# Marine corrosion & biofouling

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# Overview

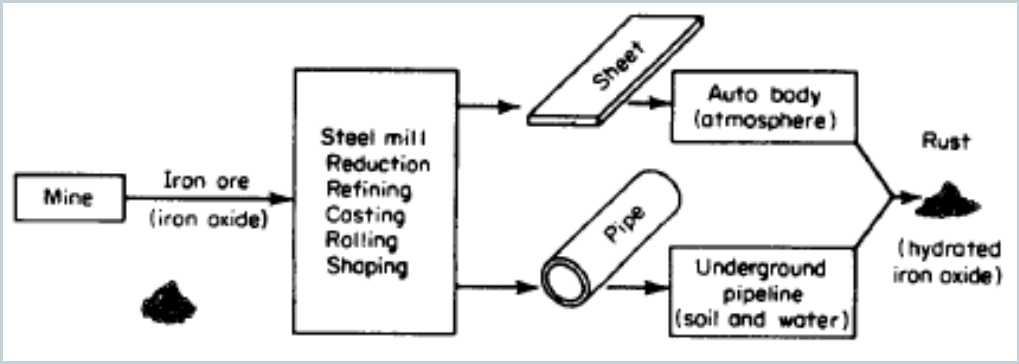


- What is corrosion?
- Problems/issues with corrosion
- Types and classification of corrosion
- Wet corrosion
- Iron rust in seawater
- Sacrificial anodes, galvanic corrosion, cathodic protection
- Biofouling

# What is corrosion?



- Corrosion is the tendency of refined metals to return to their stable natural state
- Metal corrosion is defined as the destruction or deterioration of a metal by *chemical* or *electrochemical reaction* with its environment
- Until 1960s corrosion was restricted only to metals & their alloys
- Today, corrosion encompasses: ceramics, rubber, plastics, polymers, composites & semiconductors



# Why study corrosion?



- Three reasons for studying corrosion are societal:
  - 1. Human life & safety;
  - 2. Financial costs: capital & control costs and design costs;
  - 3. Conservation of materials; some countries (eg US) import 90-100% of Cr, Co, Ni, Pt (platinum)
- and:
  - 4. Difficult to understand a phenomenon.

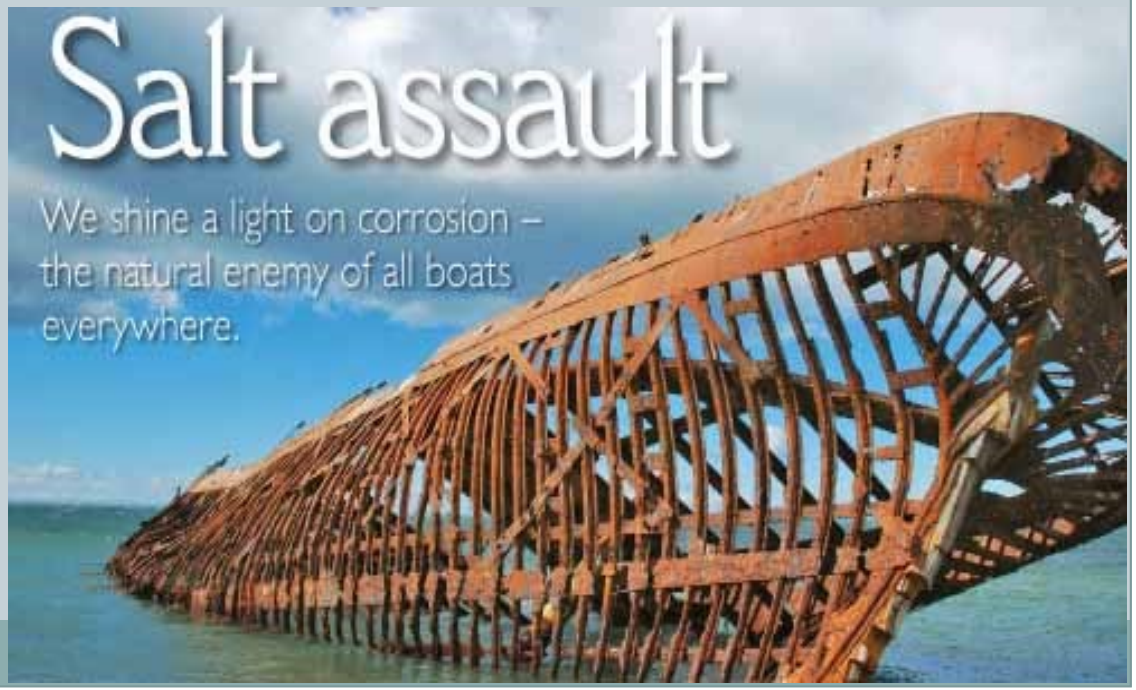
Collapse of Silver Bridge in 1967 cost the lives of 46 people.

| | 1975 Estimate of years of supply [19] | 1995 Estimate of years of supply [20] |
|---|---|---|
| Aluminum | 185 | 162 |
| Iron | 110 | 77 |
| Nickel | 100 | 43 |
| Molybdenum | 90 | – |
| Chromium | 64 | – |
| Copper | 45 | 22 |
| Zinc | 23 | 16 |

# Some corrosion-related facts



- Pipeline maintenance due to corrosion in US >$7bn/y
- Cars in Arabian Gulf begin to corrode >6 months
- 10% of aircraft maintenance in US due to corrosion
- $120b spent on maintenance of aging bldgs in US
- Automotive corrosion in US costs $23b/annum



# The problem with corrosion



- Corrosion could be partly be held responsible for:
  - 1. Plant shutdowns eg, power plants, refineries, process & nuclear plants
  - 2. Loss of resources eg, leaking containers, storage tanks, pipeline leaks, ~25% water
  - 3. Reduction in efficiency eg, blockage of tubes in HEs & small pipelines
  - 4. Corrosion products may contaminate chemicals, pharmaceuticals, dyes, goods
  - 5. Safety hazards eg, risk for bridge & buildings collapse, ship & vehicle damage
  - 6. Nuclear perils eg, Chernobyl transfer of radioactive corrosion products
- In developing countries cost of corrosion ~4-5% GDP

# Corrosive conditions



- Corrosion cannot be defined w/o reference to the environment such as:
  - Air and humidity
  - Fresh, distilled, salt and marine water
  - Natural, urban, marine and industrial atmospheres.
  - Steam and gases (eg, chlorine)
  - Ammonia
  - Hydrogen sulfide
  - Sulfur dioxide and oxides of nitrogen
  - Fuel gases
  - Acids
  - Alkalies
  - Soils.

# Corrosion related issues



- Contamination: corrosion products might contaminate process equipment, food stuff, drugs, pharmaceuticals, water, petrochemical, …
- Mechanical strength: weakening of materials can adversely affect structural capability to take load, stresses, power transmission, etc.
- Dimensional integrity: changing the size of components & structural members can affect precision, operation, load bearing capabilities, etc.
- Physical properties: corrosion can affect the thermal & electrical properties of materials and can affect operation of components, plants,
- Damage to equipment: corrosion wear & tear can impair valves, loosen joints, slacken bearings, rotating parts, etc

# Problems with corrosion

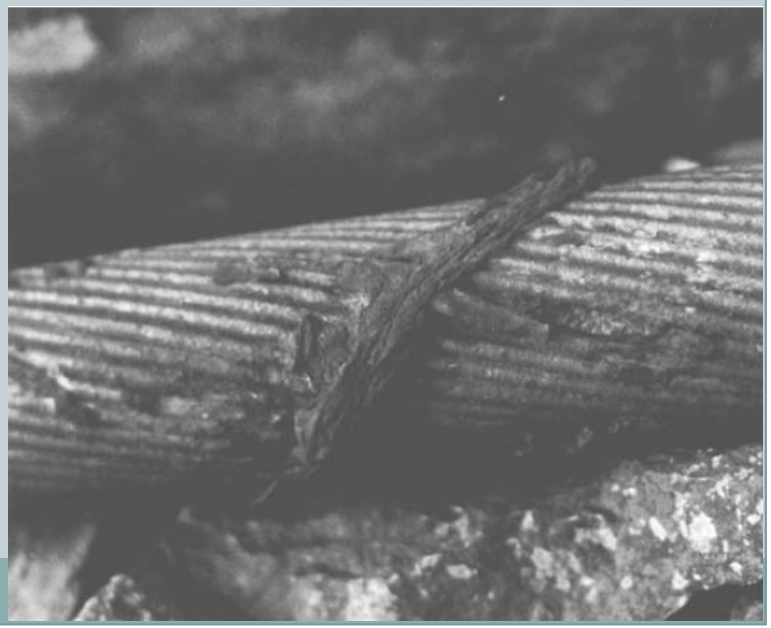


- Safety: corrosion can weaken components & make them susceptible to failure eg, airplanes, ships, bridges, oil & gas pipeline leaks, etc.
- Health: corrosion can affect potable & irrigation water quality, state of nuclear reactors, …
- Depletion of resources: metal waste from corrosion may promote metal crisis loss of oil, water, energy, even labour, etc.
- Aesthetics & appearance: material deterioration renders systems aesthetically unpleasant, ugly appearance deters buyers, etc.
- Product life & reliability: corrosion shortens intended design life eg, cars: 12 yrs; ships: 20 yrs; Eiffel tower: 2 yrs; DC-3 aircraft: 20 yrs, …

# Problems with corrosion (2)



- Corrosion proceeds unabated for a prolonged period w/t any warning
- Can lead to expensive replacement of equipment
- Could result in production losses
- Possibility of down-time (delays), etc
- Can even lead to human fatalities



# Classification of corrosion



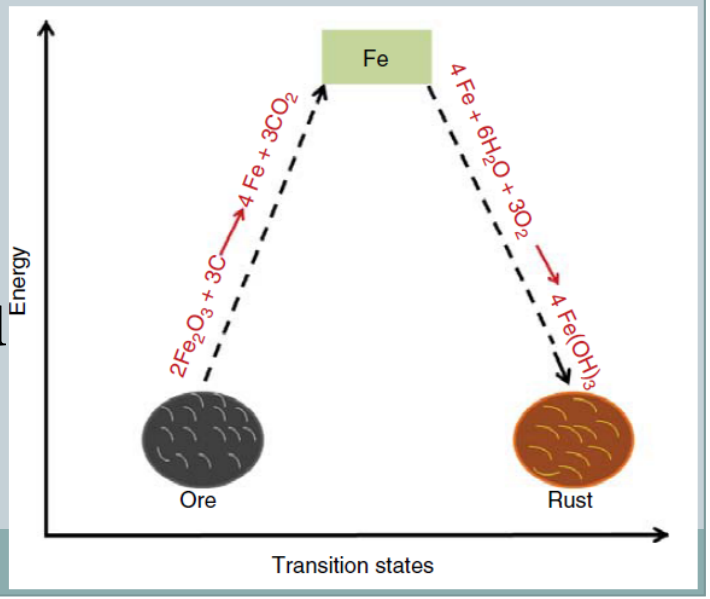
- Corrosion can be classified as:
  - 1. Wet corrosion: occurs in the presence of aqueous slts or electrolytes
  - 2. Dry corrosion: is associated with high temp. eg, attack on steel from furnace gases
- Why do metals corrode?

Refined metals possess higher energy levels compared to iron ores. Hence, the tendency to go back to low energy regime (oxides, chlorides, )

- Since corrosion releases energy, it is a *spontaneous process*. That is:

$$\Delta GE = -ve$$

where GE is Gibbs free energy: the thermodynamic potential used to calculate the max. or reversible work that may be performed by a thermodynamic stm @ isothermal & isobaric conds.



# Types of corrosion



- Corrosion on metallic materials divided into:
  - 1. Wet corrosion ie, corrosion in water with dissolved species
  - 2. Corrosion in fluids such as fused salts & molten metals
  - 3. Dry (chemical) corrosion in a dry gas at high temp.

## Factors governing wet corrosion

- Oxygen content ie, high $O_2$ level, high corrosion rate
- Seawater velocity eg, splash zone
- Temperature eg, high temp. accelerates corrosion & vise-versa
- Pollution
- Marine organisms
- Impurities in iron
- Presence of moisture
- Type of flow eg, laminar or turbulent

# Seawater environment



- Seawater consists of salts, dissolved gases, trace elements, solids, living organisms, …
- Salt content of seawater may range: 7g/kg (Baltic Sea) to 43g/kg (Persian Gulf)
- Seawater temp. range: 0°C (Antarctica) to 28°C (tropics)
- S/w corrosion can promote general thinning to local penetration



# Use of iron & steel at sea



- Unless coated inexpensive carbon steels & cast irons have high maintenance/replacement costs
- Offshore, iron/steel maintenance is very expensive
- Hence, high quality coating(s) and *cathodic protection* are essential

Carbon steel & cast iron use in the marine environment

| Type | Alloy | Application |
|---|---|---|
| Structural | Carbon steel and cast iron | Platforms, jackets, ship hulls, vessels, piling and sheeting, towers, bridges, lock gates, gratings, ladders, cranes, lifts, and loaders |
| Pressure-containing | Carbon steel, low-alloy steels, cast iron, and austenitic cast iron | Piping, vessels, pumps, and valves |

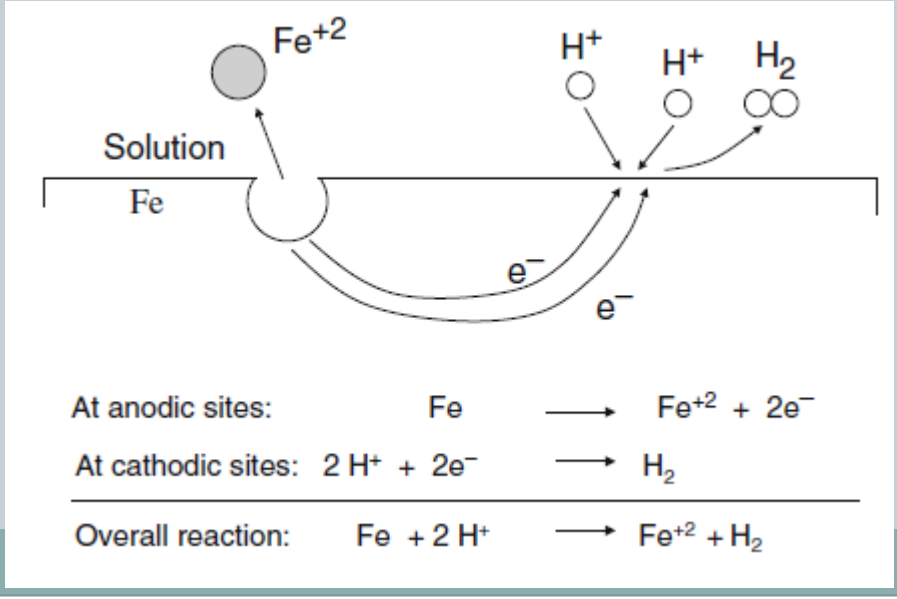
# What is corrosion?

# Coupled electrochemical reaction



- Anodic reaction:
  - 1. Species undergoes *oxidation* i.e., increase in oxidation #
  - 2. Loss of electrons at anodic site
- Cathodic reaction:
  - 1. Species undergo *reduction* i.e., decrease in oxidation #
  - 2. Gain of electrons at cathodic site i.e., electrons are used up

Iron metal immersed in a weak acid.



# Iron rust in seawater



- Iron immersed in sea water results in:

$$Fe^{2+} + 2Cl^{-} \rightarrow FeCl_2$$
$$FeCl_2 + H_2O \rightarrow FeO\ (rust) + 2HCl$$

- HCl attacks iron. To slow-down process: (a) Take steel out of water, (b) Remove NaCl, or (3) Eliminate Fe!

- Rate of corrosion in s/w slows down as corrosion products restrict diffusion of s/w to metal surface.

Role of $O_2$

- If dissolved, $O_2$ content ≤20ppb, corrosion of carbon steel is low
- Offshore $O_2$ content >50ppb, hence steel corrodes fast
- Oxygen content of 100-500ppb is common offshore!

# Wet iron (steel) corrosion



- Steel corrodes electrochemically. Iron corrosion is expressed by:

$$Fe(s) \rightarrow Fe^{+2}(aq) + 2e^-$$

- Ferric ions:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

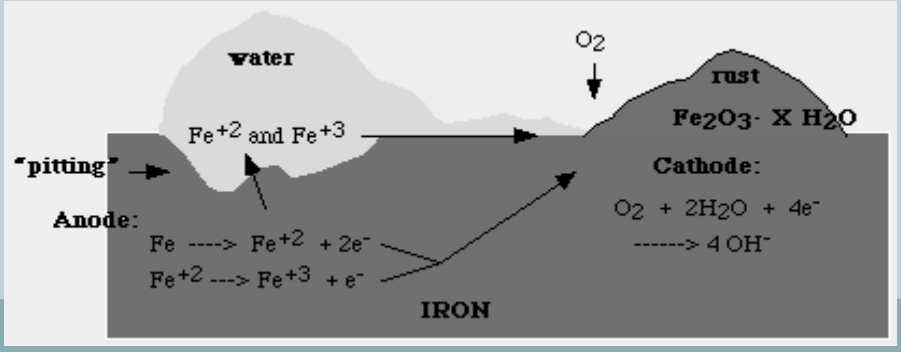
- Oxygen reduction:

$$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-$$

- The overall reaction is:

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe^{+3} + 4OH^- \rightarrow 2Fe(OH)_2$$

$$2Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 \bullet \times H_2O(s) \text{ (iron rust)}$$

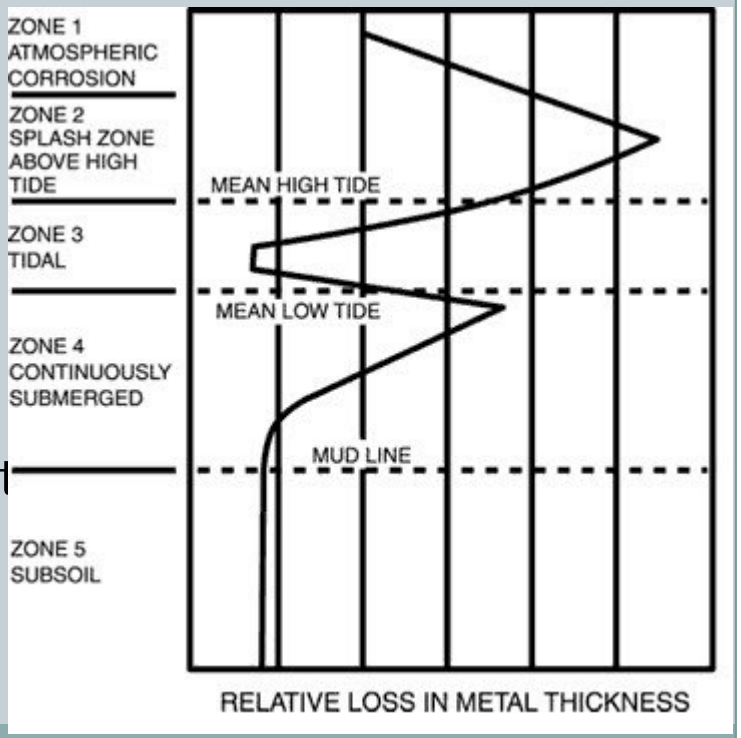


# Corrosion in the marine environment



- Carbon steels exposed to sea atmosphere corrode btw: 0.01-0.1mm/yr
- Corrosion products may expedite corrosion of other materials eg SS
- Why does corrosion peaks @ splash zone?

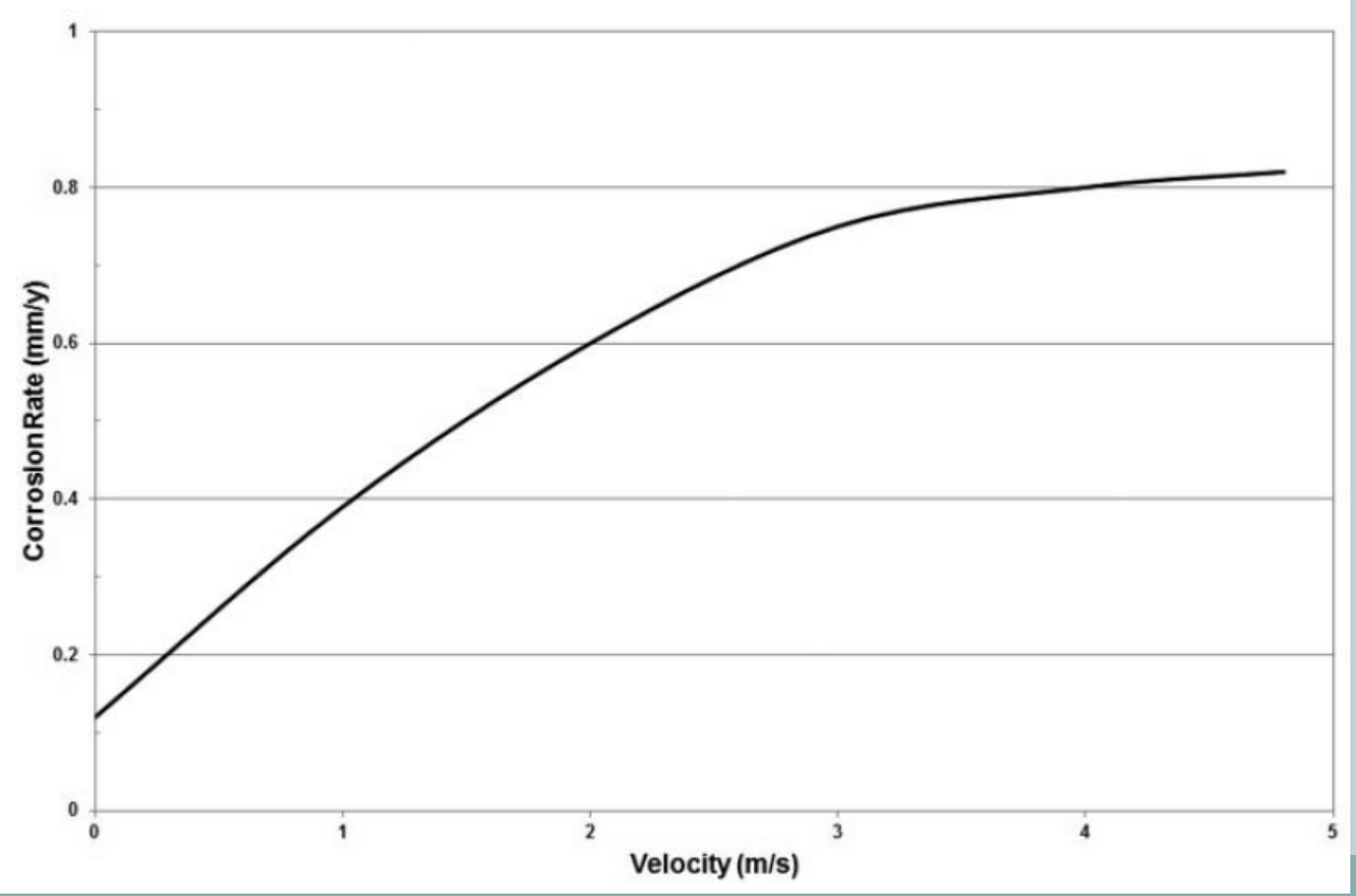
-Continuous contact with highly aerated s/w & erosive effects of *spray*, *waves* & *tidal fluctuations*. Rate for GOM: 1.4mm/yr




- CP is ineffective at splash zone because of discontinuous contact with $H_2O$; no current flows thru metal.
- At splash zone: (1) Beef-up metal thickness & (2) use good coating or sheathing (neoprene, rubber coatings, Ni, Cu alloys)

# Corrosion rate vs. seawater flow rate





# How does water $O_2$ content affect corrosion?

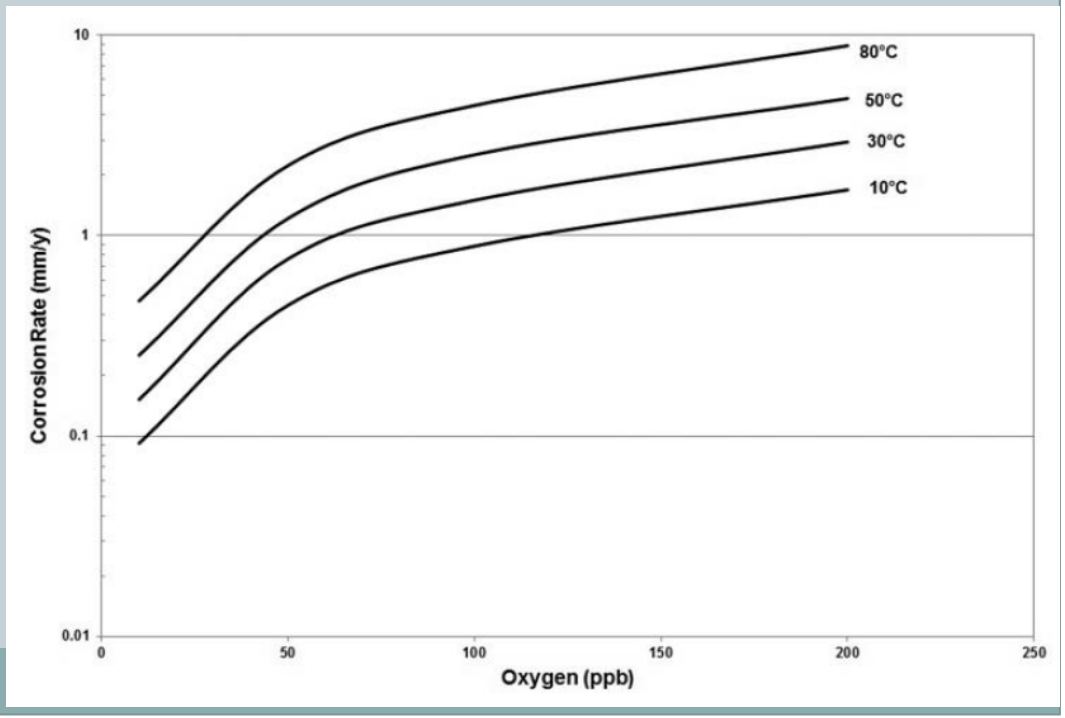


## Role of O2

- If dissolved $O_2$ content ≤20ppb, corrosion of carbon steel is low
- Offshore, $O_2$ content >50ppb, hence steel corrodes fast
- Oxygen content 100-500ppb is common offshore!

- Note that galvanized steel does not protect steel @ sea because corrosion products are soluble

Effect of dissolved $O_2$ & water temp. on corrosion rate of uncoated carbon steel.



# Faraday's law of electrolysis



- Corrosion involves concurrent electrical charge & mass transfer across a metal-electrolyte interface

- Link btw charge transfer & mass transfer is the Faraday (F), such that:

$$F \equiv \frac{96,500\,C}{equivalent} \qquad (1)$$

- Faraday's law states that the mass of metal (w) corroded is:

$$w = \frac{ItA}{nF} \qquad (2)$$

where $I$ is current (A), $t$ is time (s), $A$ is atomic weight of metal, $n$ is # of equivalents transferred/mole of metal.

- Example: Find $n$ for following anodic reactions:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$$

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^{-}$$

# Example



- Example

# Corrosion types at sea



- 1. Hydrogen embrittlement
- 2. Galvanic corrosion
- 3. Low water corrosion
- 4. Chlorine/hypochlorite
- 5. Cathodic protection
- 6. Biofouling & microbiologically influenced corrosion

# Corrosion types at sea



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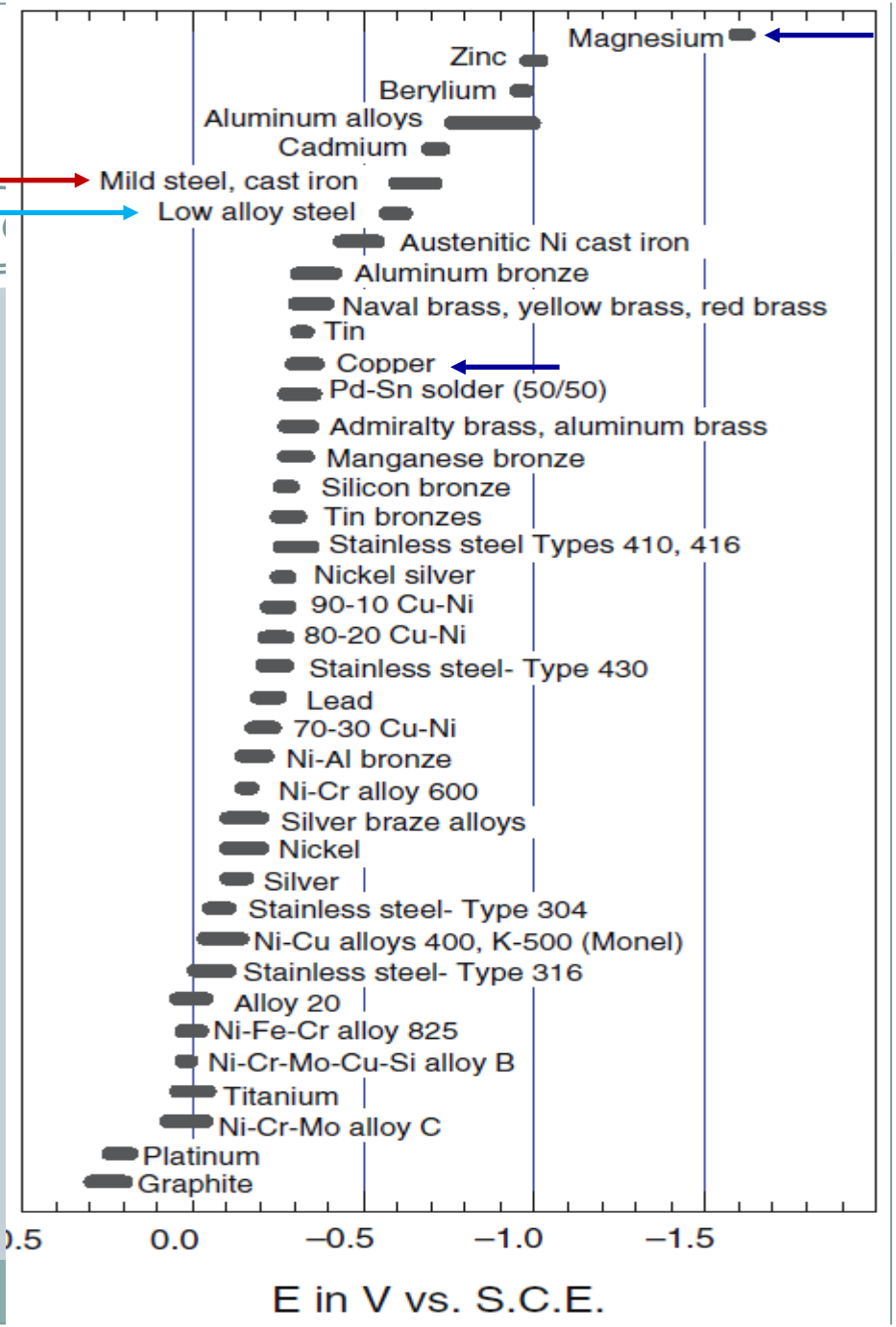
# Galvanic series in S/W

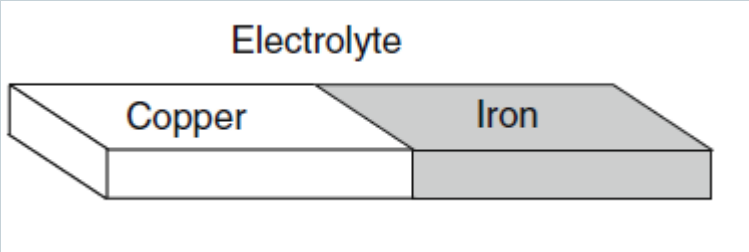
- Metals & alloys such as platinum corrode less
- Metals & alloys with higher corrosion potential $E_{corr}$ corrode more eg, Magnesium
- Most electronegative will corrode first
- Sacrificial anodes: Zn, Al, Mg
- GC ceases in absence of electrolyte



# Galvanic (bimetallic) corrosion



- When 2 metals in physical (or electrical) contact are immersed in an electrolyte 1 acts as the anode (attacked) & the other as cathode (intact)



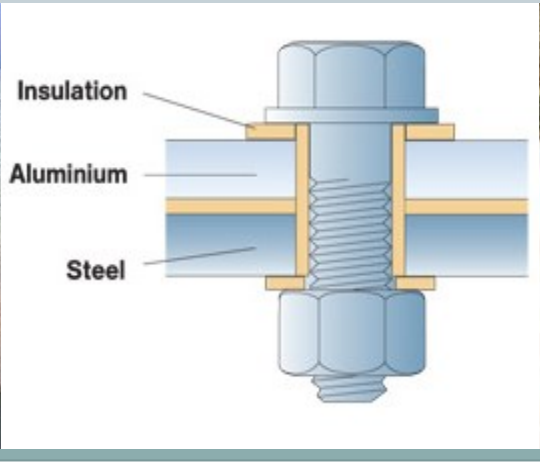

- A potential difference is set-up btw the metals. If Cu & Fe, Cu will become anodic & eaten away
- Most electropositive (anodic) will corrode at an accelerated rate
- Examples:
  - 1. Copper piping connected to a steel tank
  - 2. Zinc-coated screws in a sheet of copper
  - 3. SS screw in contact with cadmium-plated steel washer

# Guarding against galvanic corrosion



- 1. Select metals galvanically close to each other
- 2. Insulate contact btw dissimilar metals, if possible
- 3. Use organic coatings, but coat both members of the couple or coat only the cathode
- 4. Avoid unfavourable area effect of small anode & large cathode

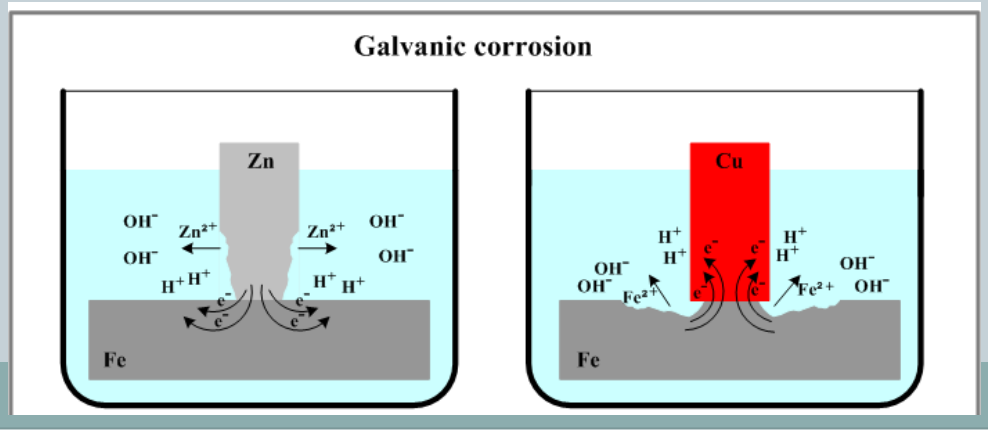
Stainless-Steel and mild-steel




# Sacrificial anodes



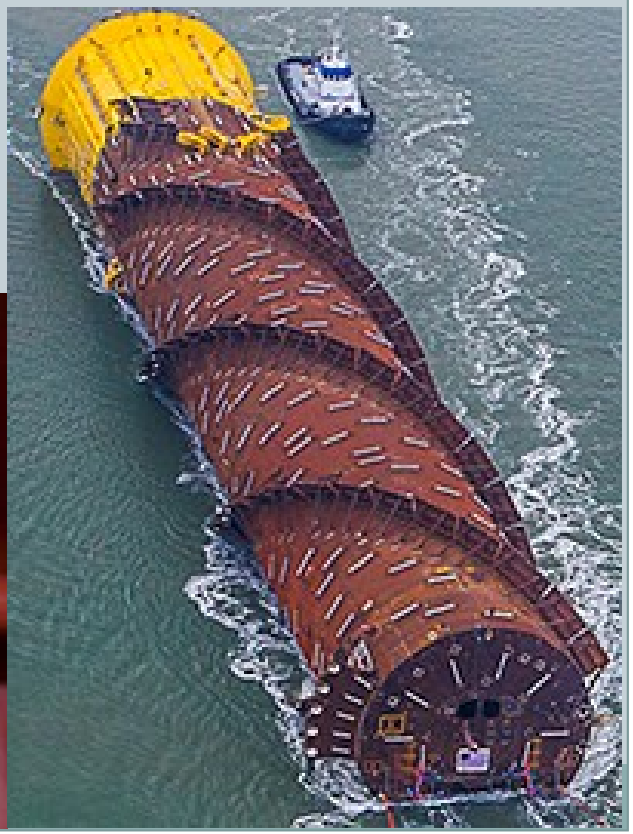
- Corrosion is greatest near the two metals' junction
- The bigger the potential difference the more severe corrosion is
- As cathode/anode areas increases so does the extent of corrosion
- Anodes are relatively inexpensive, but require replacement




# Use of sacrificial anodes



- Applications: on ships, boats, offshore platforms, pipelines, …
- Zinc is the most common sacrificial anode used
- Anodes increase weight & hull stresses



# Cathodic protection (CP)



- Idea: electrical potential of p/line material is reduced below its corrosion potential
- Corroding metal is protected by cathodic polarisation which slows down corrosion rate
- Anodic rxn:

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

- Cathodic rxn:

$$O2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

- pH in vicinity of pipeline increases and yields calcareous deposits:

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow H_2O + CaCO_3$$

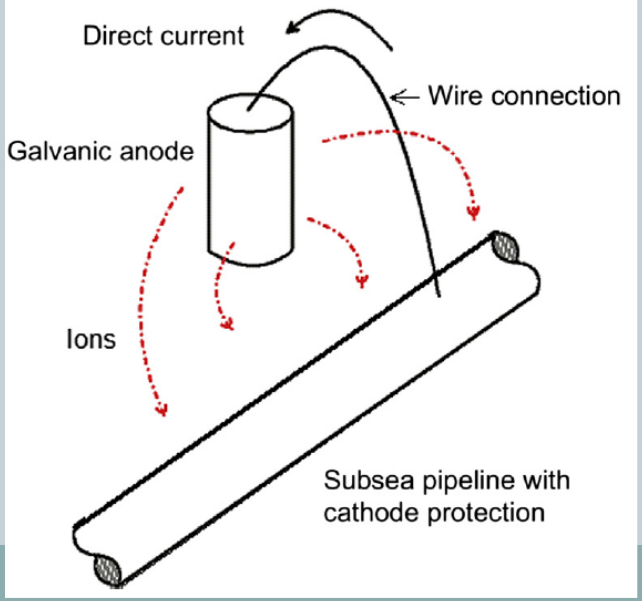
$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$

- Deposits decrease $O_2$ flux to steel and pipeline is protected

# Cathodic protection (2)



- Usually used for buried or marine pipelines
- Naked carbon steel corrodes at accelerated rate
- Usually cathodic protection is used in combination with coatings
- What happens if the coating deteriorates or fails locally?
- CP required continuous operation
- CP provides a direct current (dc) thru electrolyte to pipeline



# Cathodic protection (3)



- CP is effective against external pitting & crevice corrosion
- Subsea pipelines protected by application of $-0.80V_{Ag/AgCl}$ or more negative
- Presence of oxygen is important
- Deepwater pipelines are less prone to corrosion due to low $O_2$ levels

# Biofouling

# Biofouling



- Is the accumulation of barnacles, plants, algae or sea life on wetted surfaces
- Affects O&G industry, desalination plants, underwater structures, ship hulls, aquaculture, medical implants, bathyscaphes, …
- Can increase ship drag resistance by 60% (Vetti, 2009)
- Lower ship speed by 10% & increase fuel consumption by 40% (Vetti, 2009)
- Biofouling is estimated to cost the shipping industry $60bn/yr (Vetti, 2009)

# Biofouling



- Biofouling is to boost shipping $CO_2$ & $SO_2$ emissions btw 38-72% by 2020 (*Salta, M.* et al., 2008)
- Can weaken the structural rigidity of a marine structure
- Biofouling in pipelines can lead to entrained water



# Biofouling in oil & offshore industries



- Detrimental effects of biofouling on offshore structures can:
  - 1. Increase the mass of platforms
  - 2. Affect structural response in waves by increasing roughness
  - 3. Impact earthquake loading
  - 4. Gain in hydrodynamic loading by ~18% for 15cm thick fouling
  - 5. Obscures visual inspection of structure during maintenance
  - 6. Sharp shells & taxa may damage underwater cables & equipment
  - 7. Promote microbiologically influenced corrosion
- In US, before decommissioning a rig one needs remove biofouling in-situ

# Antifouling

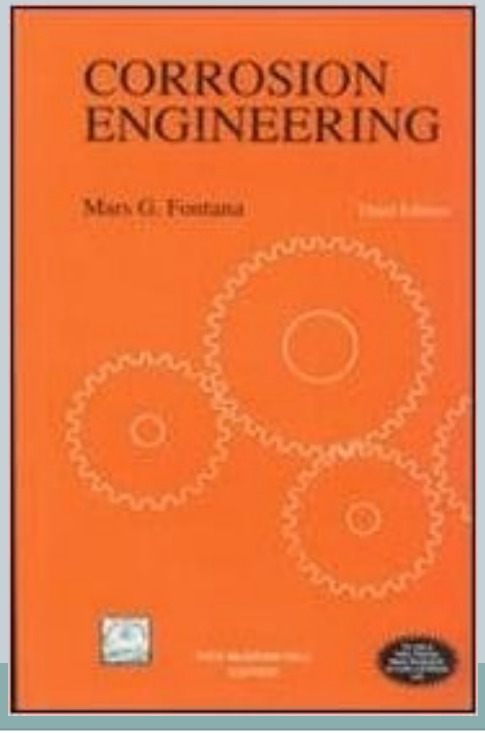


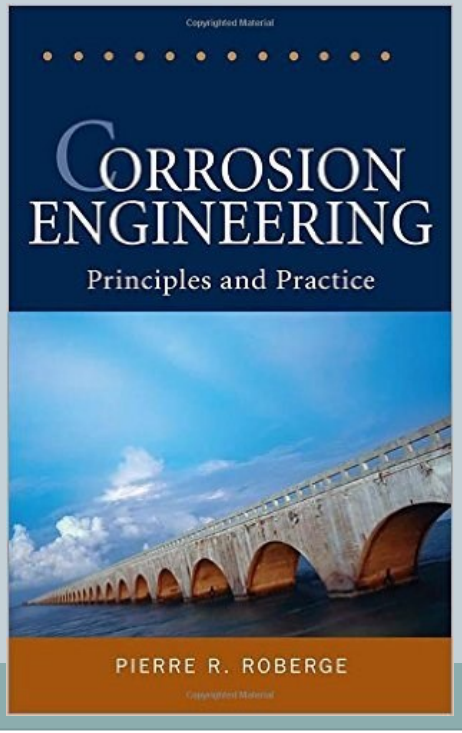
- Process of preventing the attachment of marine life on surfaces
- 1. Bio-dispersants [surfactants; polymers] are used in industrial uses
- 2. Coatings can repel or kill microorganisms:
  - Biocides eg, biofilms, toxic substances like TBT (tributyltin) banned in 1990
  - Thermal treatment eg, ship ballast systems
  - Energy methods eg, laser irradiation kills diatoms, plasma pulse for zebra mussels
- 3. Use of a slippery surface or zwitterion (electrically neutral molecules)

# Corrosion related books




- Fontana G.M. (1987) Corrosion Engineering, 3rd Ed., McGraw-Hill
- Roberge, P.R. (2008) Corrosion engineering: principles and practice, McGraw-Hill
- Waldman, J. (2015) Rust: the longest war. Simon & Schuster



Introduction: The Pervasive Menace
1. A High-Maintenance Lady
2. Spoiled Iron
3. Knives That Won't Cut
4. Coating the Can
5. Indiana Jane
6. The Ambassador
7. Where the Streets Are Paved with Zinc
8. Ten Thousand Mustachioed Men
9. Pigging the Pipe
10. Between Snake Oil and Rolexes
11. The Future

Thanks for your attention!