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

Carol Powell
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Rolled Alloys
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
How Stainless Steel Works

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
• 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.
Chlorides are again a prime requirement.
Crevice Corrosion Resistance

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

\[ \text{PREN} = \%\text{Cr} + 3.3(\%\text{Mo} + 0.5\times\%\text{W}) + 16\times\%\text{N} \]

<table>
<thead>
<tr>
<th>Alloy Type</th>
<th>PREN</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L*</td>
<td>24</td>
</tr>
<tr>
<td>Duplex</td>
<td>35</td>
</tr>
<tr>
<td>Super-duplex</td>
<td>&gt;41</td>
</tr>
<tr>
<td>Super-austenitic</td>
<td>43</td>
</tr>
</tbody>
</table>

• 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

![Cast irons – alloying elements](image)

- Iron - balance
- Others: Mn Mg
- Chromium
- Nickel
- Silicon
- Carbon

Downs and Son

16
## Copper Alloys Commonly Used in Marine Engineering

<table>
<thead>
<tr>
<th>Alloy Mix</th>
<th>Popular Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>Brasses*</td>
</tr>
<tr>
<td>Copper-zinc</td>
<td>Tin and phosphor bronzes</td>
</tr>
<tr>
<td>Copper-tins</td>
<td>Silicon bronzes</td>
</tr>
<tr>
<td>Copper-silicon</td>
<td>Aluminium bronzes</td>
</tr>
<tr>
<td>Copper-aluminium</td>
<td>Gunmetals</td>
</tr>
<tr>
<td>Copper-tin-zinc</td>
<td></td>
</tr>
<tr>
<td>Copper-nickels</td>
<td></td>
</tr>
<tr>
<td>Copper-beryllium</td>
<td></td>
</tr>
</tbody>
</table>

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

**Corrosion Rates in Seawater**

- 90/10 Copper-Nickel
- 70/30 Copper-Nickel

90-10 Copper-nickel

Good resistance to crevice corrosion even at high temperatures.
Impingement attack occurs when the breakaway velocity is exceeded.
## Typical Maximum Velocities Pipes and Tube (m/sec)

<table>
<thead>
<tr>
<th>Material</th>
<th>Piping (&gt;100 mm dia.)</th>
<th>Condensers (&lt;25 mm dia.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium brass</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>90/10 CuNi</td>
<td>3.5</td>
<td>2.4</td>
</tr>
<tr>
<td>70/30 CuNi</td>
<td>4.0</td>
<td>3.0</td>
</tr>
<tr>
<td>66-30-2-2 CuNi</td>
<td>6.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>
Other Flow Regimes

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

- Boat hulls:
  - 12-19 m/s

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

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 $\sim$75$^\circ$C

Ti Gr. 1 plates/frame seawater exchangers for cooling machinery and electronics
## Summary of Flow Behaviour μm/yr

<table>
<thead>
<tr>
<th></th>
<th>Carbon steel and cast iron</th>
<th>Cu Based alloy/Ni Resist</th>
<th>316 stainless/Ni-Cu</th>
<th>Ni-Cr-Mo Super stainless Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>125</td>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td>10m/s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2500</td>
<td></td>
<td></td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>40m/s</td>
<td></td>
<td></td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5000</td>
<td></td>
<td></td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>
## Selective Phase Corrosion 1

<table>
<thead>
<tr>
<th>Graphitisation</th>
<th>Dezincification</th>
<th>Dealuminification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast iron, ductile iron</td>
<td>Brass alloys with greater than 15% zinc</td>
<td>Aluminium bronzes with less than 4% Ni</td>
</tr>
<tr>
<td>Use austenitic cast iron</td>
<td>Use inhibited grade</td>
<td>Use nickel aluminium bronze</td>
</tr>
</tbody>
</table>

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

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

Copson U-Curve

Alloy 625LCF bellows
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**

<table>
<thead>
<tr>
<th>Potential relative to saturated calomel half cell (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.2</td>
</tr>
<tr>
<td>——————————————————————————————————</td>
</tr>
</tbody>
</table>

**Noble End**

Area effects are also important
Galvanic Corrosion of Super Duplex Stainless Steel Flange under a Graphite Gasket
Galvanic Corrosion of NAB/Ti Couple

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

Al 5083 sea water system. Al connected to a stainless steel heat exchanger
Guidelines for Avoiding Galvanic Corrosion

- 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
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

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