Nickel INSTITUTE

knowledge for a brighter future

Rolled Alloys

Overview of the Corrosion Behaviour of Metals in Seawater (and what to look for)

Carol Powell
April 2020

Seawater

- Different salts
- Dissolved gases
- Trace elements
- Suspended solids
- Decomposed organic matter
- Live organisms
- Energy (flow)

A Complex Mixture!

Corrosion Influences

Corrosion is influenced by

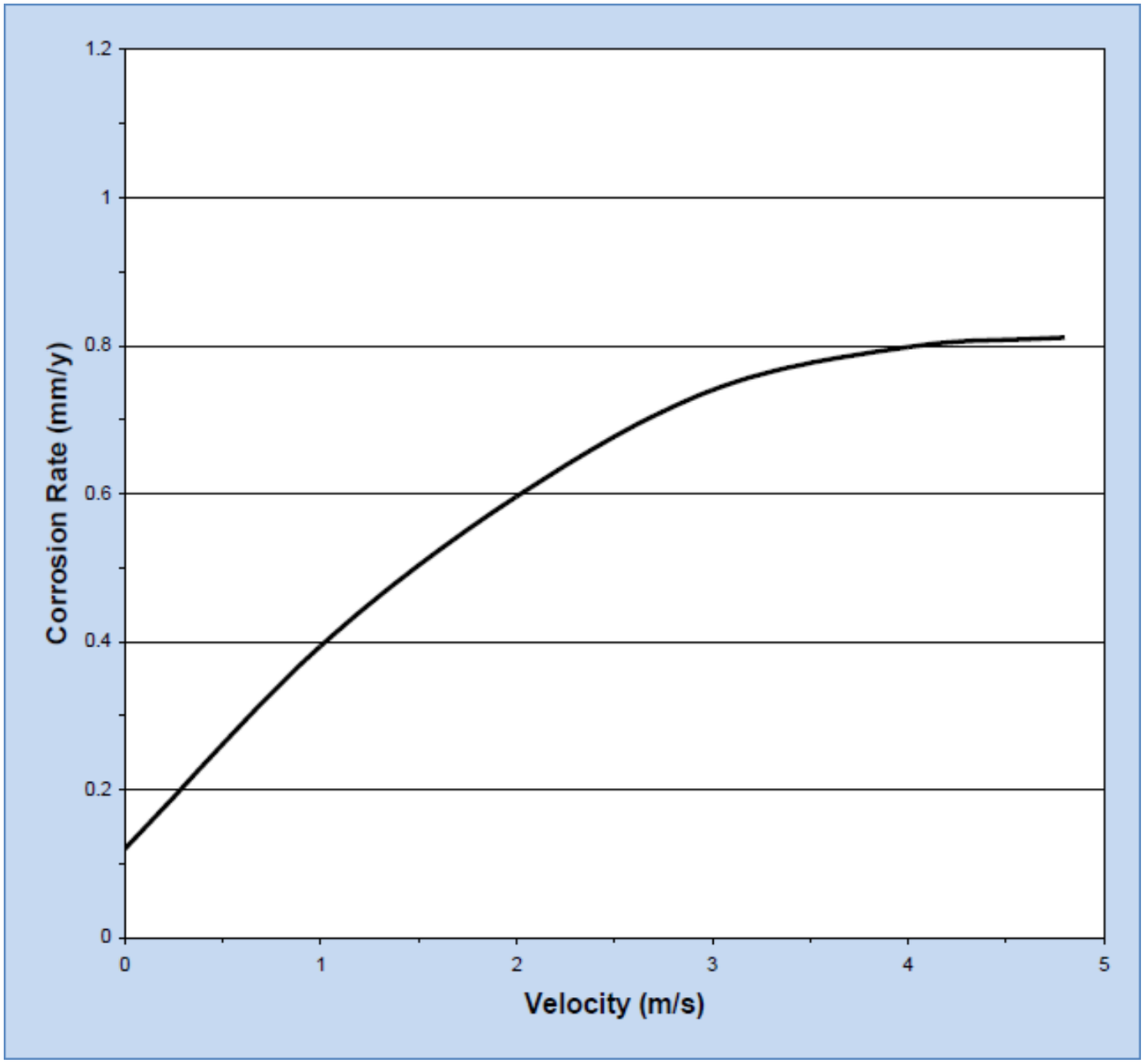
- Oxygen content
- Sea water velocity
- Temperature
- Pollution
- Marine organisms
- - Macrofouling
- - Microfouling
- Evaluation requires long term testing in live seawater

Steel Rusts

- Corrosion is governed by diffusion of oxygen to the surface
- Typically 0.1-0.2 mm/year with pits to several times this depth

Immersed under quiet conditions

Effect of Seawater Flow Rate on Steel Corrosion

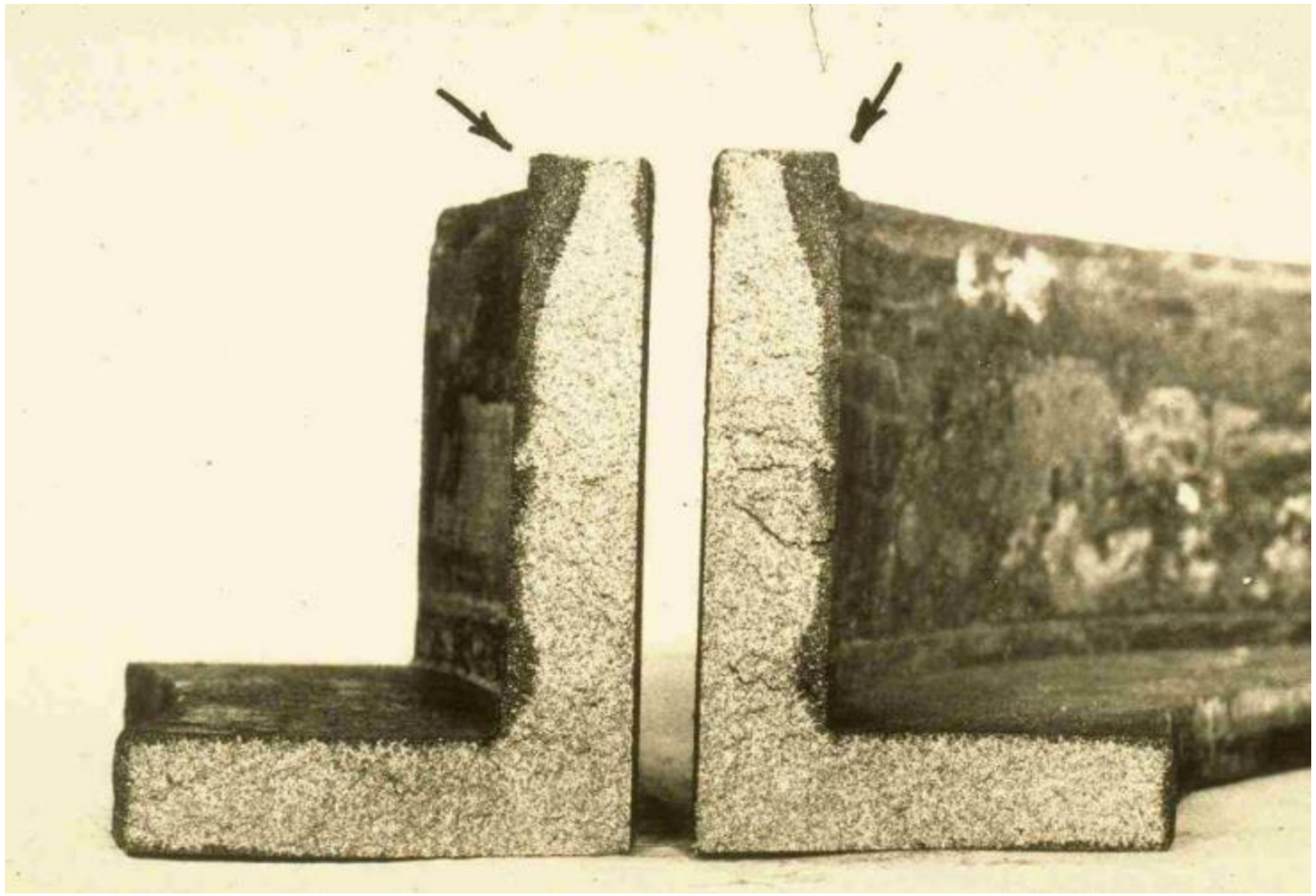


To offset corrosion in steels:

- Extra thickness for corrosion allowance
- Coatings
- Cathodic protection

Cast Iron

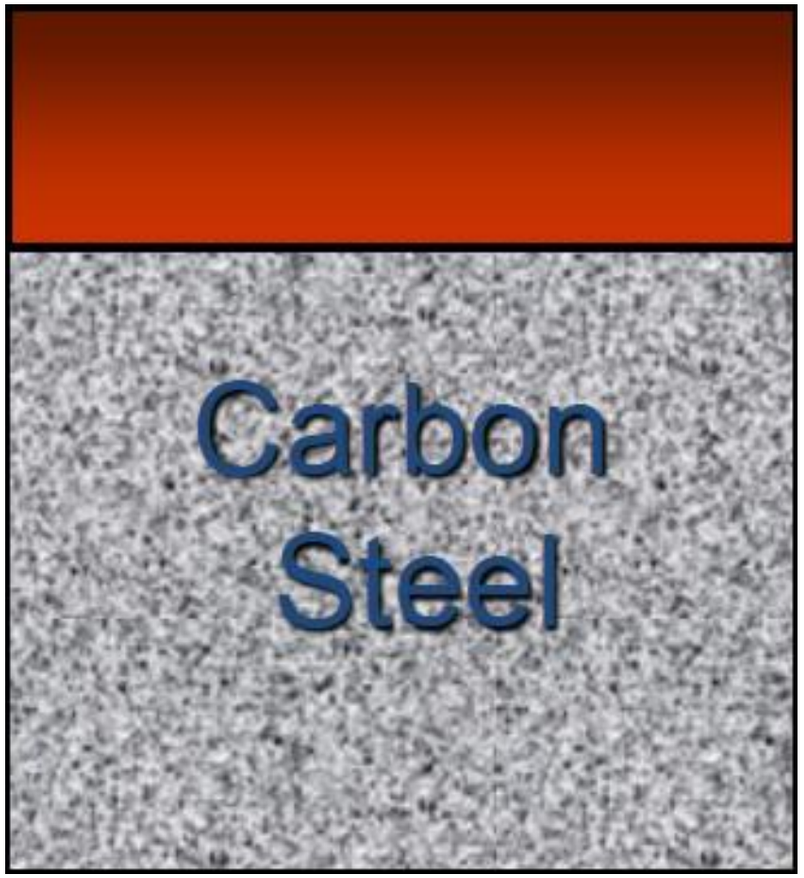
- Corrosion rates similar to steel
- Graphitisation



Rolled Alloys

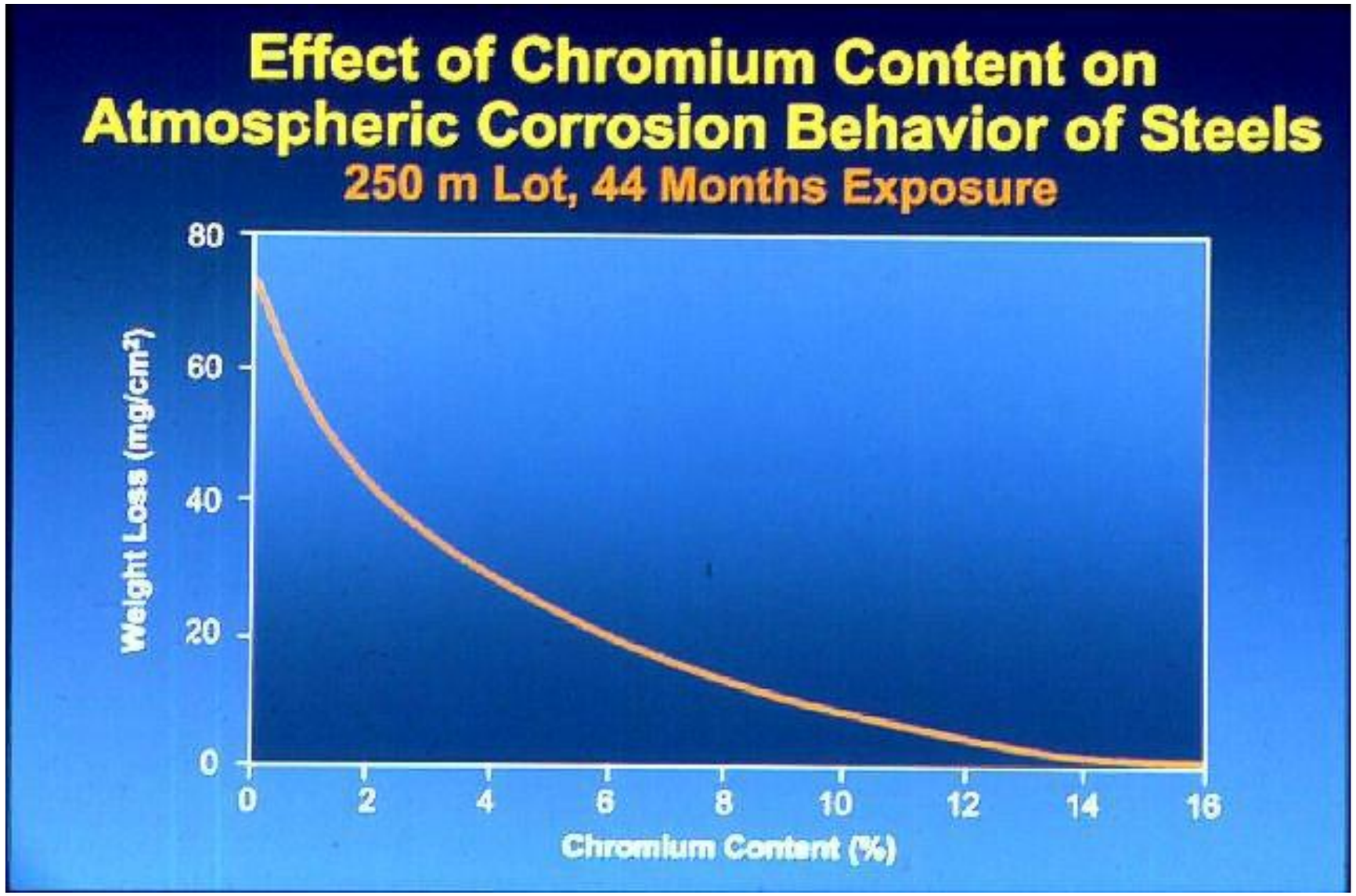
How Stainless Steel Works

Steel
Rust



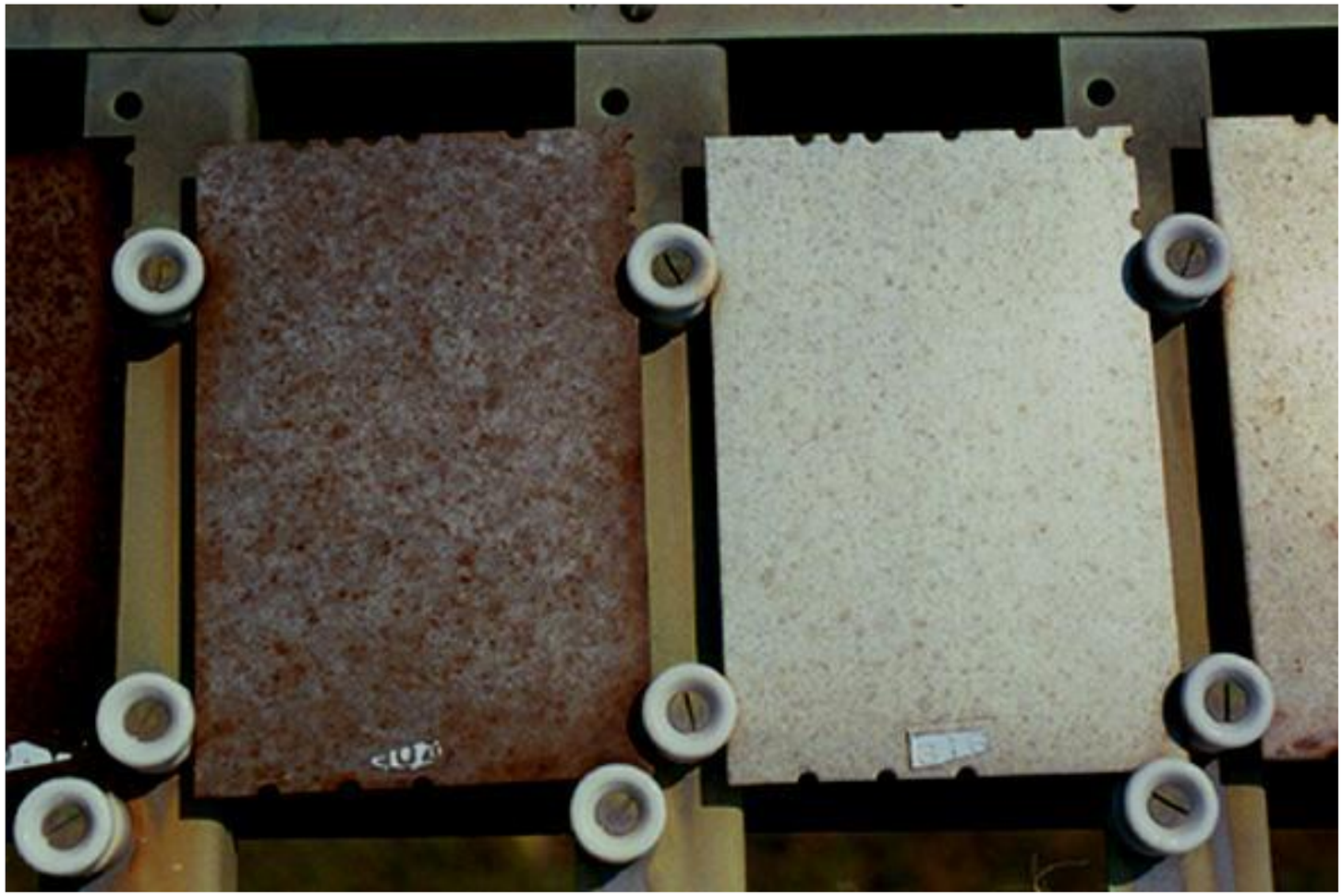
Steel + >10.5% Chromium
Passive film-Thin, strong, adherent oxide (2 - 3 nm)

Chromium Content and Stainless Steel Behaviour



>16% Cr for Marine Resistance

Effect of Molybdenum Content on Marine Exposure



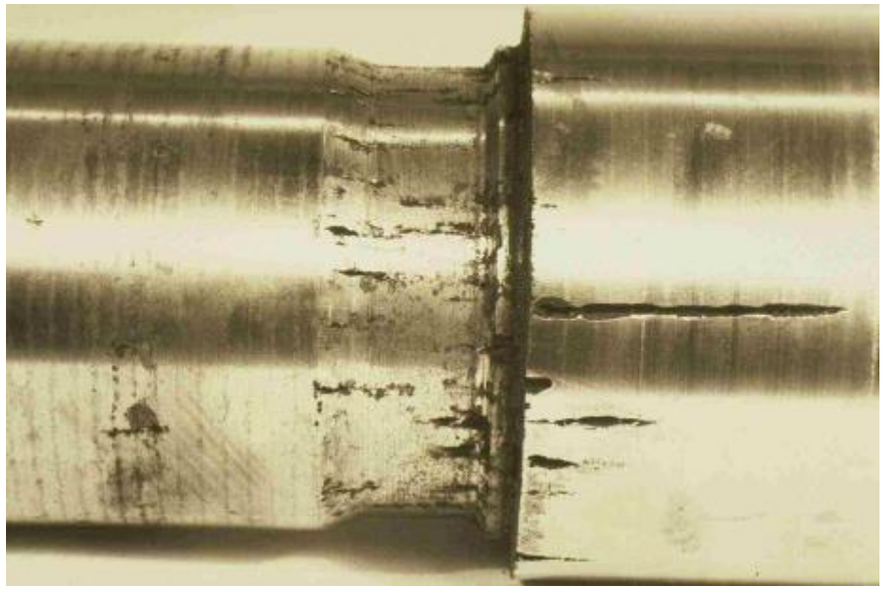
Types 304 (no Mo) (left) and 316 (Mo containing) (right) after 57 years of exposure on the US East Coast

Stainless Steel: Effect of Flow

- General corrosion rates: less than 0.002 mm/year
- Corrosion rate remains very low up to flow velocities greater than 40 m/s
- Under quiet conditions (less than 1 m/s) protective film can breakdown locally resulting in *pitting and crevice corrosion*

Pitting

- Chloride levels too high
- Over-chlorination in treated waters
- Surface contamination
- Surface inclusions exposed



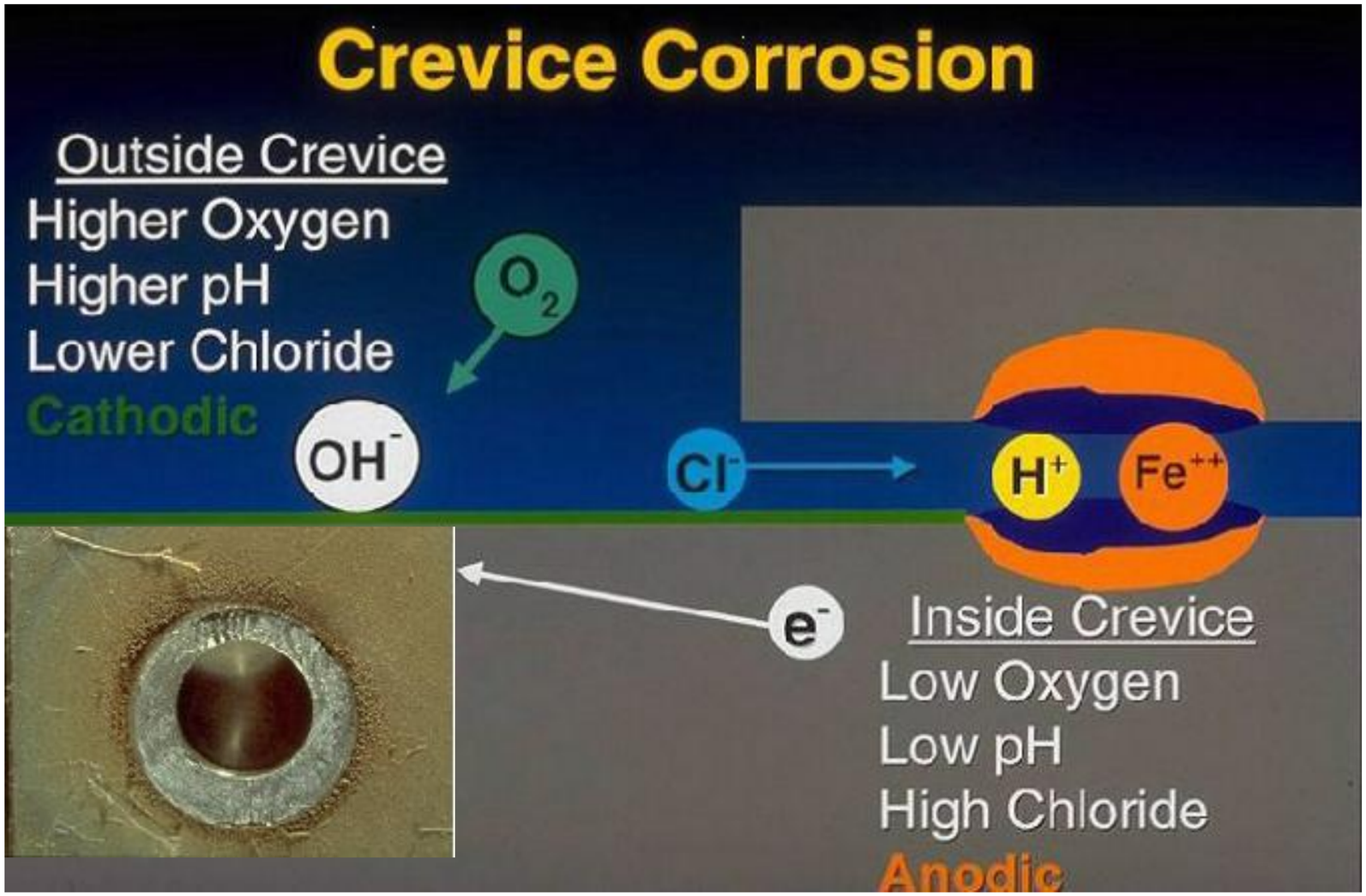
MnS Stringers in
Type 303 Stainless Steel

Crevice Corrosion

- Occurs in areas which are wet and where it is difficult for oxygen to reach, such as under the head of a bolt or o-ring, or under a deposit.
- Chlorides are a prime requirement.
- Crevice corrosion can occur when the wrong grade of stainless steel is selected for the conditions.

Type 316 used in a coupling for seawater reverse osmosis desalination. It was successfully replaced with a 6% Mo stainless steel.

Crevice Corrosion Mechanism



Chlorides are again a prime requirement

Crevice Corrosion Resistance

- Pitting Resistance Equivalent Number used to rank alloys for pitting and crevice corrosion

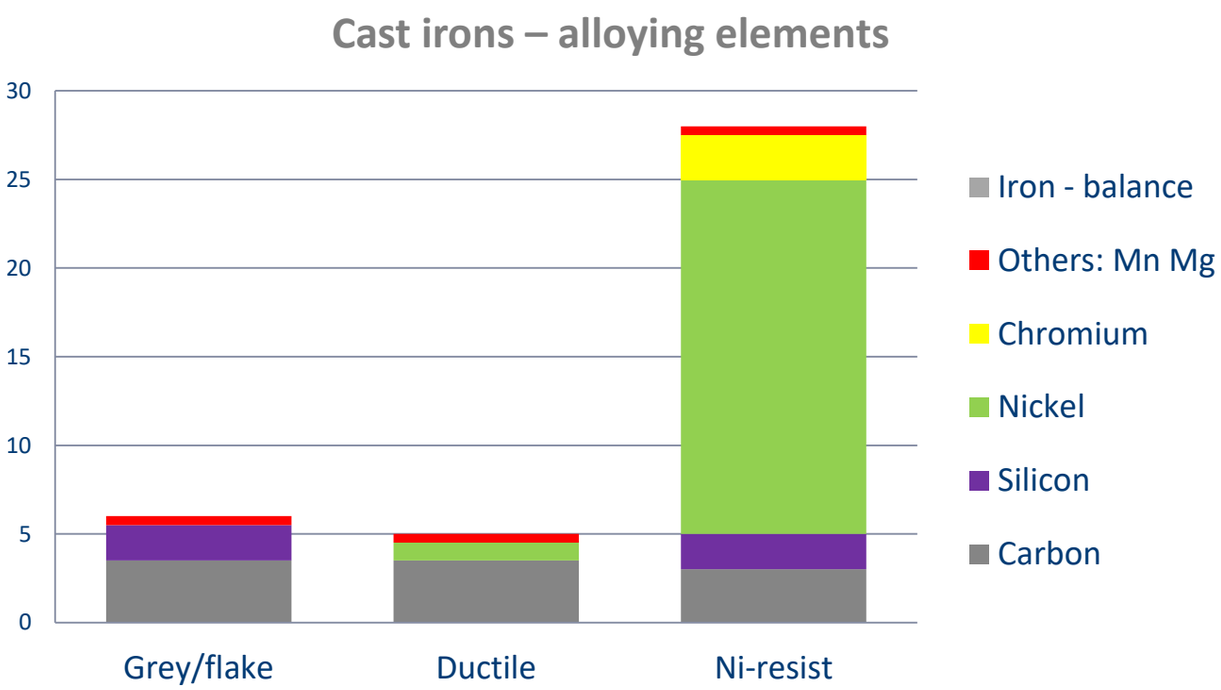
PREN=%Cr+3.3(%Mo + 0.5x%W)+16x%N	
316L*	24
Duplex	35
Super-duplex	>41
Super-austenitic	43

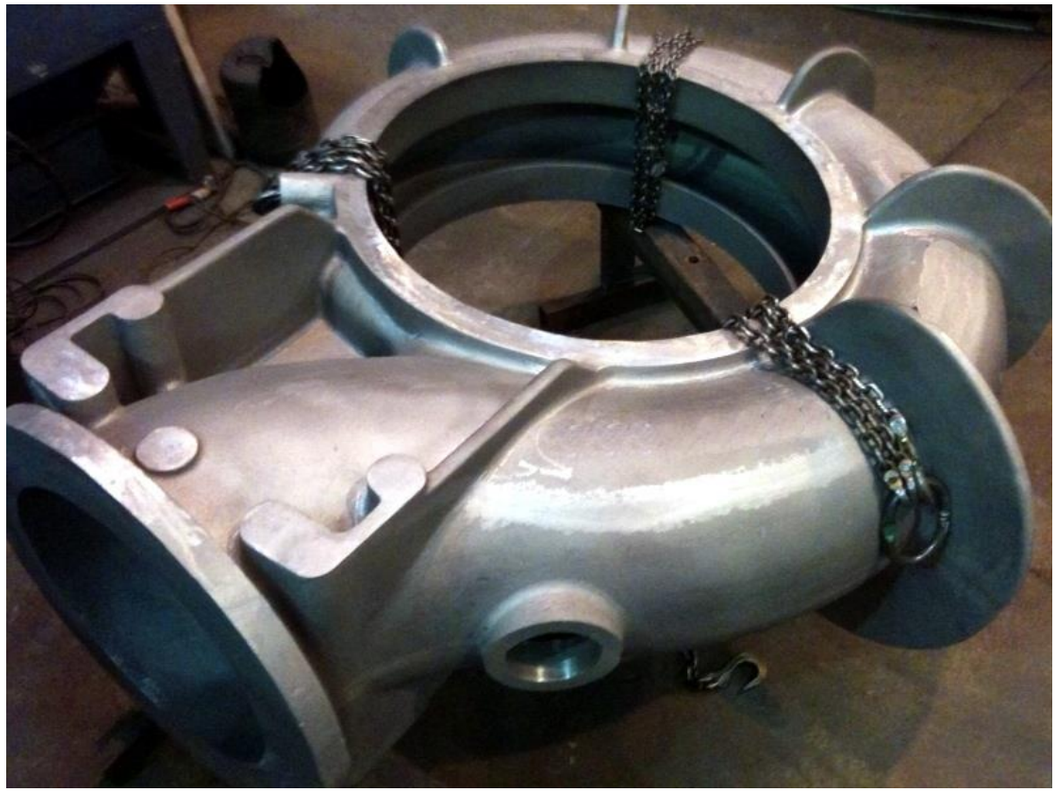
- PREN >40 resistance to localised corrosion in ambient temperature seawater
- (*L is low carbon grade required for best corrosion resistance in HAZ after welding)

Super-duplex Filter Vessel, North Sea

Austenitic Cast Irons – Ni Resist

- 15-25% nickel
- Corrosion rate of ~0.02 mm/year in low flow conditions
- Corrosion rate increases with flow rate
- Pump casings, valve bodies





Downs and Son

Copper Alloys Commonly Used in Marine Engineering

Alloy Mix	Popular Name
• Copper	
• Copper-zinc	Brasses*
• Copper-tins	Tin and phosphor bronzes
• Copper-silicon	Silicon bronzes
• Copper-aluminium	Aluminium bronzes
• Copper-tin-zinc	Gunmetals
• Copper-nickels	
• Copper-beryllium	

**Mn Bronze is a misnomer.*
It is a high strength brass

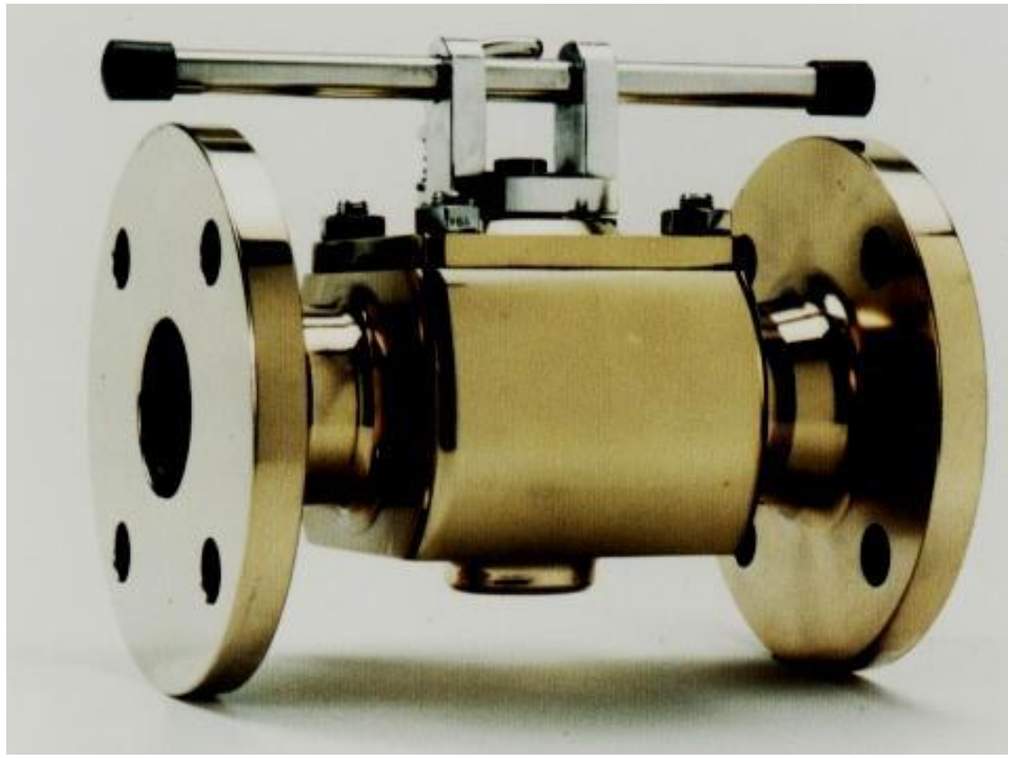
Cu-Ni Seawater inlet desalination plant

Copper Alloy Properties

- High corrosion resistance to seawater-used throughout history
  Copper-nickels and nickel aluminium bronze widely used
- High resistance to biofouling
- Fair to excellent strength
  Some wrought and cast alloys can be strengthened by heat treatment
- Fair to good flow velocity resistance
- Good galling and wear characteristics
- **High thermal conductivity**
- Caution – *polluted conditions (fitting out bays and some harbours) and very high velocities*

Copper Alloy Flow Properties

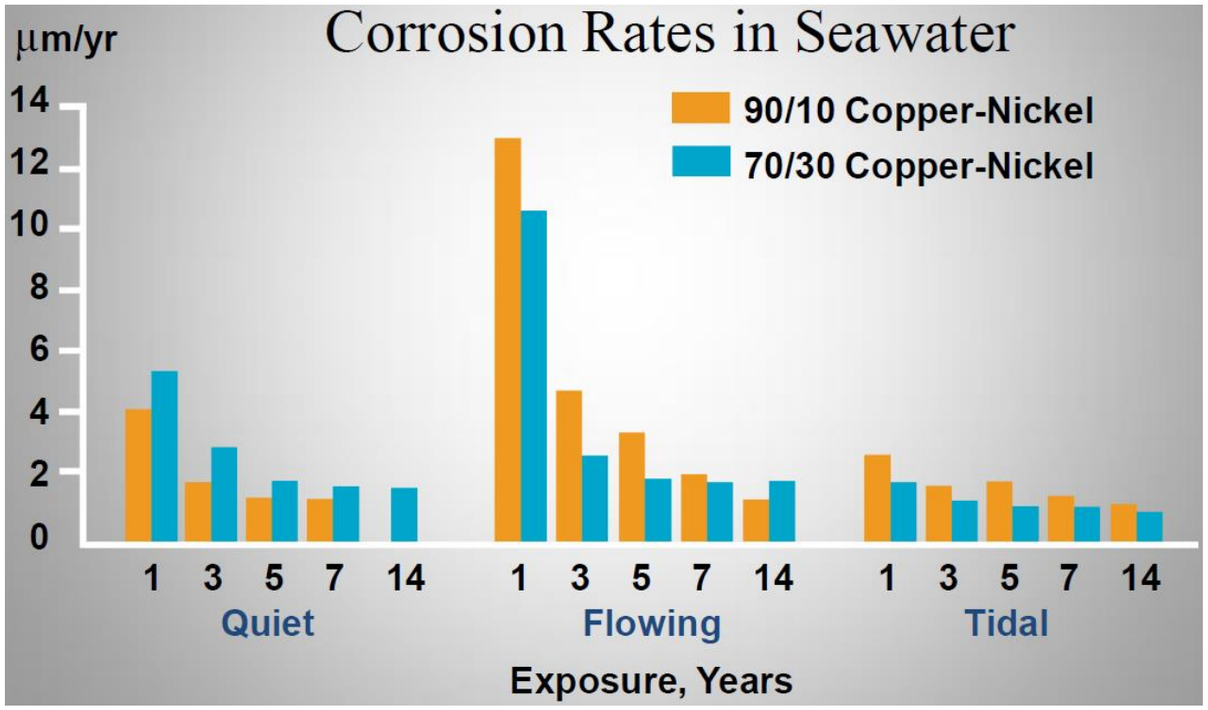
- Corrosion rate in low flow waters ~0.02 mm/year
- Moderate flow rates - low corrosion rates
- High flow rates - impingement attack



Ivan Richardson

Corrosion Properties of Copper Nickels and Surface Film

•Corrosion resistance produced by complex and protective surface films which form and mature when exposed to sea water

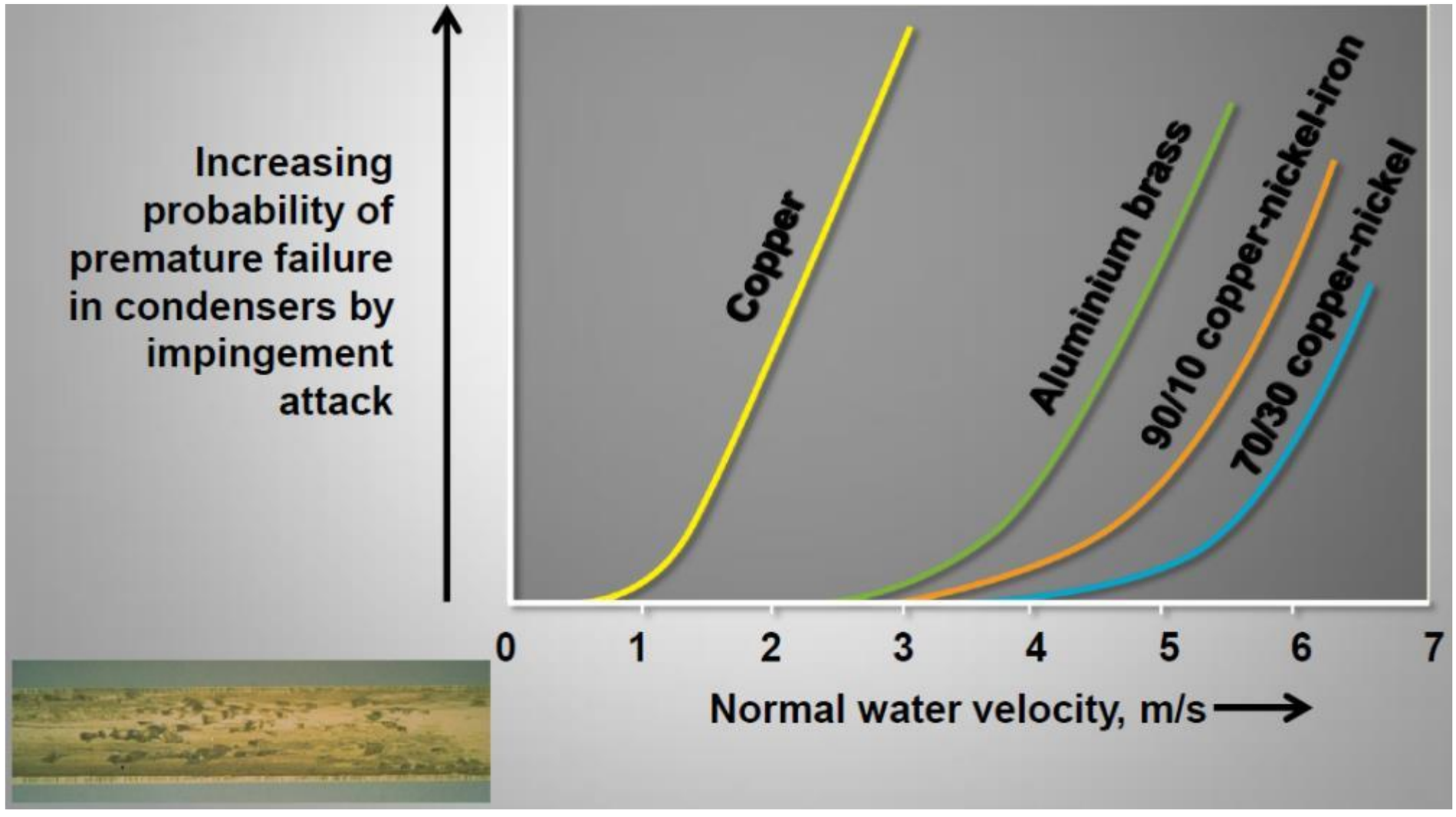


90-10 Copper-nickel

Good resistance to crevice corrosion even at high temperatures

Velocity Limitations for Copper Alloys in Seawater

- Impingement attack occurs when the breakaway velocity is exceeded



Effect of Flow

Typical Maximum Velocities Pipes and Tube (m/sec)

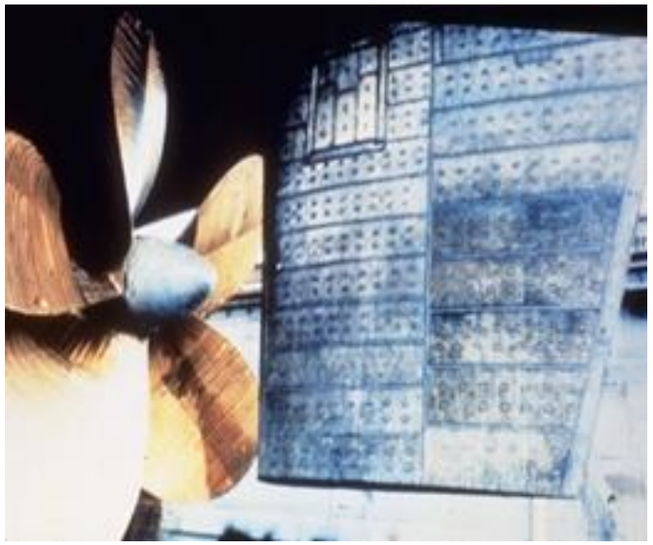
	Piping (>100 mm dia.)	Condensers (<25 mm dia.)
Aluminium brass	2.8	2.0
90/10 CuNi	3.5	2.4
70/30 CuNi	4.0	3.0
66-30-2-2 CuNi	6.5	4.5

Other Flow Regimes

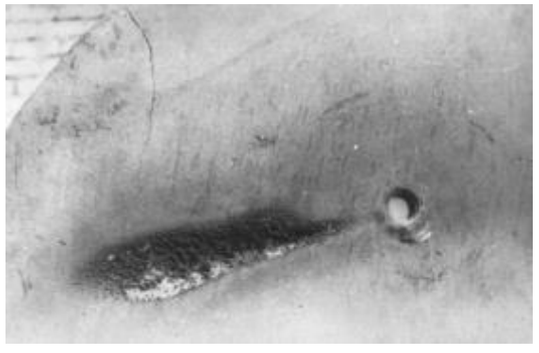
- Fire water systems:
- Intermittent
- 10-15 m/s

- Boat hulls:
- 12-19 m/s

Rolls Royce Marine



- Cavitation:



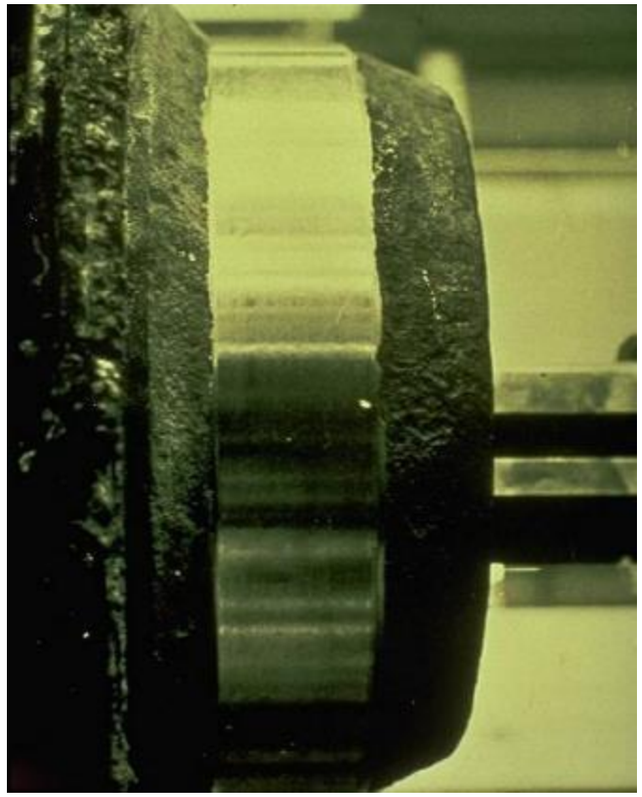
- Nickel aluminium bronze has high resistance and used for impellers and propellers

Lips BV The Netherlands

High Nickel Alloys

- Nickel-copper alloys
  e.g. alloy 400 and K500
- Nickel-chromium-molybdenum alloys
  e.g. alloy 625, alloy C276, alloy 59, alloy 686

Stabiliser boss, UK Navy-
alloy 625 overlay



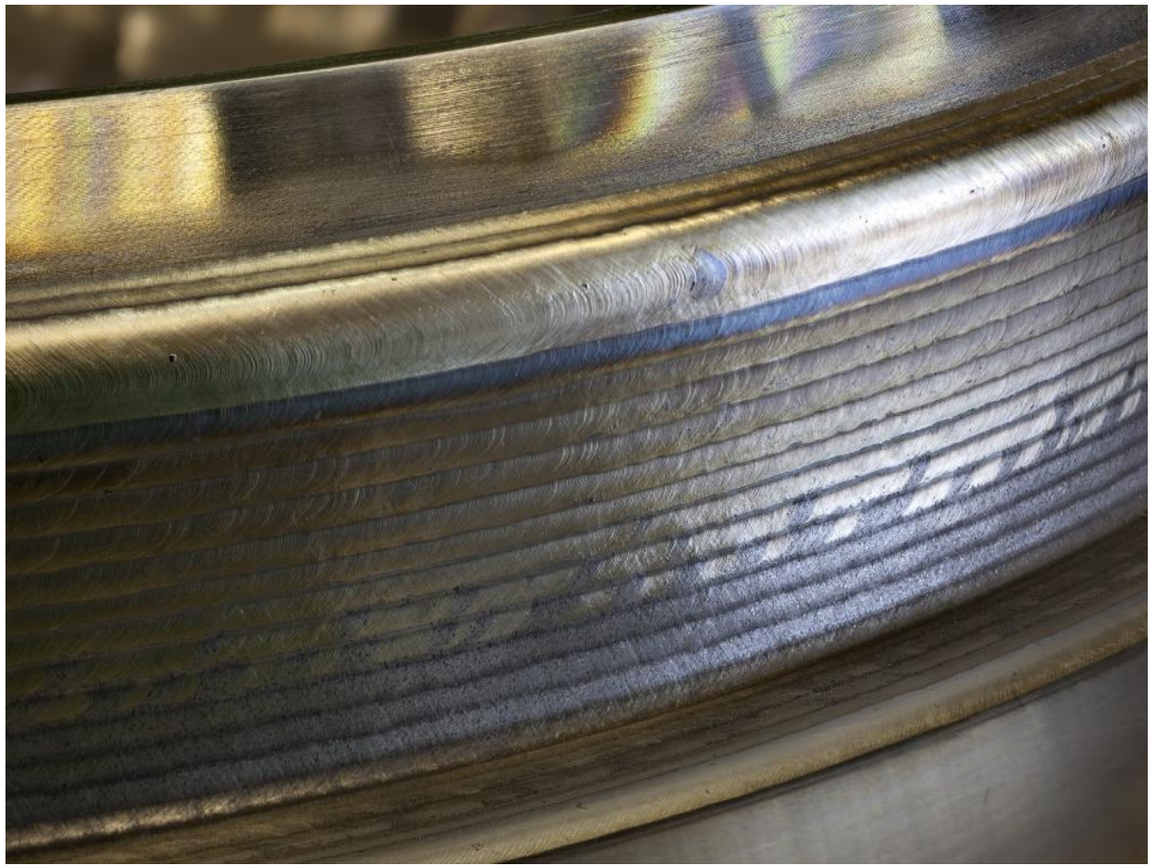
Special Metals

Nickel-copper Alloys

- Alloy K500 can be heat treated to twice the mechanical properties of alloy 400 - similar corrosion resistance
- Low general corrosion rates maintained to high flow rates
- May pit and crevice corrosion in quiet conditions unless galvanically protected
- Used for shafting, bolting, pump and valve components, sheathing of risers on offshore structures. K500 non-magnetic.

Nickel-chromium-molybdenum Alloys

- High chromium and molybdenum additions give high resistance to pitting and crevice corrosion in quiet seawater
- High corrosion resistance from low flow to high flow conditions
- Used for critical items or as a weld overlay



Arc Energy Resources

Alloy 625 TIG overlay cladding onto steel for a swivel flange

Aluminium Alloys

- Applications: fishing and patrol boats, pleasure craft, gangways, pontoons, ladders, fin-tube heat exchangers
- Alloys preferred for sea water are 5000 series, Al-Mg alloys and a few 6000 series, Al-Mg-Si alloys
- Passive surface oxide film
- Corrosion rate <0.005 mm/yr. Can suffer from pitting and crevice corrosion
- Galvanically active alloys

Titanium Alloys

- Passive TiO_2 surface film
- Unaffected by Cl^- and S^- or chlorination
- Negligible corrosion rates to flow rates in excess of 36 m/s
- Resistant to pitting and crevice corrosion below ~75°C

RTI International Metals Inc.

Ti Gr. 1 plates/frame seawater exchangers for cooling machinery and electronics

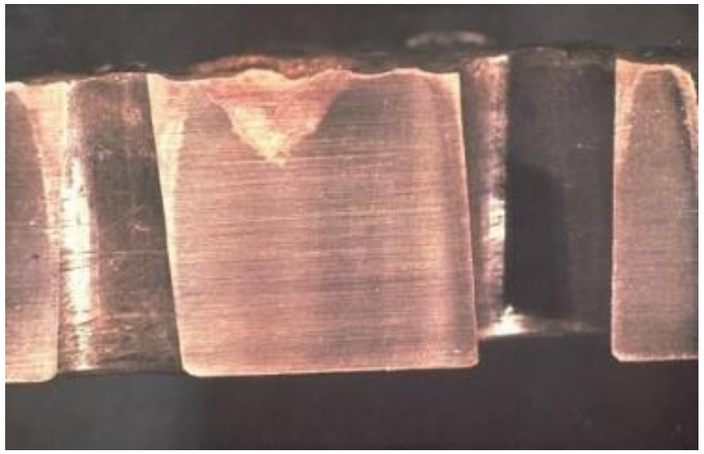
Summary of Flow Behaviour µm/yr

	Carbon steel and cast iron	Cu Based alloy/Ni Resist	316 stainless/Ni-Cu	Ni-Cr-Mo Super stainless Titanium
Low				
	125	25	2	<1
10m/s				
	2500	250	<1	<1
40m/s				
	5000	500	<1	<1

Selective Phase Corrosion 1

Graphitisation	Dezincification	Dealuminification
Cast iron, ductile iron	Brass alloys with greater than 15% zinc	Aluminium bronzes with less than 4% Ni
Use austenitic cast iron	Use inhibited grade	Use nickel aluminium bronze

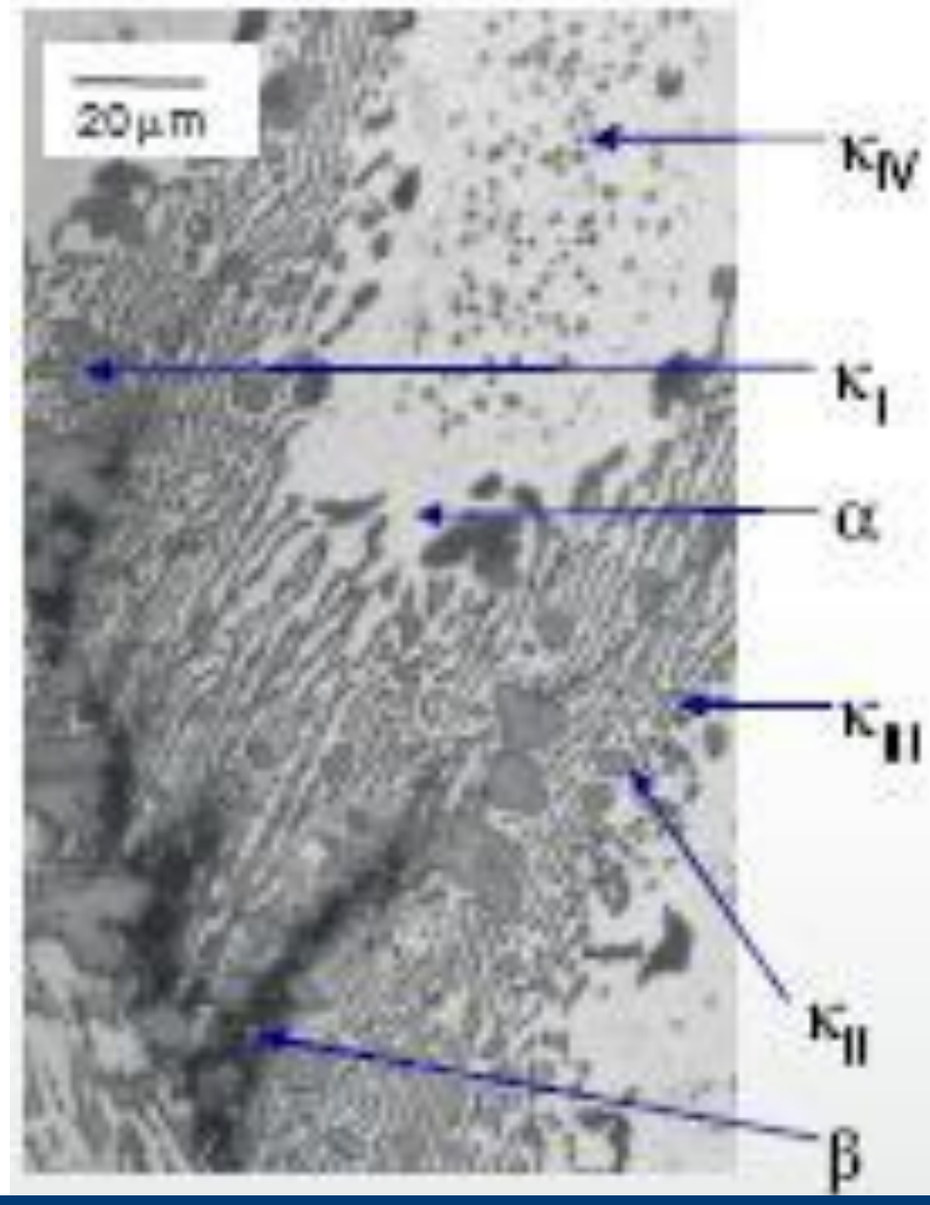
Valve stem made from 60-40 brass



Naval brass tube plate after 11 years

Complex Structure of NAB
-Correct Heat Treatment important

- Final heat treatment can be beneficial, particularly after welding
- Cast: 675°C
- Wrought:725°C



Selective Corrosion in Stainless Steels

Rolled Alloys

Sigma Phase in Superduplex

Use correct heat treatment

Stress Corrosion Cracking

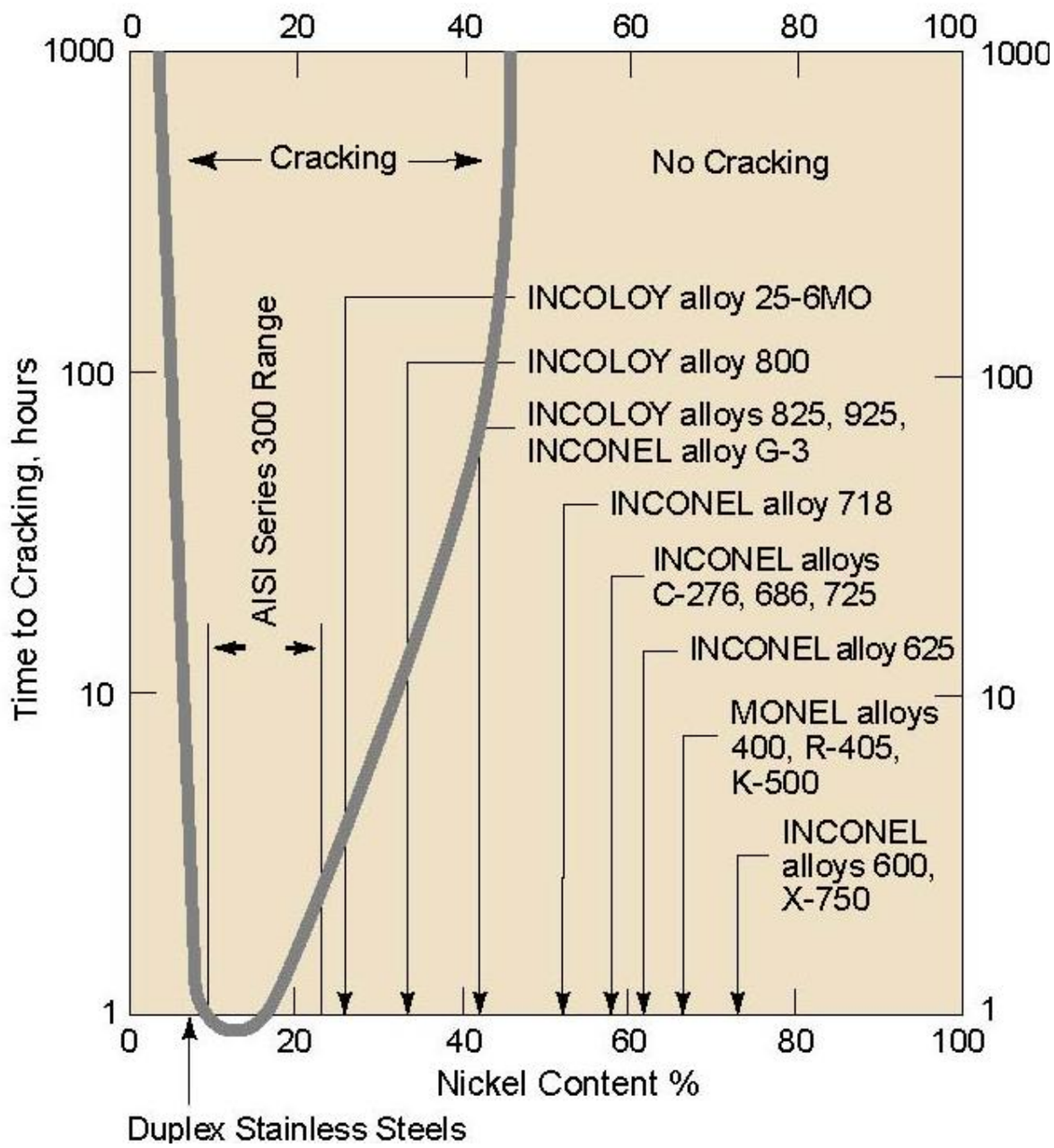
- Susceptible alloy
- Tensile stress
- Specific environment
  - temperature
  - chemical

    - chlorides - stainless at >50°C

    - ammonia - copper alloy

    - warm seawater - Ni Resist

Chloride stress corrosion cracking



Alloy 625LCF bellows

Ex Special Metals

Copson U-Curve

SCC of Austenitic Cast Iron in Warm Sea Water

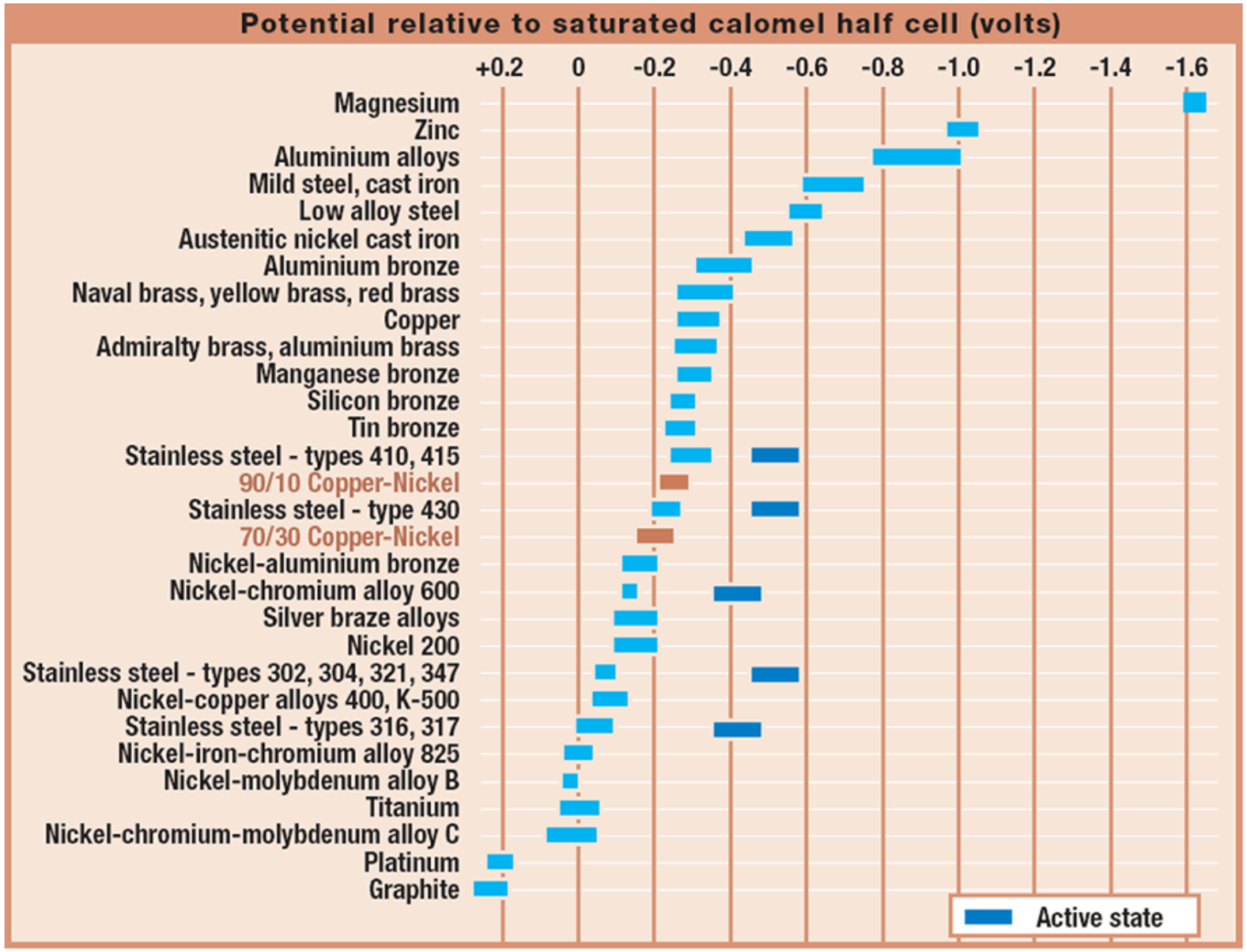
Avoid by stress relief

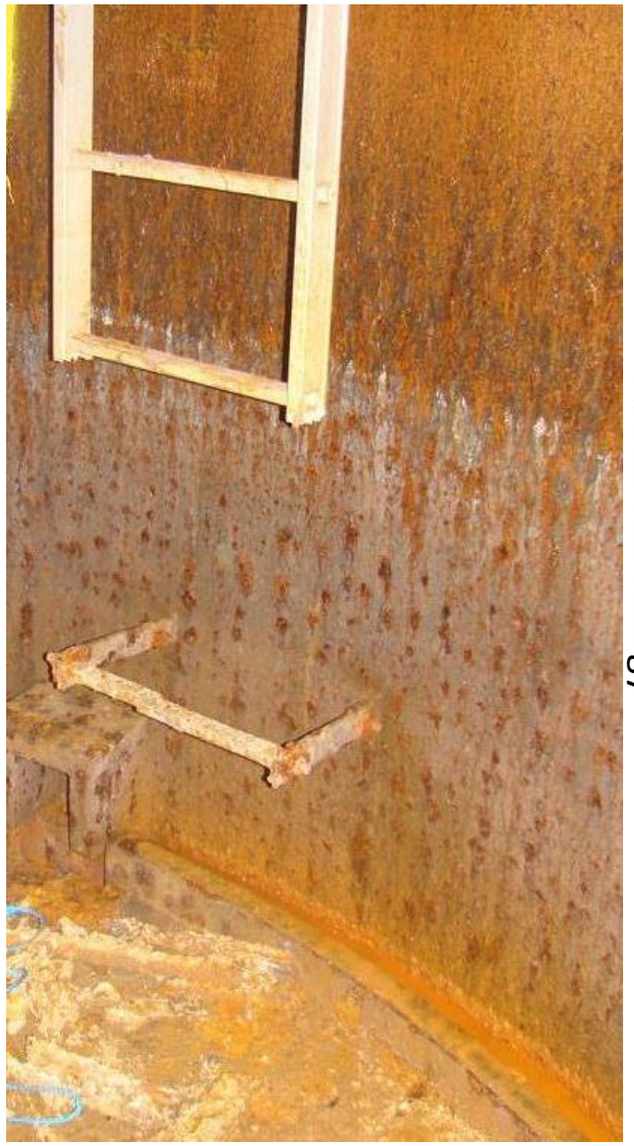
Galvanic Corrosion

- Two or more metals in electrical contact
- Immersed in seawater
- Sufficient potential difference between the metals for a current to flow
- The more noble metal, the cathode, will have a lower corrosion rate than it normally would
- The less noble metal, the anode, will corrode more than it normally would

Galvanic Series

Active End





FORCE Technology

Noble End

Area effects are also important

Galvanic Corrosion of Super Duplex Stainless Steel Flange under a Graphite Gasket

Rolled Alloys

Galvanic Corrosion of NAB/Ti Couple

Rolled Alloys

Ti Susceptible to hydriding

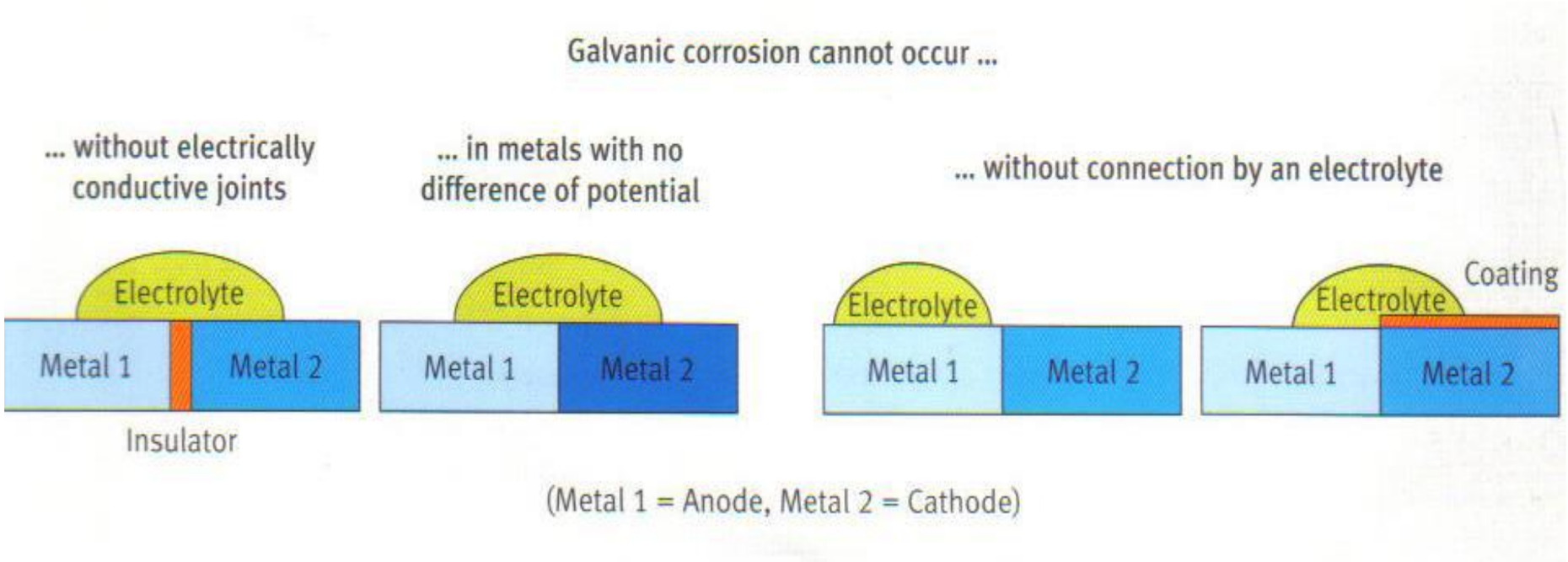
- Limit CP to -0.8V (vs Ag/AgCl) if >70°C
- Less severe applications limit -1.05V

Galvanic corrosion of aluminium/ stainless steel couple

Courtesy Lloyds Register

Al 5083 sea water system. Al connected to a stainless steel heat exchanger

Guidelines for Avoiding Galvanic Corrosion

- 

Euro Inox

- Ensure the less noble material is present in a much larger surface area than the more noble material
- When coatings are used to protect against galvanic corrosion, do not coat anode alone

Biofouling

Macrofouling has low adherence to many copper alloys

Of these, copper and copper-nickels have the highest resistance

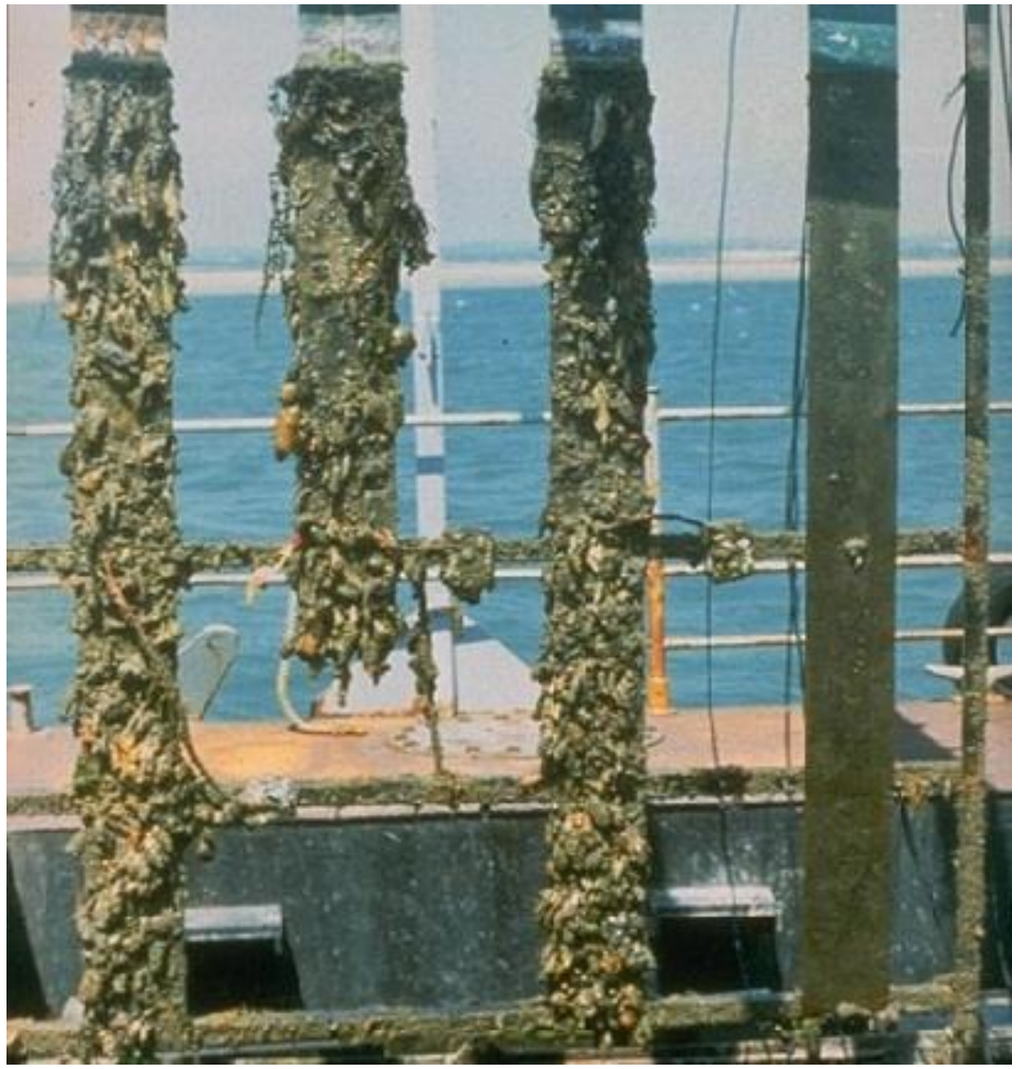
Corrosion Program, 22 Months Immersion in Sea Water, Levington Marina, Suffolk

Copper Alloys Ltd

① CuAl9Ni5Fe5 ② CuNi15Mn5AlFe ③ CuNi30Cr2 ④ CuNi14Al3Fe ⑤ CuNi3Si ⑥ CuNi30 ⑦ CuNi15Sn8 ⑧ CuNi14Al3Fe ⑨ Ni-Cu 400
⑩ Ni-Cu K500 ⑪ Alloy 625 ⑫ Alloy 718 ⑬ Alloy 825 ⑭ 6%Mo St.St. ⑮ Superduplex ⑯ Superduplex ⑰ Superduplex ⑱ Duplex ⑲ 316L
⑳ 304L ㉑ 17-4 PH ㉒ Ti Gr. 2 ㉓ Ti Gr. 5 ㉔ CuNi15Mn5AlFe ㉕ CuAl9Ni5Fe4Mn ㉖ CuAl10Ni5Fe4 ㉗ 316 ㉘ 321

90-10 Copper-nickel Exposure Panels – Langstone Harbour

Before exposure



12 months' later

Biofouling Resistance: Copper Alloys

- High resistance to macrofouling
- Will form slimes
- Any macrofouling which does colonise is loosely attached and easily removed
- Insulate from less noble alloys

90-10 Cu-Ni,
2-year exposure

The Footloose

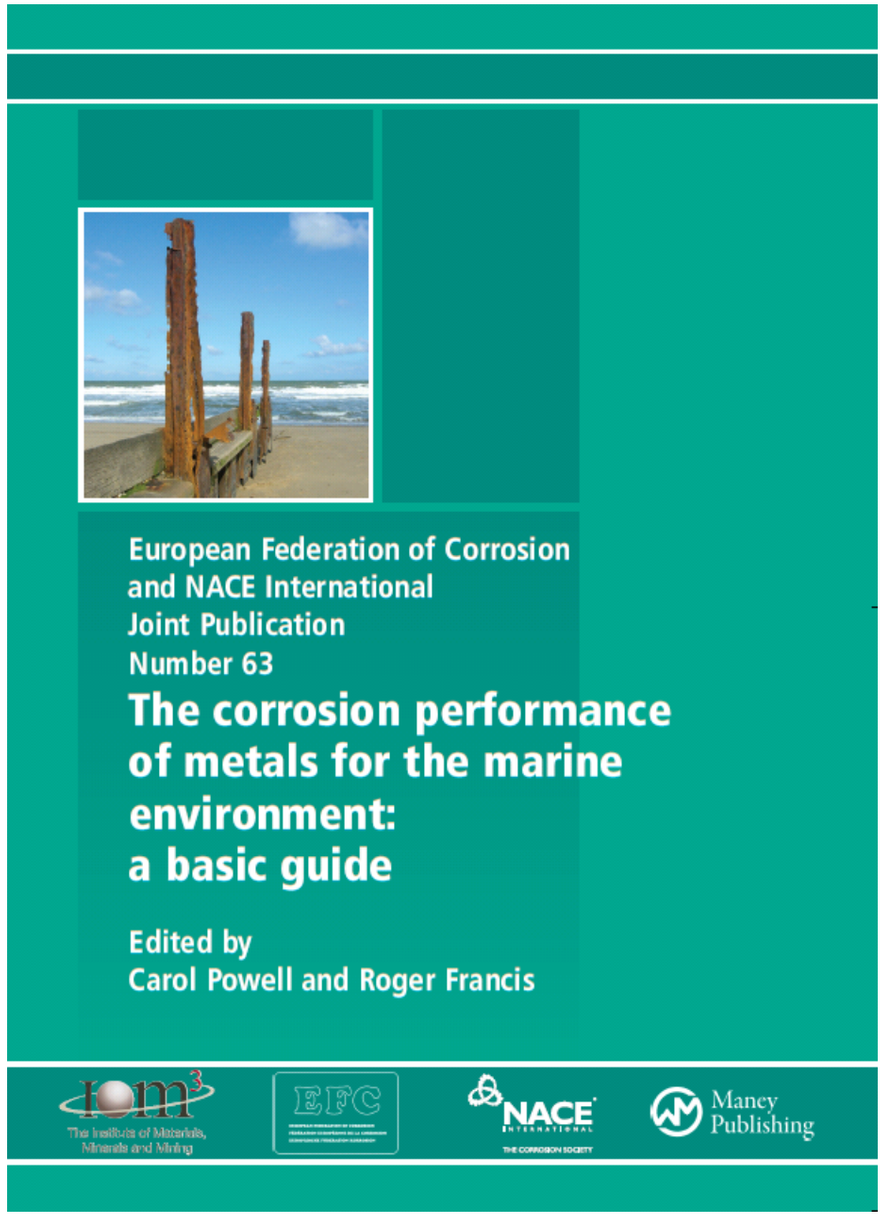
Foil after 20 years, Vancouver (hull given a light spray wash)

Courtesy Chris Cowland

The Corrosion Performance of Metals for the Marine Environment: A Basic Guide

- Chapter 1: Introduction
- Chapter 2: Iron and Carbon Steel
- Chapter 3: Stainless Steel
- Chapter 4: Copper Alloys
- Chapter 5: Nickel Alloys
- Chapter 6: Aluminium Alloys
- Chapter 7: Titanium Alloys
- Chapter 8: Galvanic Corrosion

(Available from Amazon and NACE)



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