Electrochemistry

CHEM 5390

Corrosion

Metals (except Au) are thermodynamically unstable with respect to their oxides in air and water.

Metals are not found in nature in their metallic form but rather in the form of some compound, i.e. oxide, sulfide, silicate, …ores

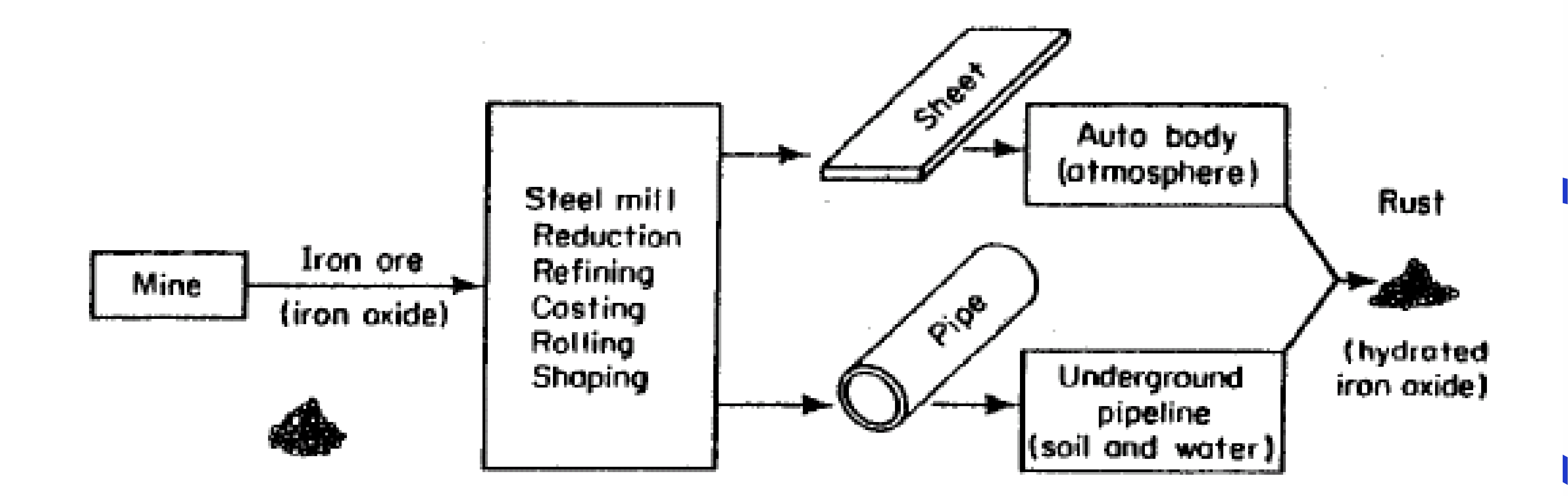
Corrosion

Corrosion represents the natural tendency of all systems toward a state of minimum Gibbs energy.

Corrosion processes are electrochemical in nature

Corrosion

Corrosion: Metallurgy in Reverse



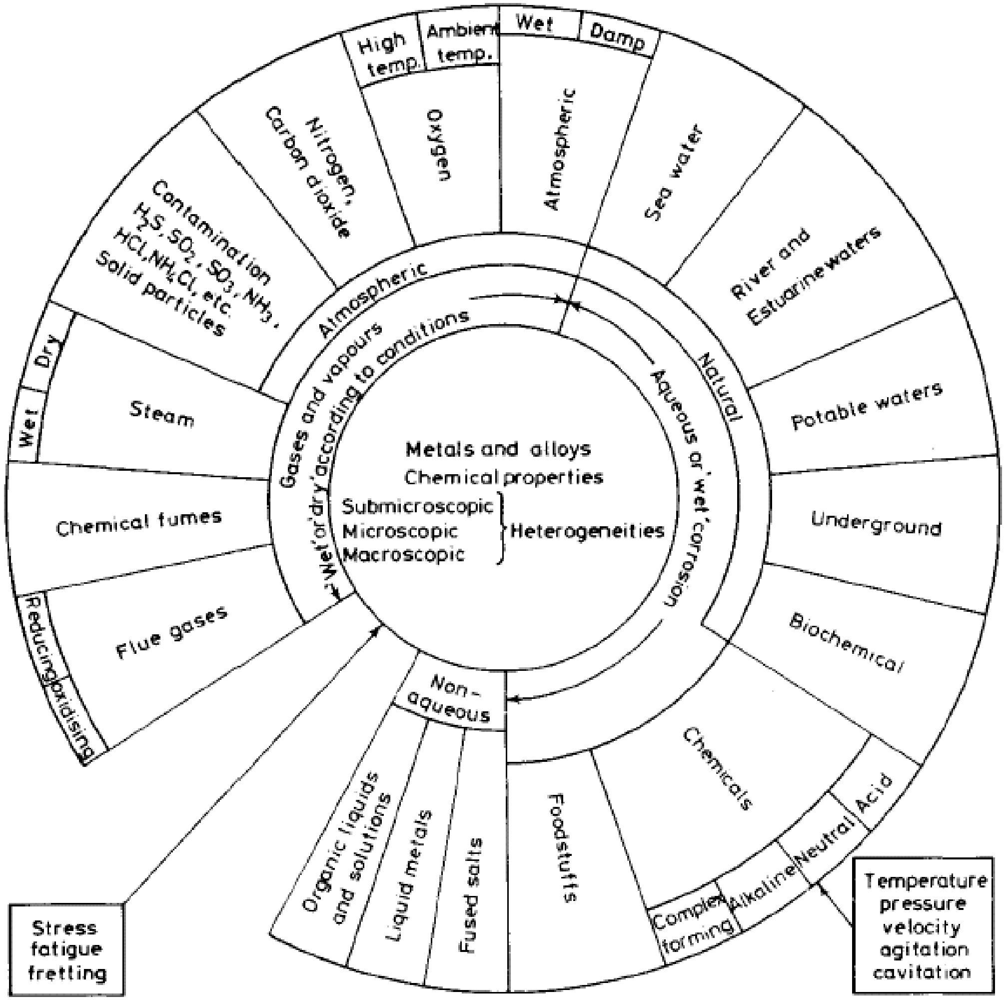
Corrosion

Technology depends on our ability to slow down the rate of corrosion.

The cost for industries to prevent corrosion is huge per year in the World.

Corrosion

Environments in Corrosion



[1]Sheir, L.L., R.A. Jarman, and G.T. Burstein, eds. Corrosion. 3rd ed. Vol. 1. 2000, Butterworth-Heinemann: Oxford.

Corrosion

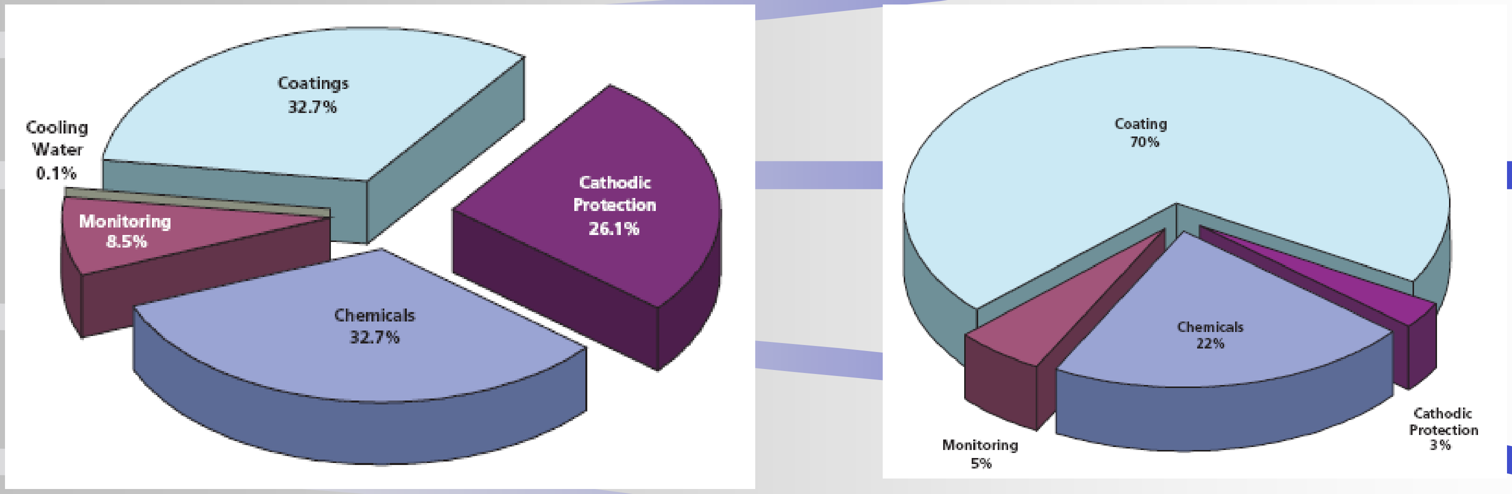


Figure 1. Percentage of direct cost for specific corrosion control technologies in (left) on-shore production for 2000 and 2001 and (right) off-shore production for 1998 and 2001 [5].

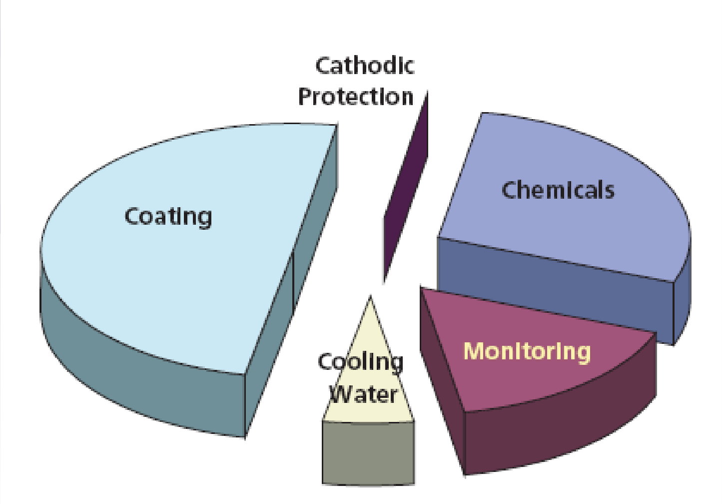


Figure 2: Relative percentage of direct cost for specific corrosion control technologies in refineries [5].

Corrosion

Damage caused by corrosion is not just esthetic (i.e. rust spots) but an engineering and safety problem.

Combination of high humidity and high temperature and certain harsh environments favors corrosion.

The presence of chloride ions is detrimental to almost all metals and interferes with many corrosion protection methods.

Corrosion

Rate of Corrosion depends on:

- – chemicals present (environment)
- – type of material (metal, ceramic, polymer)
- – temperature
- – exposure time
- – stress …. etc

Corrosion

Type of material and corrosion

- Metals
  - *tend to dissolve (Corrosion)*
  - *form non-metallic film (Oxidation)*
- Ceramics
  - *relatively inert, but under certain conditions corrosion may occur.*
- Polymers
  - *may dissolve in solvents, swell, UV - degradation.*

Corrosion

One of the worst types of corrosion is local corrosion from design error – when two different types of metals are in contact without isolating them electrically.

Corrosion

Galvanic Corrosion

Galvanic corrosion (also called “dissimilar metal corrosion”) refers to corrosion damage induced when two dissimilar materials are coupled in a corrosive electrolyte.

In a bimetallic couple, the less noble material becomes the anode and tends to corrode at an accelerated rate, compared with the uncoupled condition and the more noble material will act as the cathode in the corrosion cell.

Corrosion

Galvanic Corrosion

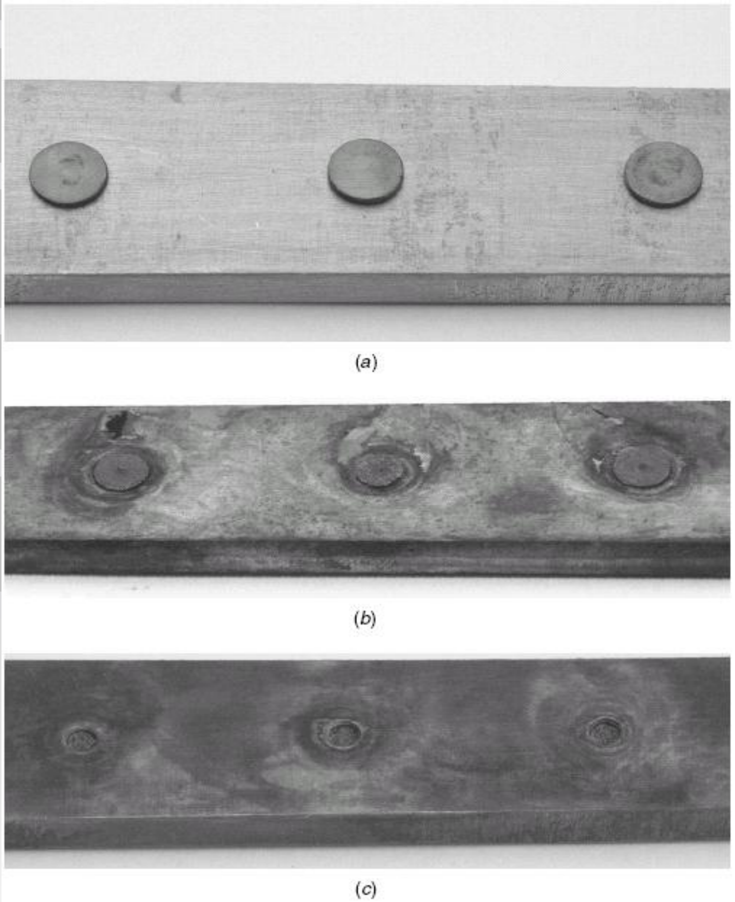


Fig. 2.14. Steel rivets on a copper bar: (*a*) at the start of the experiment; (*b*) 6 months after being submerged in 3% sodium chloride solution; and (*c*) after 10 months in the same solution.

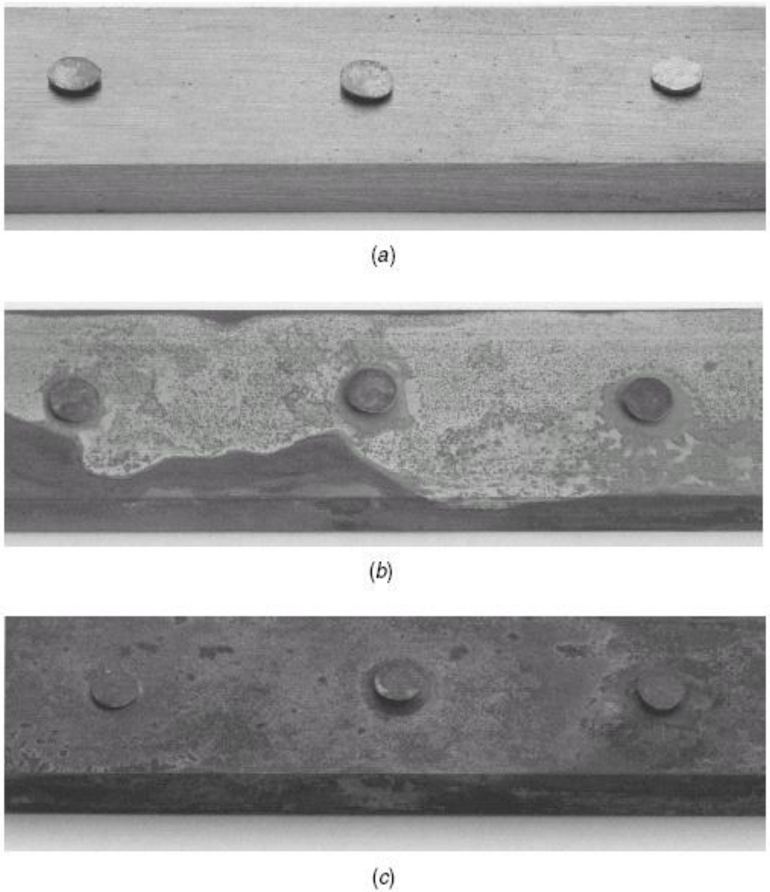


Fig. 2.15. Copper rivets on a steel bar: (*a*) at the start of the experiment; (*b*) 6 months after being submerged in 3% sodium chloride solution; and (*c*) after 10 months in the same solution.

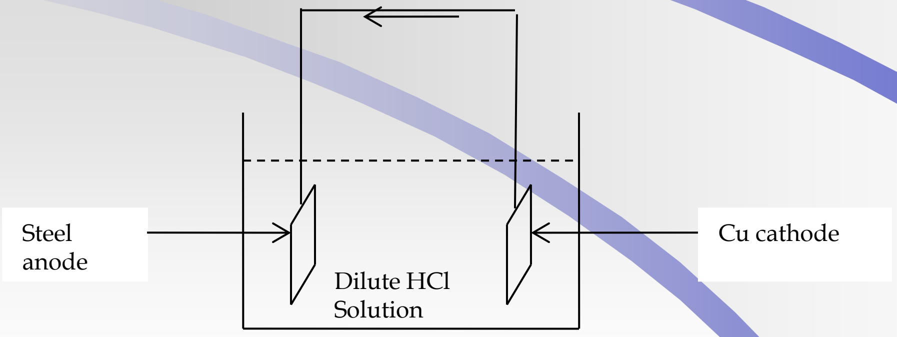
Corrosion

Other dissimilar electrode cells or galvanic cells

- Dry cell
- Local action cell
- A brass fitting connected to a steel pipe
- A bronze propeller in contact with the steel hull of a ship

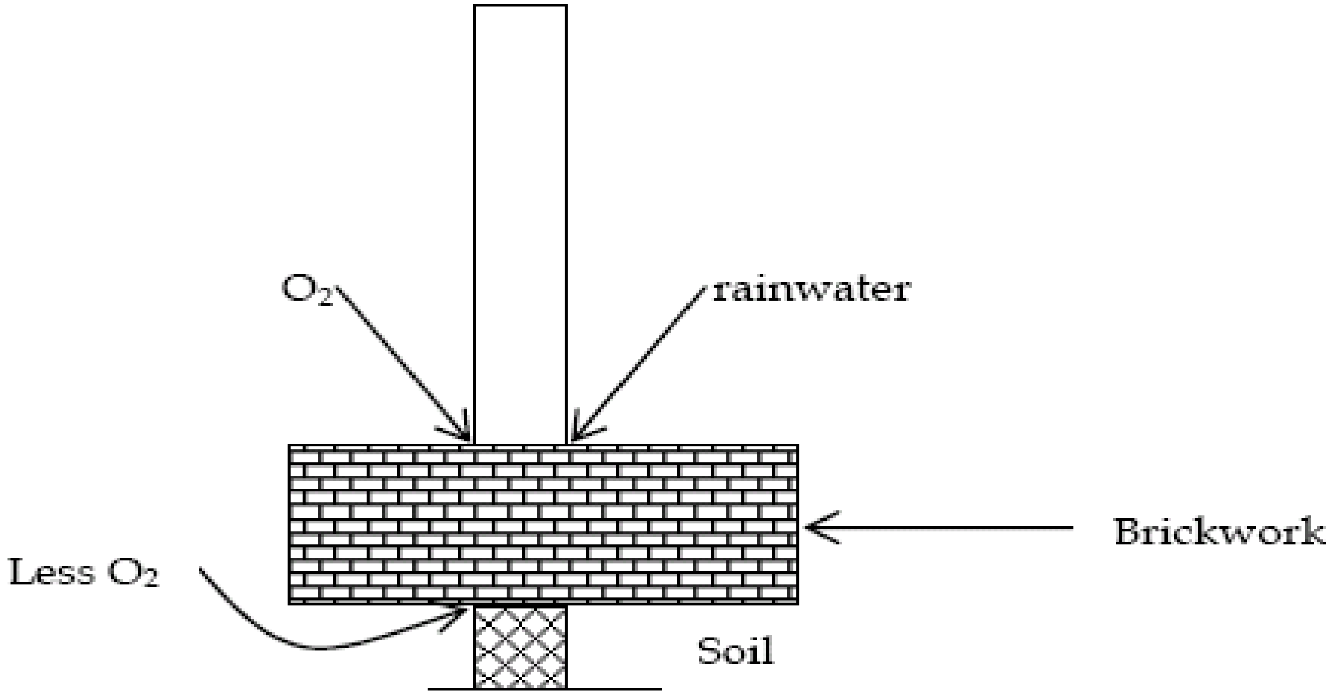
Corrosion

Copper plates and steel rivets – creates a battery where Cu is the cathode and steel is the anode – short circuit when water is present.



Corrosion

Corrosion at the bottom of the electrical poles



Corrosion

Most fundamental step in corrosion is oxidation of metal to its lowest stable valence state.

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

This reaction cannot occur by itself without another reaction – since high negative charge would accumulate on the metal.

Corrosion

Anodic Reaction: $Fe^0{}_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + 2e^-$ Deterioration of metal

Typically H_2 evolution or oxygen reaction will accompanying these reactions.

Cathodic Reaction: $2H^+{}_{(aq)} + 2e^- \rightarrow H_2O_{(l)}$ Chemical

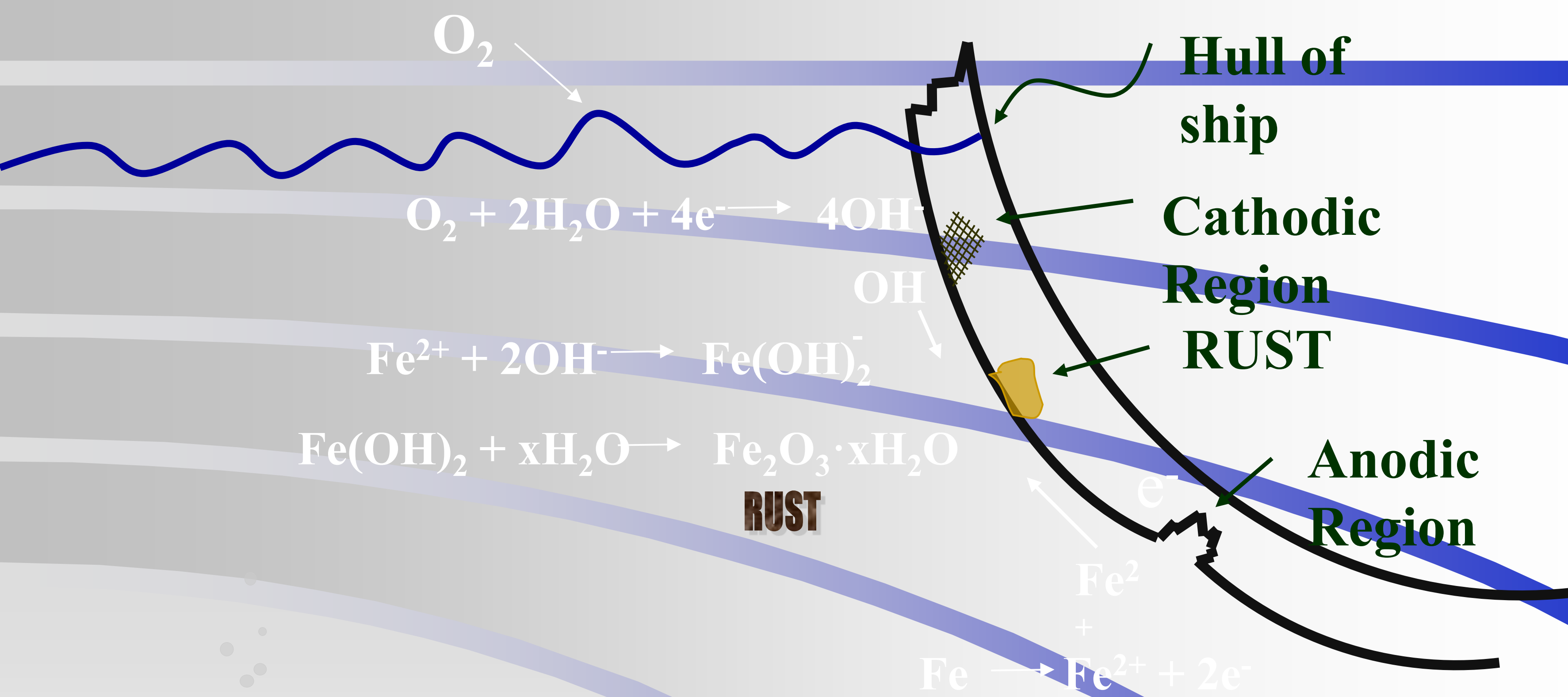
$O_{2\,(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-{}_{(aq)}$ Atmospheric

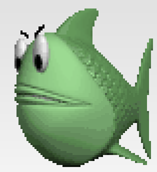
Overall Reaction:

$Fe^0{}_{(s)} + 2H^+{}_{(aq)} \rightarrow Fe^{2+}{}_{(aq)} + H_2O_{(l)}$ Chemical

$2Fe^0{}_{(s)} + O_{2\,(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}{}_{(aq)} + 4OH^-{}_{(aq)}$ Atmospheric

Corrosion to a Ship's Hull





Electrons Migrate from Anodic to Cathodic Region

Corrosion

Types of Corrosion

1. General corrosion or uniform attack
2. Pitting
   i. Impingement attack or erosion-corrosion
   ii. Fretting corrosion
   iii. Cavitation erosion
3. Selective Corrosion
4. Intergranular Corrosion
5. Cracking
   i. Corrosion fatigue
   ii. Stress corrosion cracking (SCC)

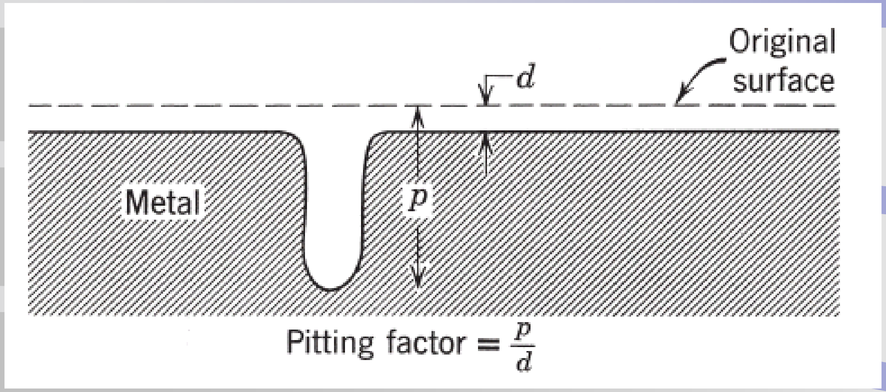
Corrosion

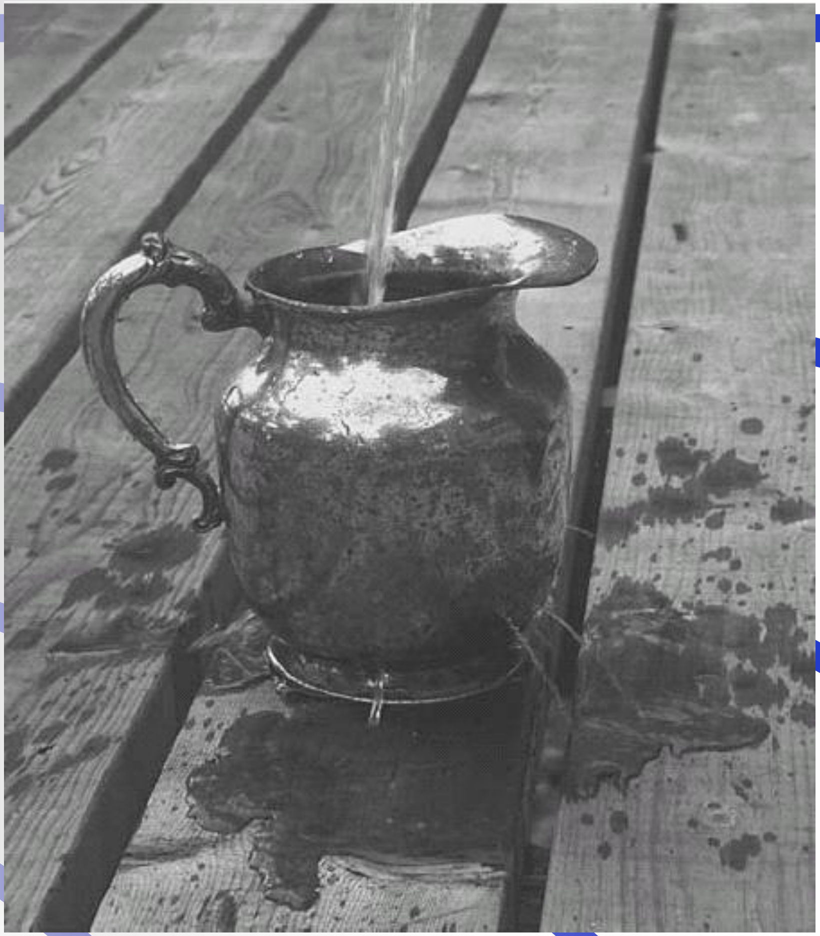
Uniform Corrosion

This type of corrosion includes the commonly recognized rusting of iron or tarnishing of silver. " Fogging " of nickel and high - temperature oxidation of metals are also examples of this type.

Corrosion

Pitting





Iron buried in the soil corrodes with formation of shallow pits, whereas stainless steels immersed in seawater characteristically corrode with formation of deep pits.

Corrosion

Pitting

This is a localized type of attack, with the rate of corrosion being greater at some areas than at others.

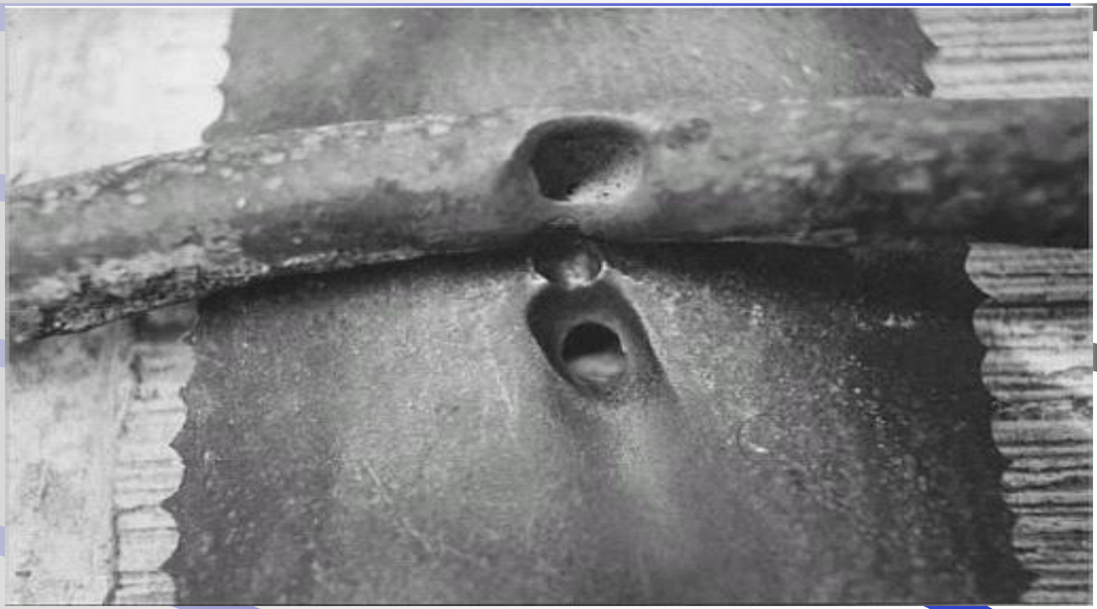
Depth of pitting is sometimes expressed by the *pitting factor* , the ratio of deepest metal penetration to average metal penetration as determined by the weight loss of the specimen.

A pitting factor of unity represents uniform attack.

Corrosion

Pitting - Erosion-Corrosion

When subjected to high – velocity liquids, materials undergo a pitting type of corrosion called *impingement attack* , or *erosion corrosion* .



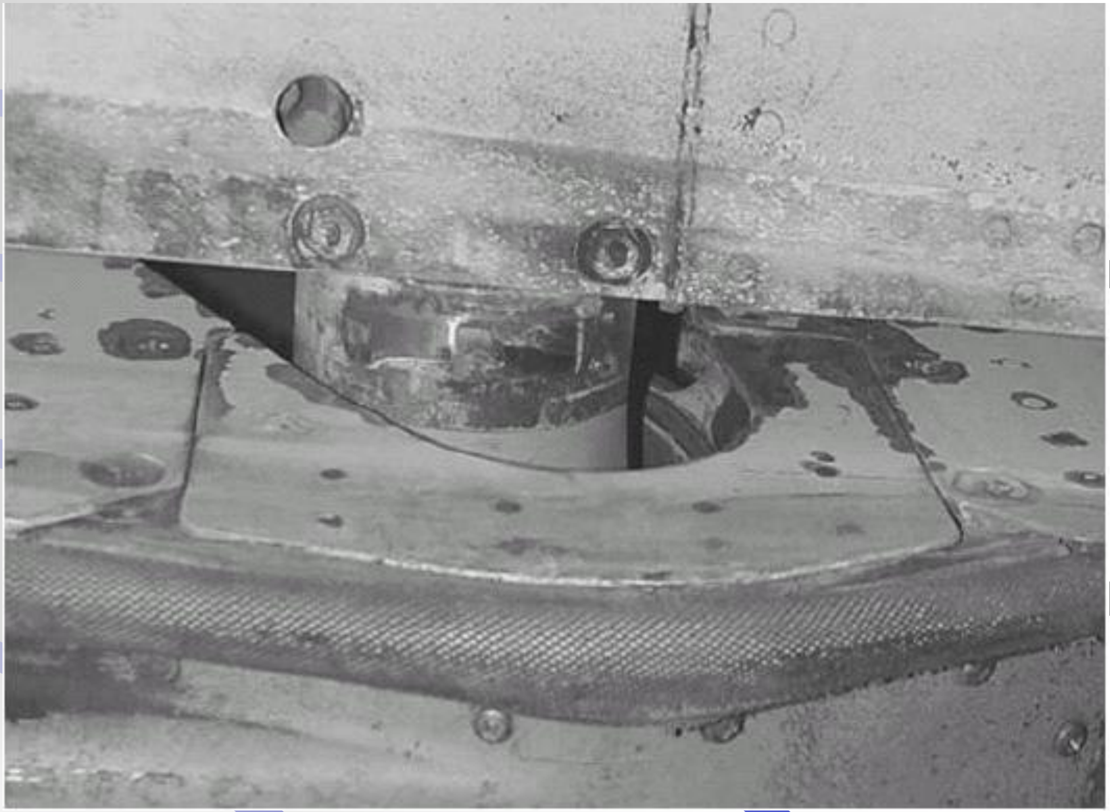
Copper and brass condenser tubes, for example, are subject to this type of attack.

Corrosion

Pitting - Fretting Corrosion

Fretting corrosion , which results from slight relative motion (as in vibration) of two substances in contact, one or both being metals, usually leads to a series of pits at the metal interface.

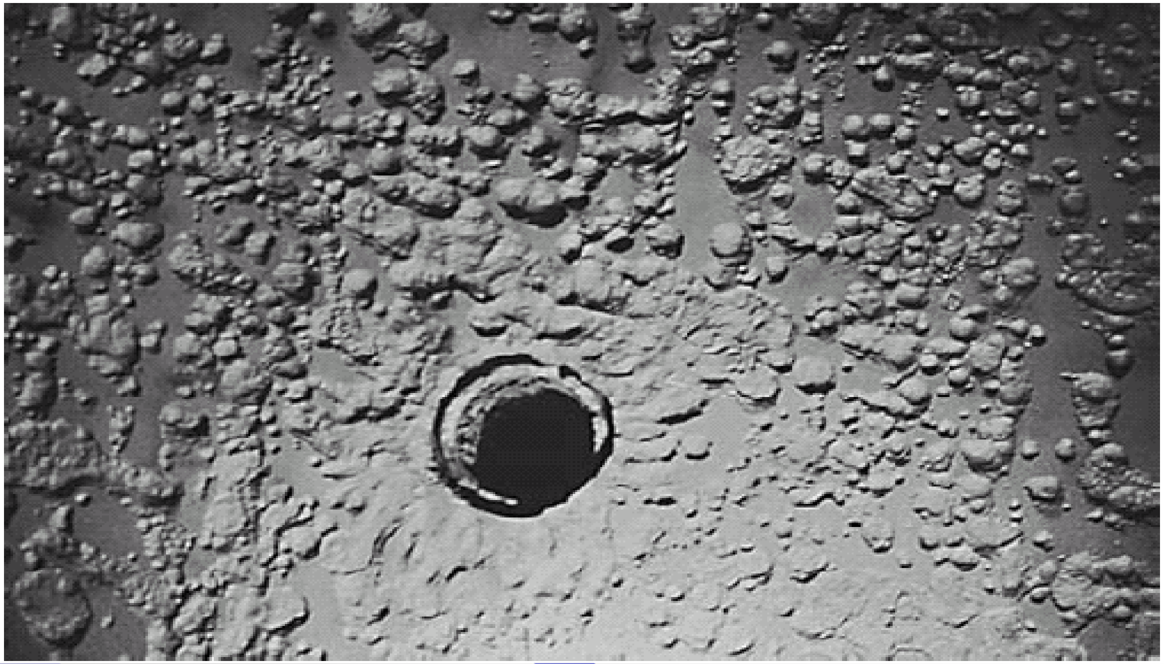
Metal - oxide debris usually fills the pits so that only after the corrosion products are removed do the pits become visible.



Corrosion

Pitting - Cavitation Erosion

Cavitation – erosion is the loss of material caused by exposure to cavitation, which is the formation and collapse of vapor bubbles at a dynamic metal – liquid Interface.



For example, in rotors of pumps or on trailing faces of propellers. This type of corrosion causes a sequence of pits

Corrosion

Selective Corrosion

Dealloying is the selective removal of an element from an alloy by corrosion.

One form of dealloying, dezincification, is a type of attack occurring with zinc alloys (e.g., yellow brass) in which zinc corrodes preferentially, leaving a porous residue of copper and corrosion products.

The alloy often retains its original shape, and may appear undamaged except for surface tarnish, but its tensile strength and ductility are seriously reduced.

Dezincified brass pipe may retain sufficient strength to resist internal water pressures until an attempt is made to uncouple the pipe, causing the pipe to split open.

Corrosion

Selective Corrosion

Parting is similar to dezincification in that one or more reactive components of the alloy corrode preferentially, leaving a porous residue that may retain the original shape of the alloy.

Parting is usually restricted to such noble metal alloys as gold – copper or gold – silver and is used in gold refining.

For example, an alloy of Au – Ag containing more than 65% gold resists concentrated nitric acid as well as does gold itself.

However, on addition of silver to form an alloy of approximately 25% Au – 75% Ag, reaction with concentrated HNO_3 forms silver nitrate and a porous residue or powder of pure gold.

Corrosion

Selective Corrosion

Copper - base alloys that contain aluminum are subject to a form of corrosion resembling dezincification, with aluminum corroding preferentially.

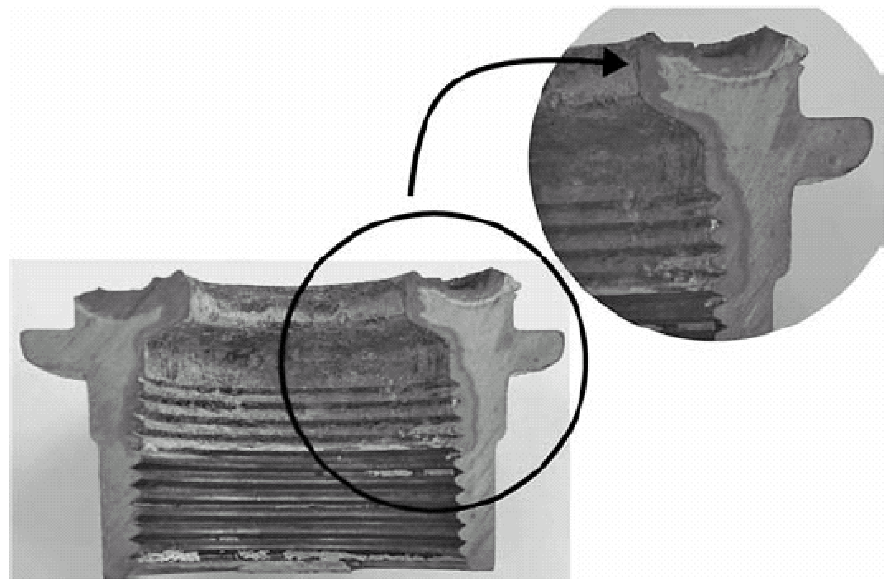


FIGURE 6.35 Layer dezincification of a brass fitting: parent material Cu 59.3 percent, Zn 35.7 percent, Pb 4.9 percent, leached area: Cu 95.0 percent, Zn 0.7 percent Pb 4.1 percent. (Courtesy of Defence R&D Canada-Atlantic)

Corrosion

Intergranular Corrosion

This is a localized type of attack at the grain boundaries of a metal, resulting in loss of strength and ductility.

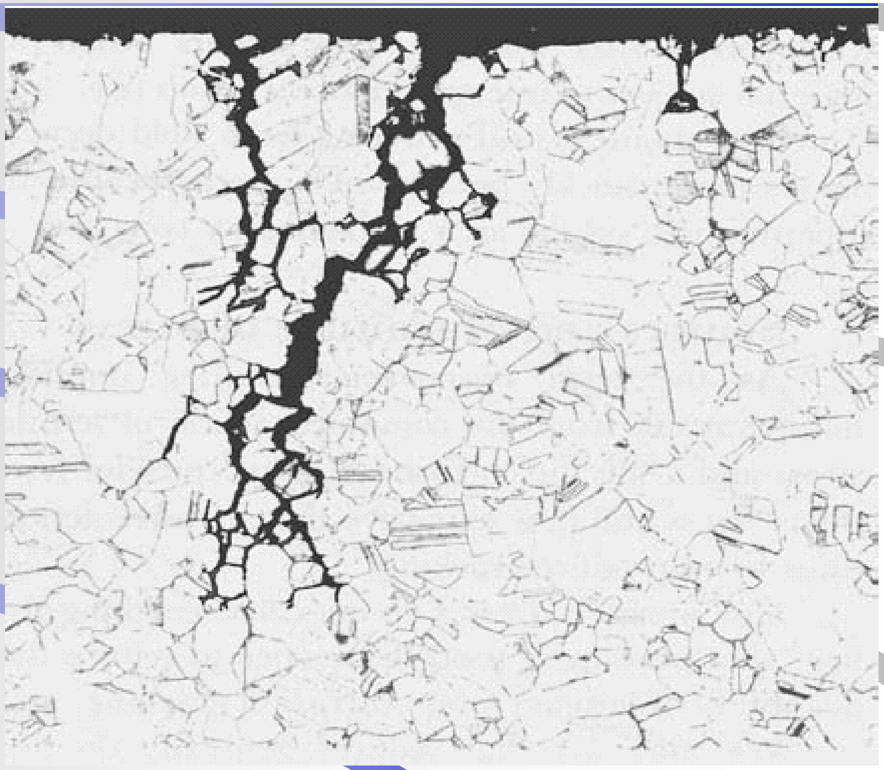
Grain – boundary material of limited area, acting as anode, is in contact with large areas of grain acting as cathode.

The attack is often rapid, penetrating deeply into the metal and sometimes causing catastrophic failures.

At elevated temperatures, intergranular corrosion can occur because, under some conditions, phases of low melting point form and penetrate along grain boundaries.

Corrosion

Intergranular Corrosion



Improperly heat - treated 18 - 8 stainless steels or Duralumin – type alloys (4% Cu – Al) are among the alloys subject to intergranular corrosion.

When nickel - base alloys are exposed to sulfur - bearing gaseous environments, nickel sulfide can form and cause catastrophic failures. This type of attack is usually called *sulfidation* .

Corrosion

Cracking - Corrosion Fatigue

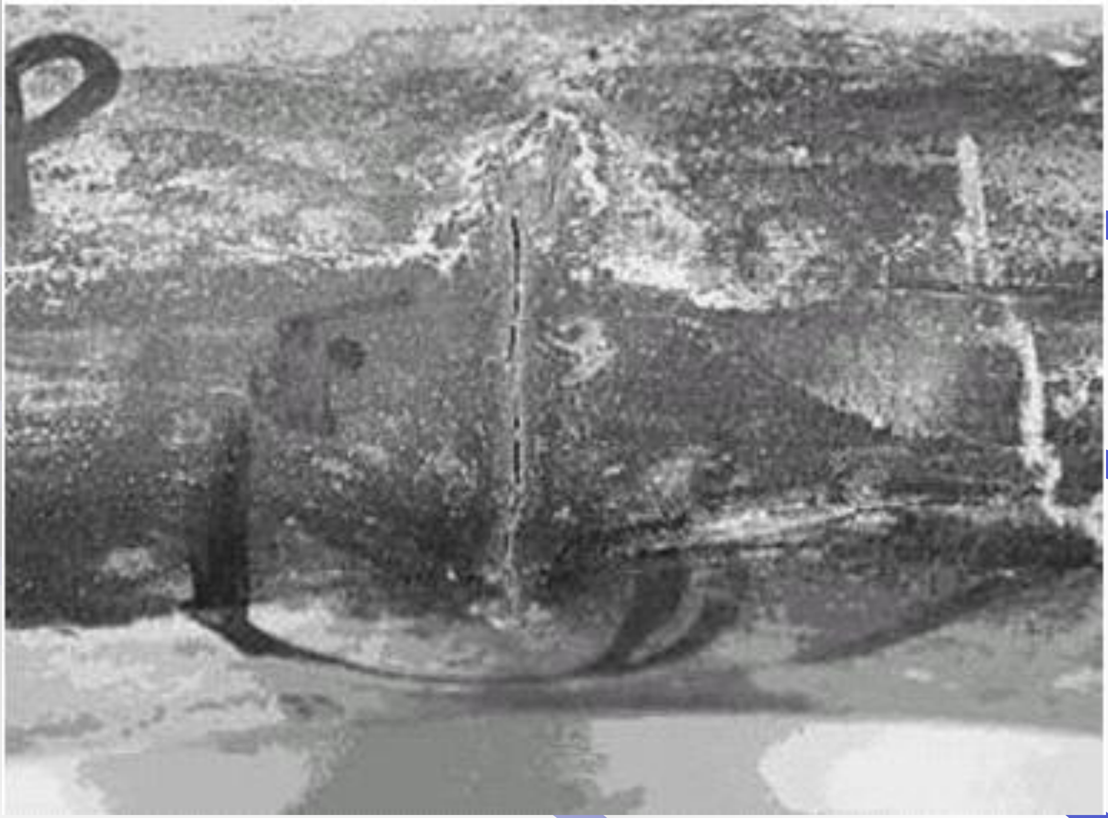
If a metal cracks when subjected to repeated or alternate tensile stresses in a corrosive environment, it is said to fail by *corrosion fatigue* .

In the absence of a corrosive environment, the metal stressed similarly, but at values below a critical stress, called the *fatigue limit* or *endurance limit* , will not fail by fatigue even after a very large, or infinite, number of cycles.

A true endurance limit does not commonly exist in a corrosive environment: The metal fails after a prescribed number of stress cycles no matter how low the stress.

Corrosion

Cracking - Corrosion Fatigue



Corrosion

Cracking - Stress corrosion cracking (SCC)

If a metal, subject to a constant tensile stress and exposed simultaneously to a specific corrosive environment, cracks immediately or after a given time, the failure is called *stress - corrosion cracking* .

The stress may be residual in the metal, as from cold working or heat treatment, or it may be externally applied.

Failures of this kind differ basically from intergranular corrosion, which proceeds without regard to whether the metal is stressed.

Corrosion

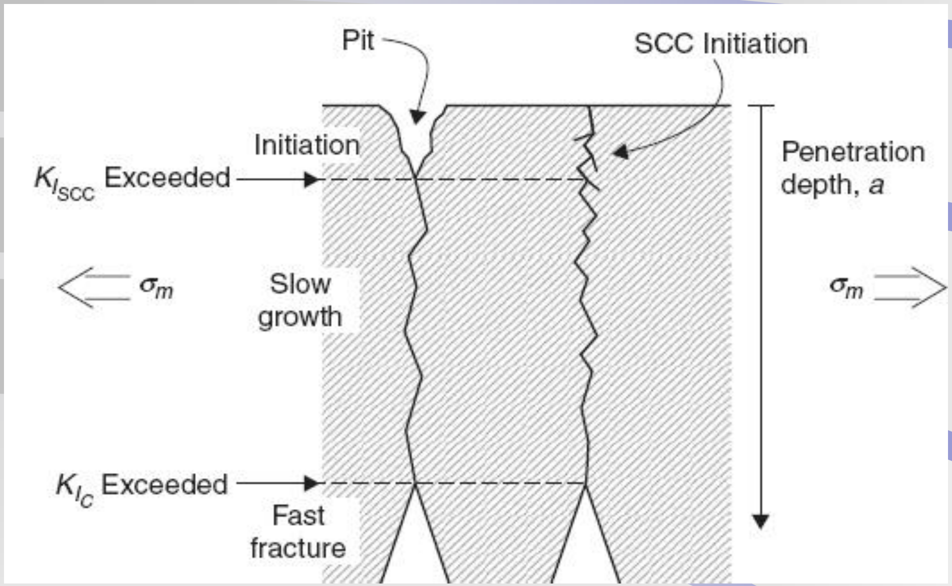
Cracking - Stress corrosion cracking (SCC)

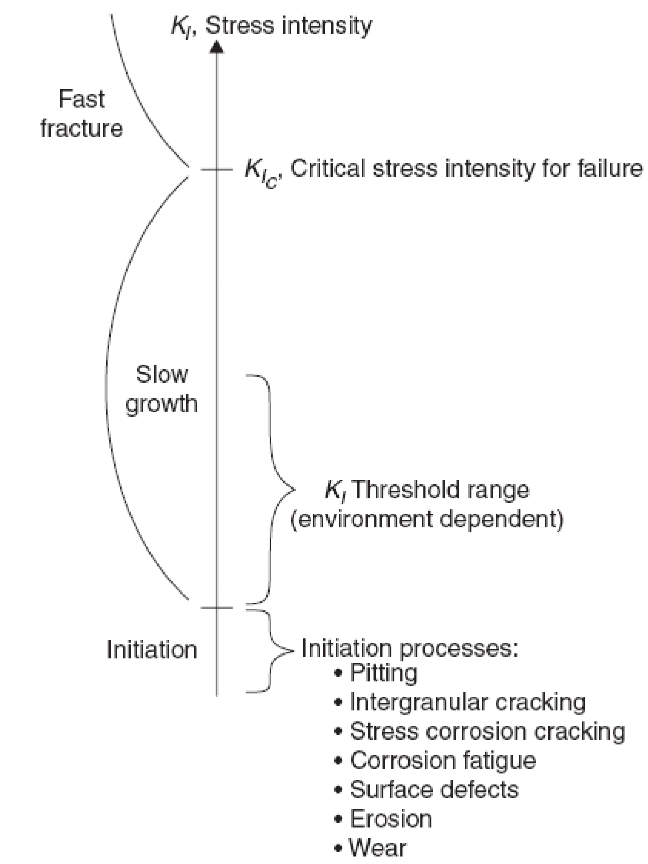
Almost all structural metals (e.g., carbon - and low - alloy steels, brass, stainless steels, Duralumin, magnesium alloys, titanium alloys, nickel alloys, and many others) are subject to stress - corrosion cracking in some environments.

Fortunately, either the damaging environments are often restricted to a few chemical species, or the necessary stresses are sufficiently high to limit failures of this kind in engineering practice.

Corrosion

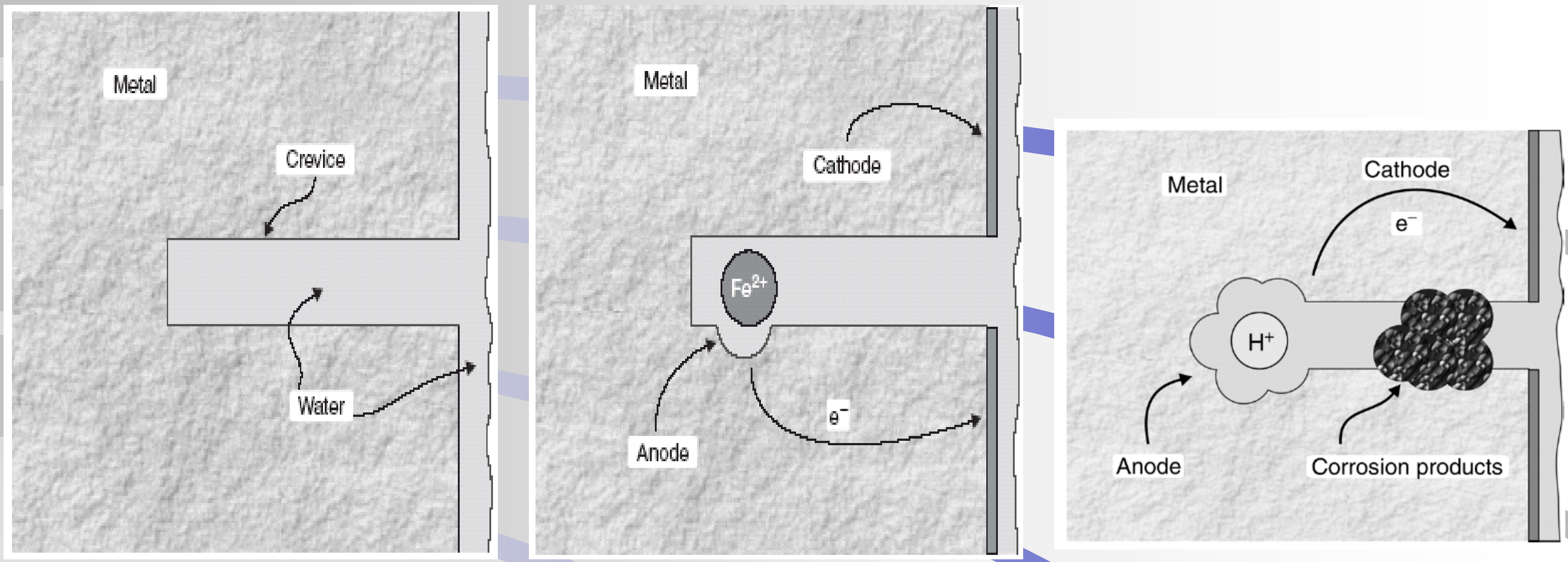
Cracking - Stress corrosion cracking (SCC)





Corrosion

Crevice Corrosion



Corrosion

Hydrogen Damage

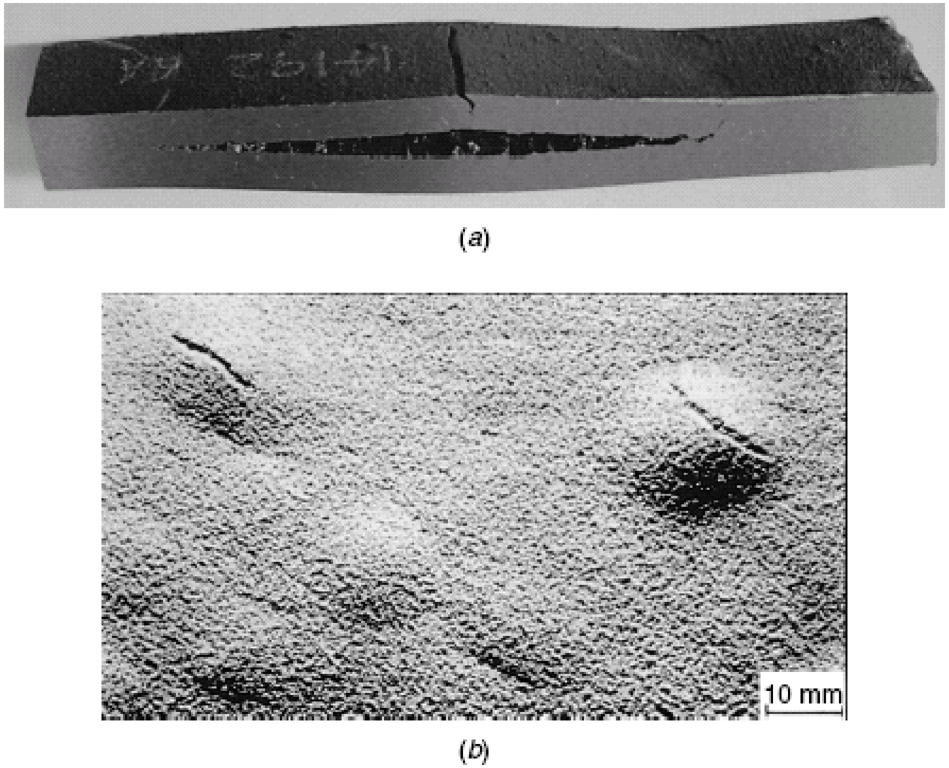
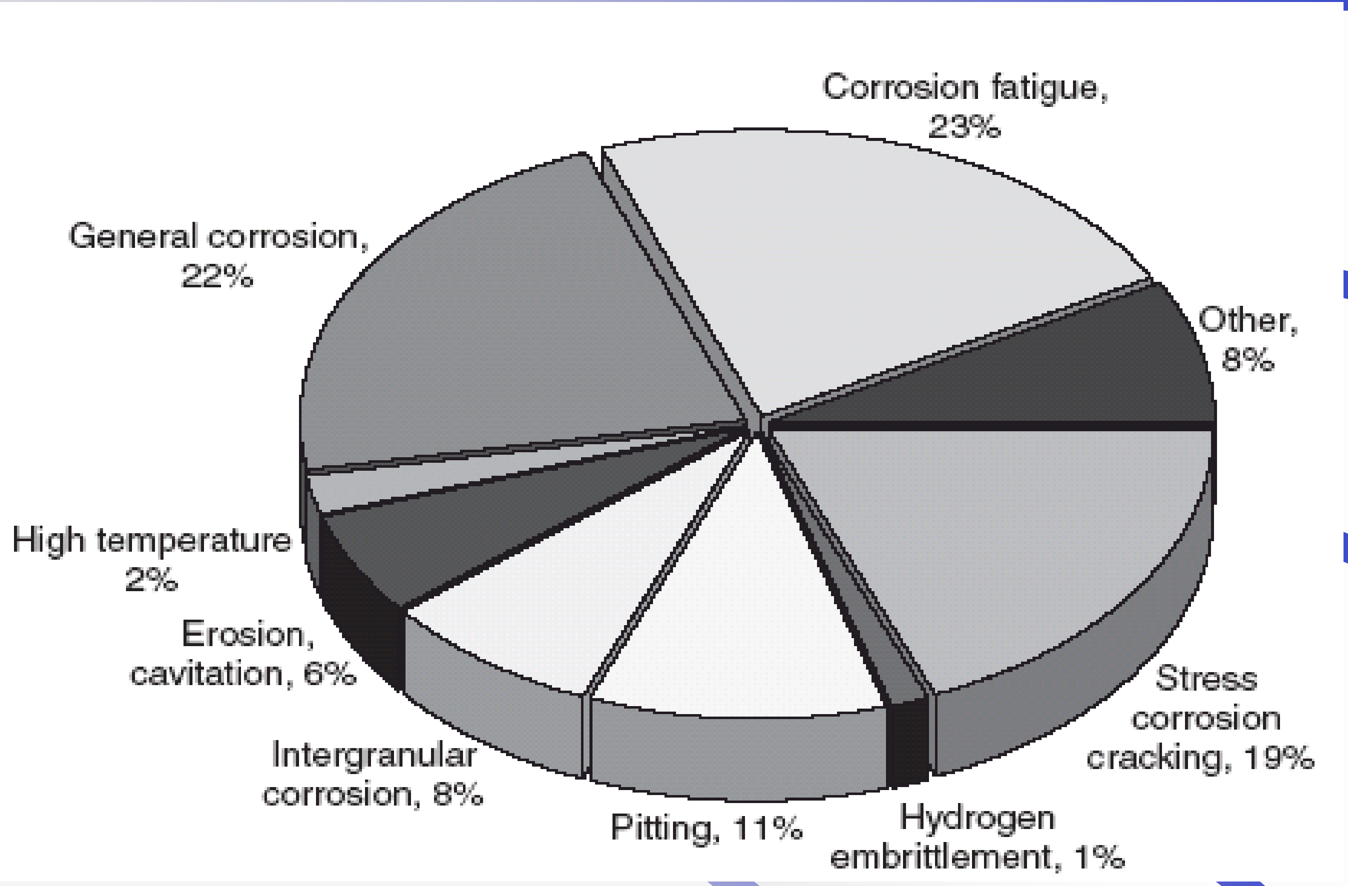


Fig. 2.29 (*a*) Hydrogen induced cracking with midwall cracks running parallel to the pipeline wall. (*b*) Surface blisters may also contain cracks. (Courtesy of MACAW's Pipeline Defects, published by Yellow Pencil Marketing Co.)

Corrosion

Failure Statistics in USA



Corrosion

Corrosion Rate and Classification of Metals

- mm/y – millimeters penetration per year
- gmd – grams per square meter per day
- ipy – inches penetration per year
- mpy – mils penetration per year (1000 mil = 1 inch)
- mdd – milligrams per square decimeter per day

Corrosion

Corrosion Rate and Classification of Metals

- Mils per year (mpy) = 534W/DAT

- mm/y =87.6W/DAT

  – W = weight loss in mg
  – D = density of specimen material in g/cm^3
  – A = area in cm^2
  – T= exposure time in hours

Corrosion

Classification of metallic materials according to their rate of uniform attack

A. <0.005 ipy (<0.15 mm/y) – Metals in this category have good corrosion resistance and can be used for critical parts

B. 0.005 to 0.05 ipy (0.15 mm/y to 1.5 mm/y) – Metals in this group are satisfactory if a higher rate of corrosion can be tolerated

C. >0.05 ipy (>1.5 mm/y) – Usually not satisfactory

Corrosion

Variables that affect the corrosion rate:

- Fluid velocity: usually corrosion rate↑ as velocity ↑
- Temperature: most chemical reaction rates ↑ as T ↑ hence so do most corrosion rates.
- Composition: increasing concentration of corrosive species (e.g.. H+ ions) usually increases corrosion rate (*except in passivation)*.
- Microstructure: cold-worked regions of a metal are more susceptible to corrosion than the annealed regions.
- Alloying: Alloys tend to have higher corrosion rates than their pure metals (*except when passive films form - stainless steels)*.

Corrosion

Some Corrosion Failure Examples

Aloha Incident

1988 - 19-year old Boeing 737 operated by Aloha Airlines lost a major portion of the upper fuselage in full flight at 24000 ft

Corrosion

Aloha Incident

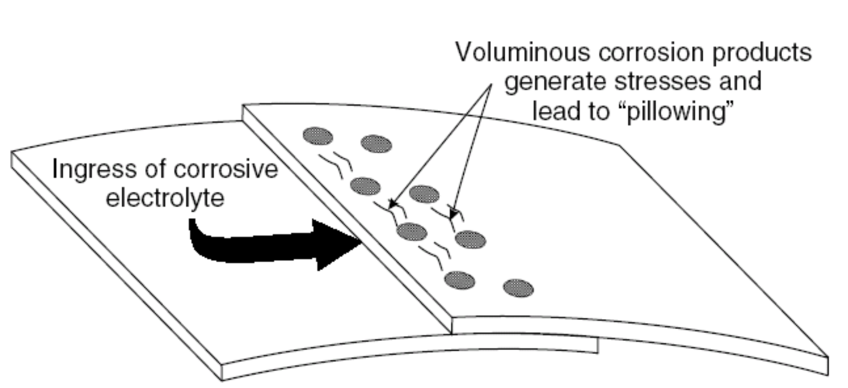
The prevalent corrosion product identified in corroded fuselage joints is hydrated alumina, $Al(OH)_3$, with a particularly high volume expansion relative to aluminum.

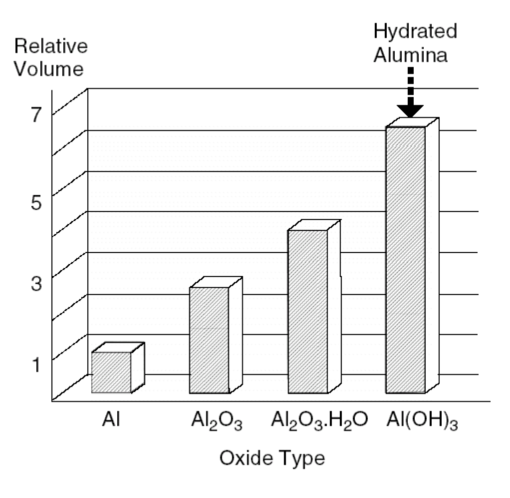
This build-up of voluminous corrosion products can lead to an undesirable increase in stress levels near critical fastener holes and subsequent fracture due to the high tensile stresses resulting from the “pillowing”.

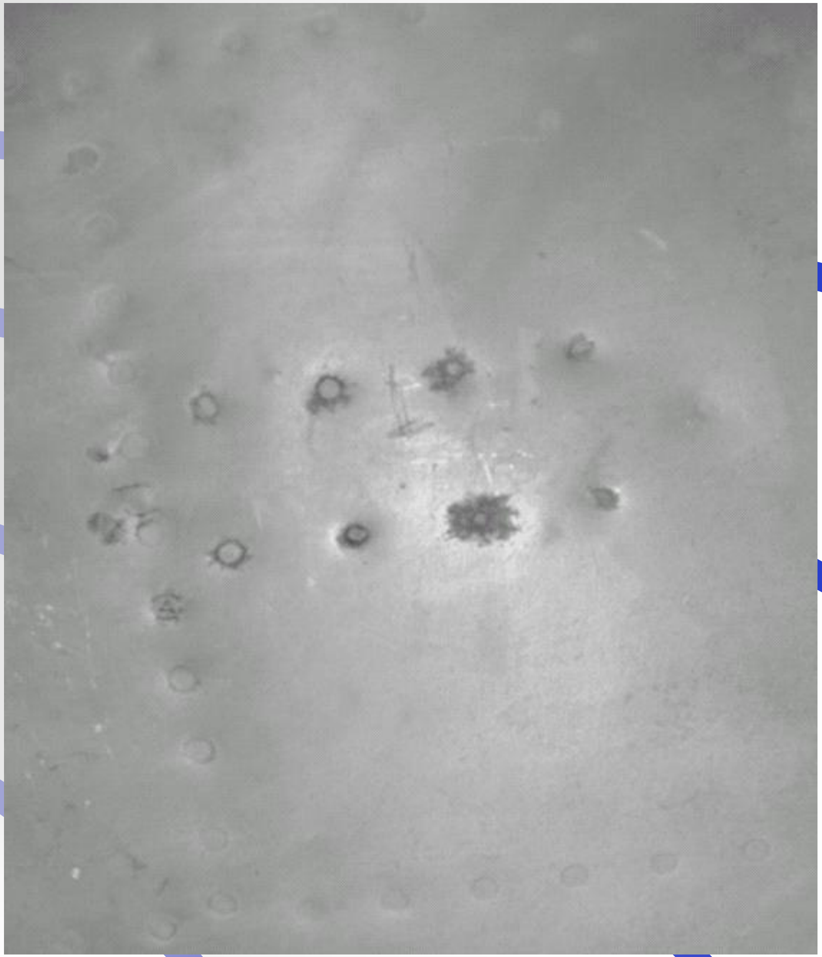
Corrosion

Aloha Incident

The "pillowing" process - the faying surfaces are forced apart.







Corrosion

Carlsbad Pipeline Explosion

At 5:26 a.m. on August 19, 2000, a 75-cm diameter natural gas transmission pipeline operated by El Paso Natural Gas Company (EPNG) ruptured adjacent to the Pecos River near Carlsbad, New Mexico.

The released gas ignited and burned for 55 min. Twelve persons who were camping under a concrete-decked steel bridge that supported the pipeline across the river were killed and their three vehicles destroyed. Two nearby steel suspension bridges for gas pipelines crossing the river were extensively damaged with $1 million in property and other damages or losses .

Corrosion

Carlsbad Pipeline Explosion

- A 15-m section of the pipe was ejected from the crater in three pieces measuring ~1, 6, and 8 m in length. The largest piece was found 90 m northwest of the crater in the direction of the suspension bridges.

- Investigators visually examined the pipeline that remained in the crater as well as the three ejected pieces.
- All three ejected pieces showed evidence of internal corrosion damage, but one of the pieces showed significantly more corrosion damage than the other two.
- Pits were visible on the inside surface of this piece, and at various locations, the pipe wall evidenced significant thinning.
- **Significant reduction in pipe wall thickness due to severe internal corrosion.**

Corrosion

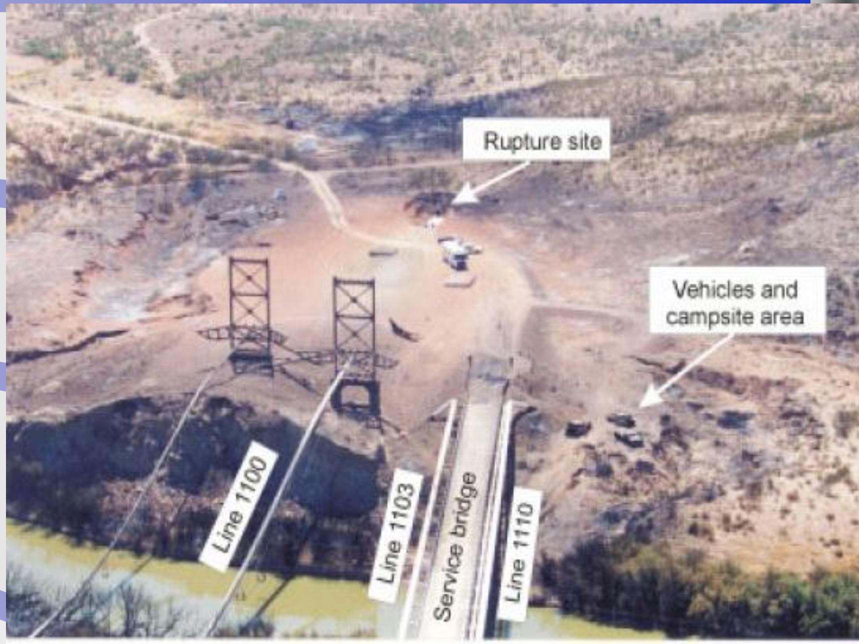
Carlsbad Pipeline Explosion

- Interconnecting pits were observed on the inside of the pipe in the ruptured area.
- Typically, these pits showed the striations and undercutting features that are often associated with microbial corrosion.
- A pit profile showed that chloride concentration in the pits increased steadily from top to bottom.
- Increased chloride concentration can result from certain types of microbial activity.
- All four types of microbes (sulfate reducing, acid-producing, general aerobic, and anaerobic) were observed in samples collected from two pit areas in the piece of line where internal corrosion was discovered after the accident.

Corrosion

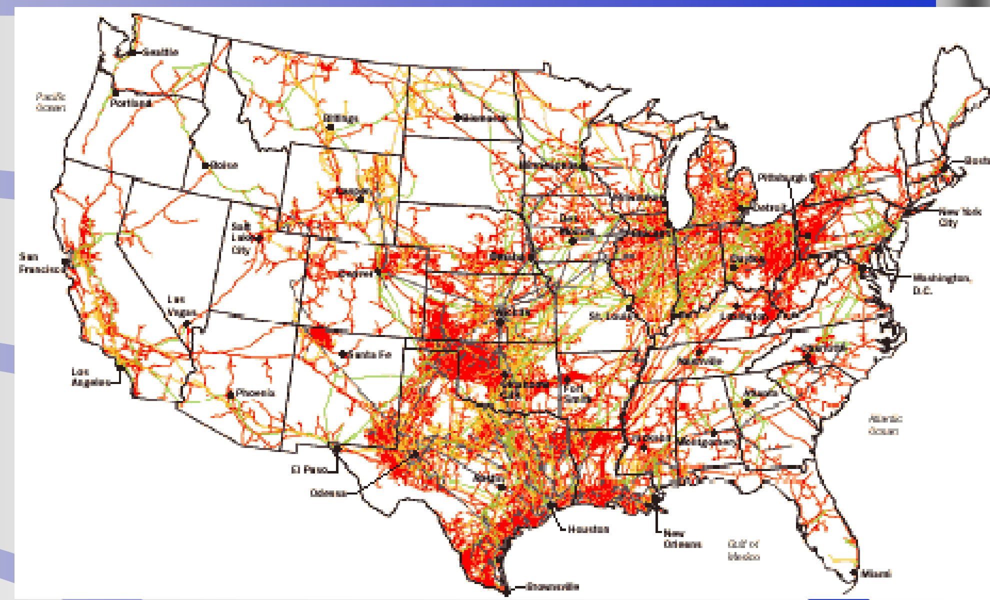
Carlsbad Pipeline Explosion

Figure 5. Post-rupture fire. At lower left of fireball can be seen the 85-foot-tall support structures for the pipeline suspension bridges.



Corrosion

Carlsbad Pipeline Explosion



Corrosion at the rupture site was likely caused by a combination within the pipe line of microbes and such contaminants as moisture, chlorides, oxygen, carbon dioxide, and hydrogen sulfide.

Corrosion

Prevention of Corrosion

- Separate reactants with coatings
  - ✓ Paint, grease, oils, and polymers
  - ✓ Coat with less active metals (tin cans, noble metals)
- Exclude Water
- Exclude Oxygen
- Self Protective Coatings

Aluminum → Al_2O_3

Magnetite → Fe_3O_4

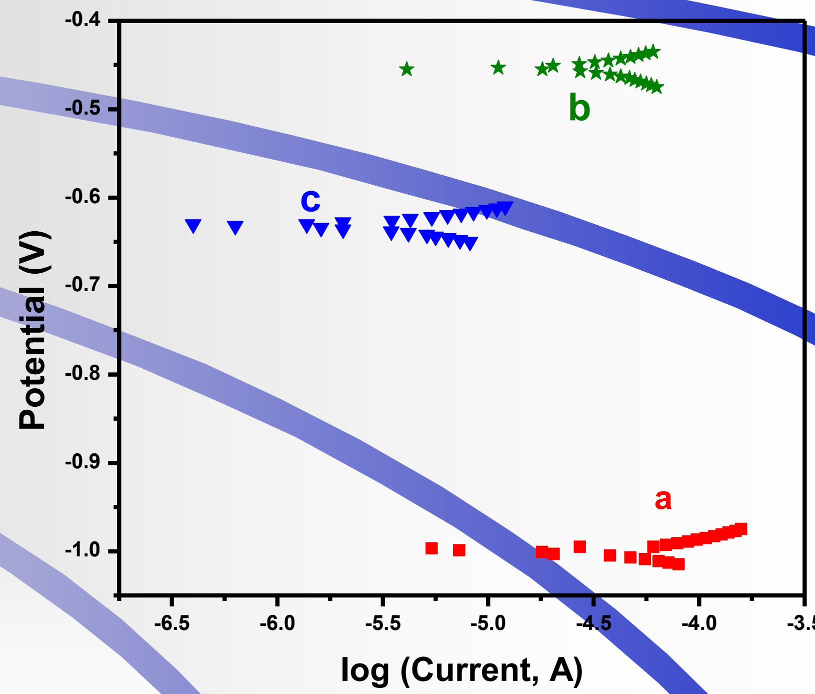
Stainless Steel → Cr oxides

Corrosion

Coating Material	Application
Zinc-Nickel Alloy	Salt Corrosion
Copper-Nickel Alloy	Microbial Induced Corrosion
Nickel-Molybdenum Alloy	High Temperature Corrosion

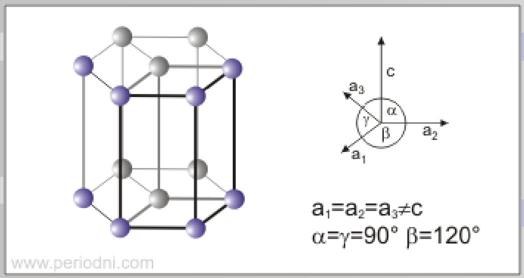
Corrosion

- Zn-Ni
  - Strong corrosion resistance when coated onto steel
  - High salt resistance
    - Microcracking

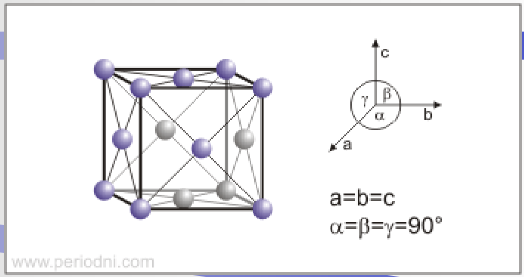


a: Zn only
b: Ni only
c: Zn-Ni ɣ phase alloy

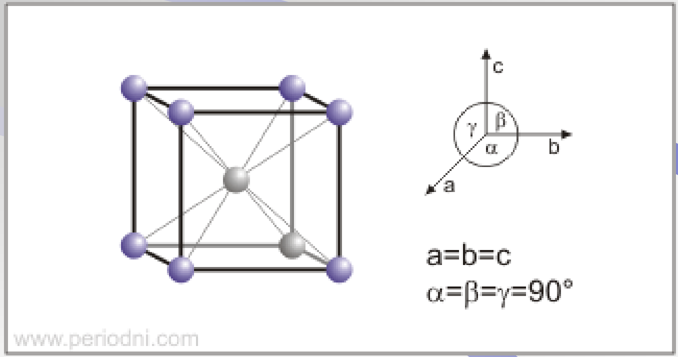
Corrosion



Zinc: hexagonal



Nickel: Face Centered Cubic



Zn/Ni γ Phase Alloy: Body Centered Cubic

η- 1% Ni

α– 30% Ni

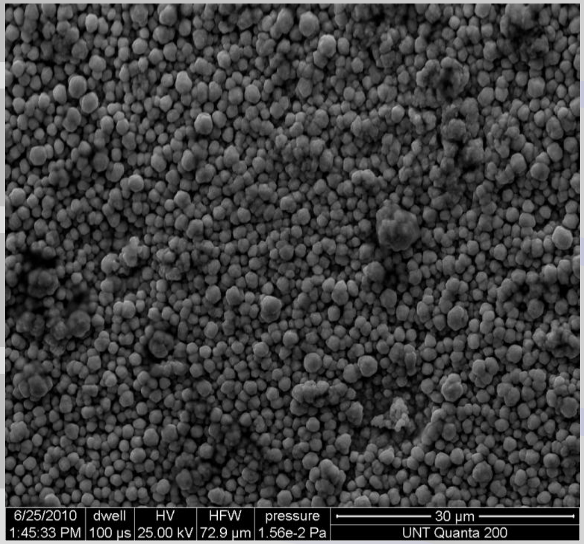
β– 30% Ni

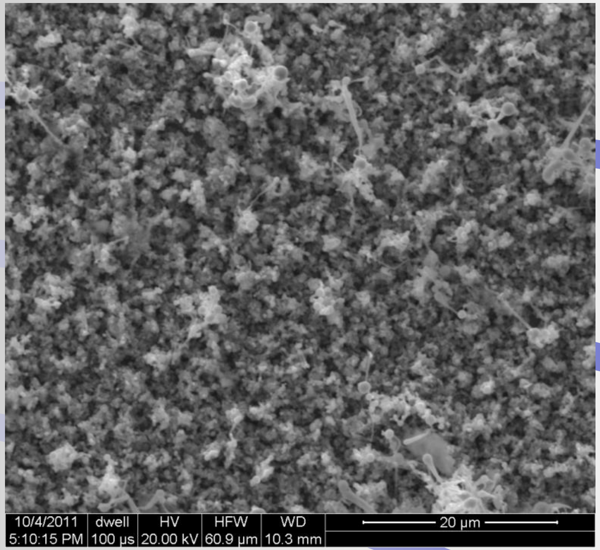
δ- Ni_3Zn_{22}

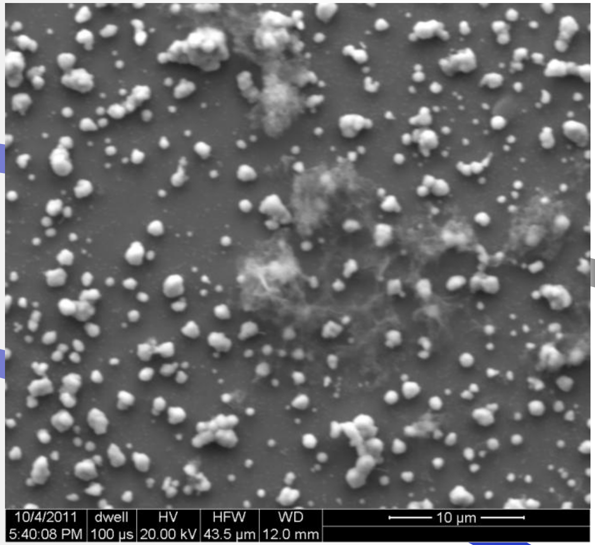
γ- Ni_5Zn_{21}

Corrosion

Zn-Ni Phase Alloys







Corrosion

- Cu-Ni
  - Microbial corrosion resistance

Copper ions resist the growth of bacteria, viruses, fungi, algae and other microbes on the surface of the coating by reducing adhesion.

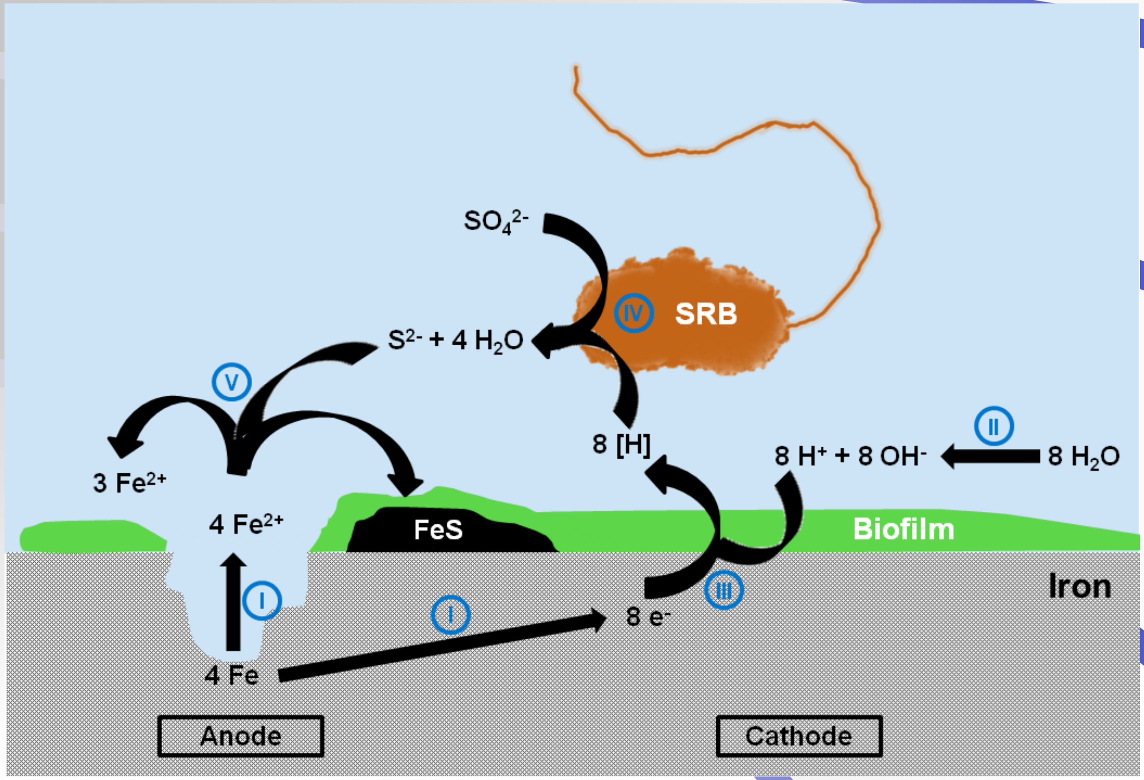
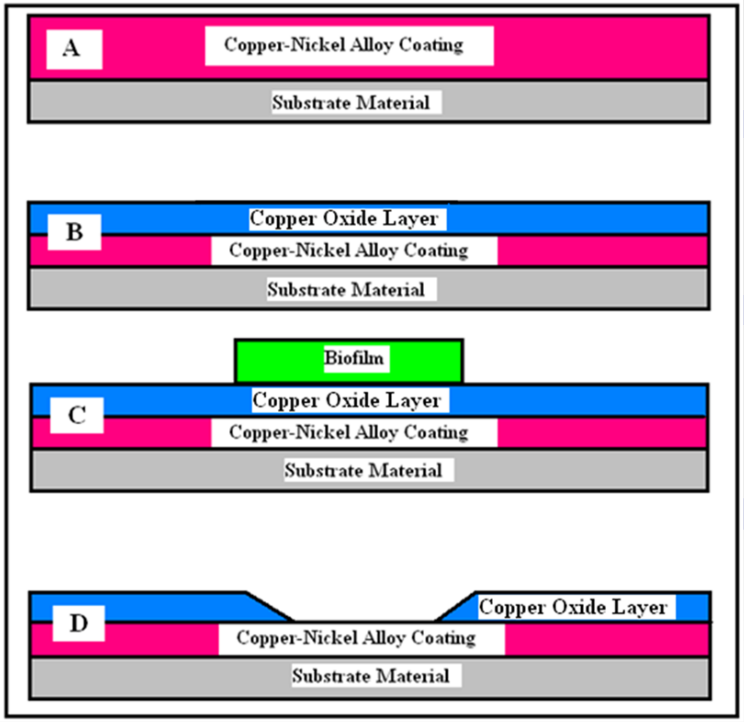


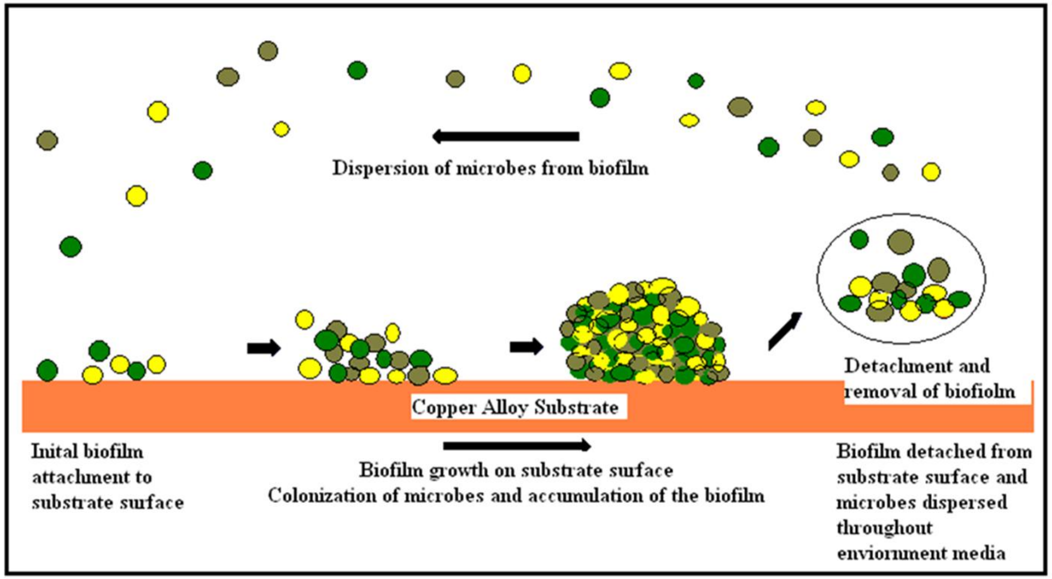
Figure 2.8: Microbial induced corrosion of iron.

Corrosion

- Cu-Ni
  - Microbial corrosion resistance

Copper ions resist the growth of bacteria, viruses, fungi, algae and other microbes on the surface of the coating by reducing adhesion.





Corrosion

- Cu-Ni

Particle Sizes of the 70-30 Cu/Ni Coatings Calculated from the Scherrer Equation using X-ray Diffraction.

Coatings	Particle size (nm)
Cu-Ni (70-30)	62 ± 6
70-30 Cu-Ni 0.05% MMT	16 ± 5
70-30 Cu-Ni 0.1% MMT	15 ± 4
70-30 Cu-Ni 0.2% MMT	15 ± 5

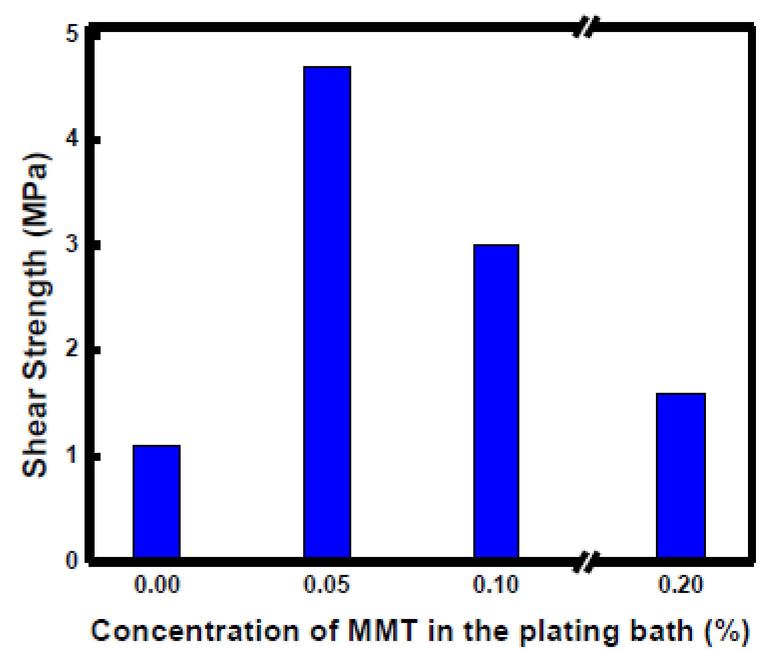
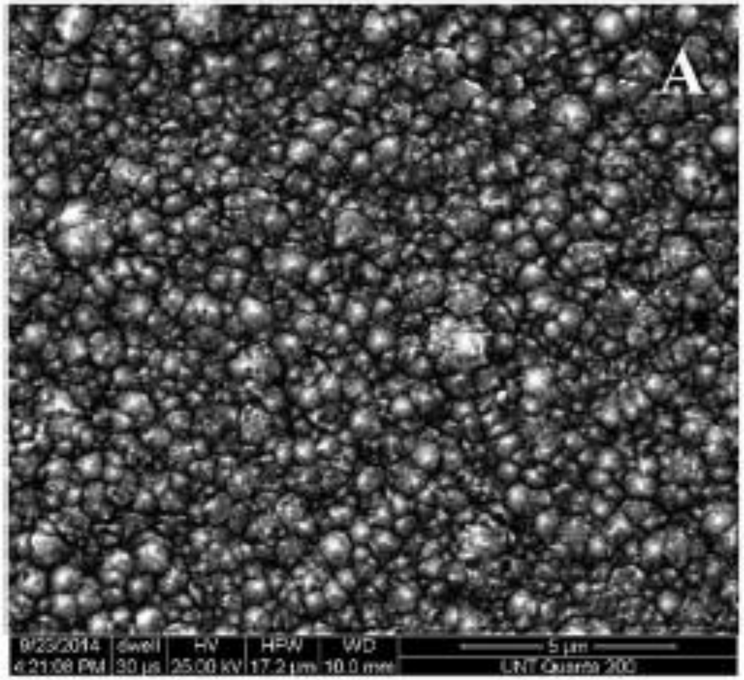


Fig. 5. The sheer adhesion strength of different coating layers versus the percentage of MMT in the plating solution.

Corrosion

- Cu-Ni



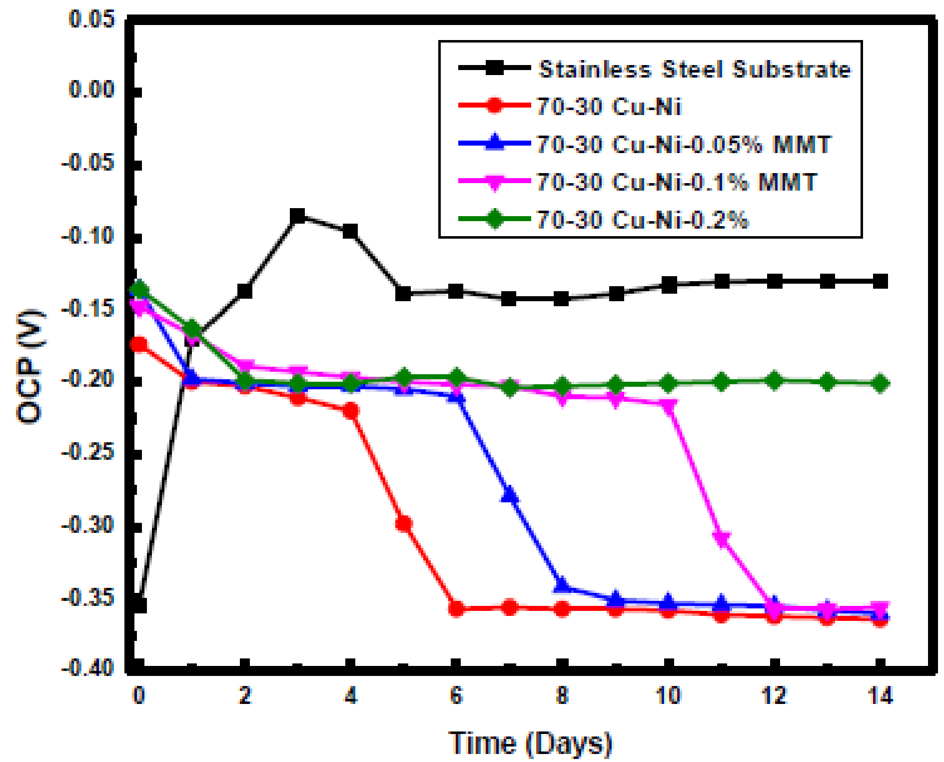


Fig. 6. Plot of the immersion test for the 70-30 Cu–Ni coatings with and without MMT

Corrosion

- Ni-Mo
  - Harsh environments corrosion protection
  - Sibor

Nickel alloys containing 9–16% Mo are highly resistant to all forms of corrosion in seawater.

Deposition of Ni-Mo alloys from aqueous solutions containing only Ni^{2+} and MoO_4^{2-} is not possible without using the proper complexing agent due to the formation of the multimolecular heteropolymolybdate $(NiMo_6O_{24}H_6^{4-})_n$ complexes which are very difficult to reduce.

The electrodeposition of Ni-Mo has been tried from electrolytes of different complexing agents e.g. acetate, tartarate, pyrophosphate, citrate and ammonia. We added MMT and borate which seemed to be the most promising with respect to quality, adhesion and mechanical properties.

Corrosion

- Ni-Mo

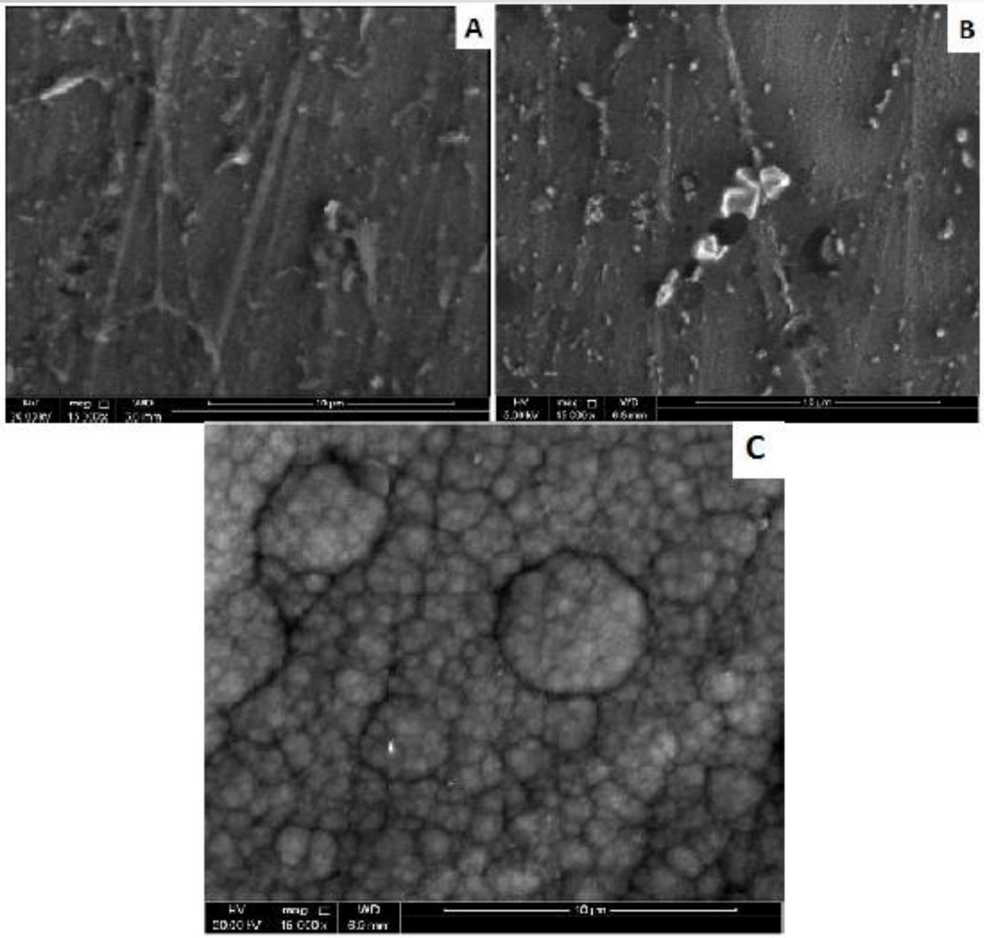


Figure 7. SEM micrographs of: A) pure Ni, B) Ni:Mo 10:1 and C) Ni:Mo 5:1.

Corrosion

- Ni-Mo

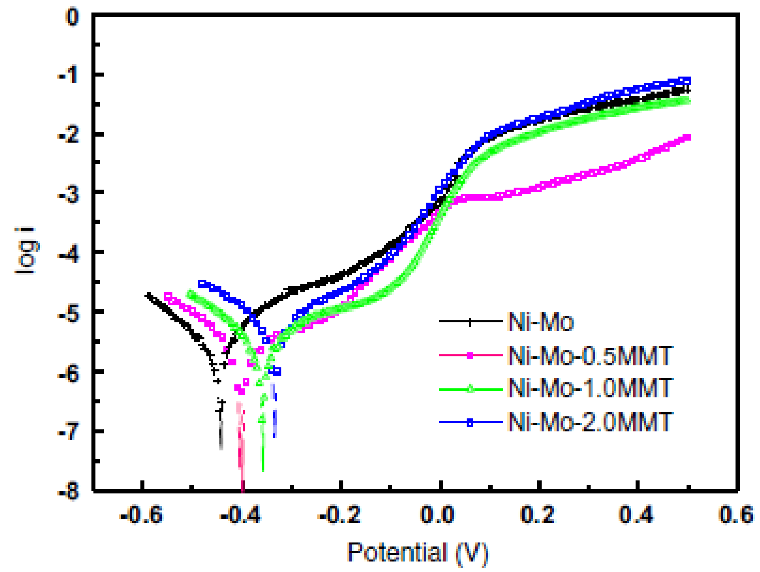
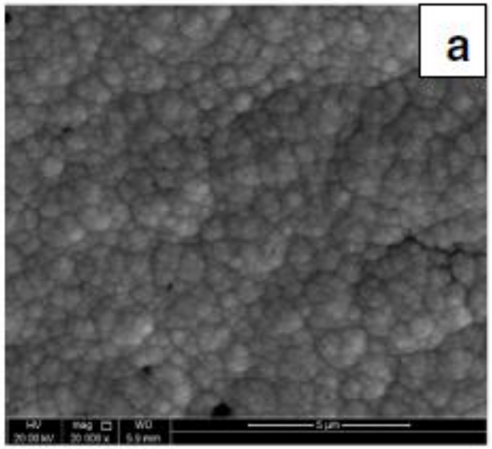
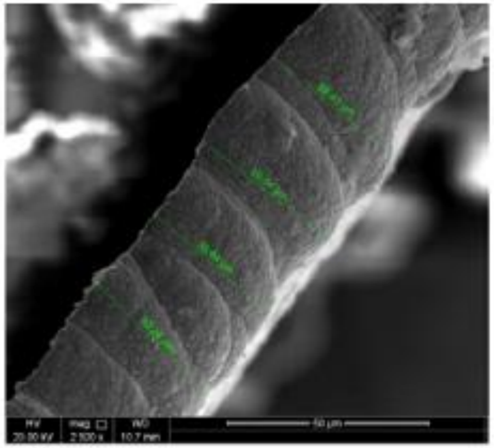


Fig. 7. Potentiodynamic polarization curves of Ni–Mo and different Ni–Mo–MMT nano-composite coatings after 24 h immersion in 3.5% NaCl solution.





Class Assignment

- Final – Dec 9th   8-10 am