevent fowling and
provide additional protection for brass propeller and
shafts.

Ships (Cont)

- Sacrificial anodes also used to protect water intakes for coolant systems
- Anodes must never be over painted
- Anode replacement requires vessel to be dry-docked
- Impressed current protection is now favoured

Offshore Platforms



These are often unpainted steel structures and are usually protected using large numbers of sacrificial anodes
Aluminium anodes are becoming more prevalent
Ca and Mg ions in sea water precipitate insoluble protective layers on exposed Fe

Buried Pipelines

- Pipeline many 1000s of kms long
- Sacrificial Anode Protection is ideal
- Anodes buried at set distances from pipe
- Regular spacing to maintain protection
- A serious defect far from an anode can be a problem
- Internal potential monitoring to assure against failure

Marine Pipelines

- Sacrificial Anode Bracelets used
- Spacing of ca 150 m
- Potential disaster is pipe fails
- Monitoring of pipe potential by robotic submarine vehicles
- Potential must be maintained well below -850 mV vs SSC

ICCP

Impressed Current Cathodic Protection

- Potentiostatic arrangement of a 3 electrode cell
- The potential of the anode and cathode are altered by passing current between them
- Reference electrode monitors potential difference
- Anode and cathode are insulated

Choosing the Right Potential

- Corrosion rate drops as impressed current increases and E_{corr} drops
- The protection potential E_p is typically -850mV vs SSC
- Lower potentials risk the formation of hydrogen gas
- Potentiostat maintains a constant potential by altering i_p which is very important

Using Impressed Current Protection

- Similar basic principle to sacrificial anodes
- Three important differences
 - Anode is insulated
 - Non consumable electrodes
 - Control electronics
- Anodic reaction is water or chloride oxidation
$$2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}$$
$$\text{Cl}_2 + 2\text{e}$$
$$2\text{Cl}^- =$$

Anode Types

- Early anodes were based on scrap iron but these dissolved
- Modern anodes very inert
- Silver/lead alloys
- Platinised niobium
- Platinised titanium

Reference Electrodes

- Usually Silver silver chloride half cell
- Silver wire (Ag) coated with silver chloride (Ag^+) has stable potential
- Siting of reference electrodes can be difficult

Ships

- Preferred since no dry dock time
- Not always successful!!
- Used in conjunction with barrier coating
- As coating degrade current increases
- 1 to 1000 Amps on a supertanker
- Anodes located forward and aft positions
- Can be problems of consistent protection

Offshore Rigs

- Sacrificial anodes preferred since no electronics
- Electrical and anode systems in ICCP often destroyed in bad weather
- Has been used in some cases
- Conaco Murchison platform protects 80,000 square metres with just 100 ICCP anodes

Pipelines

- Often used
- Can be solar or wind Powered
- Must be combined with a routine inspection

Concrete



Corrosion in concrete results in serious destruction
Steel is normally passive but ingress of CO_2 (lowering pH)
and chloride ions leads to rapid corrosion

ICCP in concrete structures

- Large structures such as bridges and buildings protected from reinforcement corrosion by ICCP

Anodic Protection

- Reverse of cathodic impressed current Protection
- Metal is forced into the passive region by an impressed current
- Growth of protective passive layer
- Lower corrosion rate

Advantages and disadvantages

- Can be used to protect metal in oxidising and acidic environments
- More flexible than cathodic protection
- Can be dangerous!!
- Pushing E_{corr} to high level is risky if system fails or it drops a fraction
very rapid corrosion

