WELCOME

Corrosion Issues in Power Plants

Ashwini K Sinha
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Training Program (Virtual) Organized by Excellence Enhancement Centre, Delhi
6th Aug. 2021

Corrosion and Water Management Consultants
"Improving Plant Performance, Availability & Reliability by Chemical Interventions"

PRESENTATION OUTLINE

About Myself

Name: Ashwini K. Sinha (Retired as Addl. GM (NETRA), NTPC in July 2012)

Qualifications: M.Sc (Electrochemistry)
P.G. Dip. In Corrosion Science & Technology, Univ. of Ferrara (Italy)

Affiliations: Member NACE International, Life Fellow Member SAEST, IAAPC
Core Member of CII-Avantha Corrosion Management Committee

Experience: 44 years experience in Corrosion Analysis, Monitoring and Control in Power Plants. 5 Years BHEL (R&D), Hyderabad. 30 years with NTPC (R&D) (now “NTPC Energy Technology Research Alliance **(NETRA). Free Lance Consultant in the areas of Corrosion & Water Management (since 2012).**

Specialization: Corrosion Assessment, Failure Investigations, Corrosion Monitoring, Corrosion Audit, Design of Cathodic Protection Systems for Underground Pipelines; Condenser Water Boxes; RCC Structures such as Cooling Towers; **etc, Selection of Anticorrosive Coatings, Development & Implementation of Cooling Water Treatments, Waste Water Recycling & Treatment, Chemical Cleaning of** Condensers; Boilers; Pipelines; PVC Film Type Fill Packs of Cooling Towers**; etc, Material Selection, Water Management, etc.** Research Studies on **Extraction of Moisture from Flue Gases, Ash Mineralization by Flue Gas, etc.**

About Myself

Major Association - International,

1. Plants under O&M by NOMAC –

- USC Plant (Coal & Gas Based, Seawater Cooled), Dubai, and Umm Al Quwain Independent Water Treatment Plant, UAE
- CCPP (Coastal, Air Cooled), Salalah, Sohar3 CCPP (Seawater Cooled), IBRI CCPP (Air Cooled) & PV; Barka IWPP Oman;
- Tanger Wind Farms (Coastal), Morocco,
- Boujdour PV, Layuoune PV, NOOR 1 CSP, NOOR 4 PV; Morocco,
- Vin Hao 6 PV (Coastal, Salt Pan), Vietnam,
- Egypt Energy PV; Benban Egypt for Solar Energy PV; Nile Energy PV; Egypt,
- Shuaibh IWPP (Seawater Cooled CCPP), Jeddah;
- DEWA CSP and PV Plants, Dubai; UAE
- Sardarya CCGT, (Snow area), Uzbekistan;
- Al Dur 2, IWPP (Seawater Cooled CCPP), Bahrain
- Bokpoort CSP, South Africa

2. Sembcorp IWPP (Seawater Cooled CCPP), Salalah, Oman
3. Failure of SS Tubes at Oman Food Products, Salalah, Oman
4. Condenser tubes and Boiler Tube Failures at CCPPs (3 No.), Iran

About Myself

Major Association - National

1. NTPC and NTPC Subsidiary Companies (almost all stations till 2012, Meja)
2. Adani Power- Mundra (Seawater), Tiroda, Kawai, Udupi (Seawater), etc
3. Sembcorp (Seawater), Nellore
4. Rajasthan RVUNL - Kalisindh, Dholpur CCPP, Kota Thermal, Chhabra (TPP & SC), Suratgarh
5. Mahagenco – Chandrapur STPS, Koradi (SC), Bhusawal
6. CLP Jhajjar (SC) and Paguthan CCPP
7. Haldia Energy Limited, Haldia, Dhariwal Infrastructure Ltd., Chandrapur
8. Vedanta Limited, CPP & IPP, Jharsuguda, TSPL Bhatinda and Balco, Korba
9. GSECL Sikka TPS (Seawater), Jamnagar
10. Essar Sallaya Project (Seawater), Jamnagar
11. NABHA Power, Rajpura, Punjab
12. IOCL Refinery - Dibrugarh, Guwahati, Panipat
13. Lanco Kondapally, Gurugram, Udupi (now with Adani Power)
14. HMEL Refinery, Bhatinda, Punjab
15. Reliance Power - Rosa Power, Shajahanpur, Sasan UMPP
16. Jindal Power, Raigarh; JSPL, Odisha
17. Neyveli Lignite Corp. and NTPL, Neyveli, TN
18. Hindalco – Mahan, Sambalpur
19. Pipavav CCPP (Seawater), Gujarat
20. Tuticorin TPP (Seawater), Panipat Thermal Power Plant

CWMC

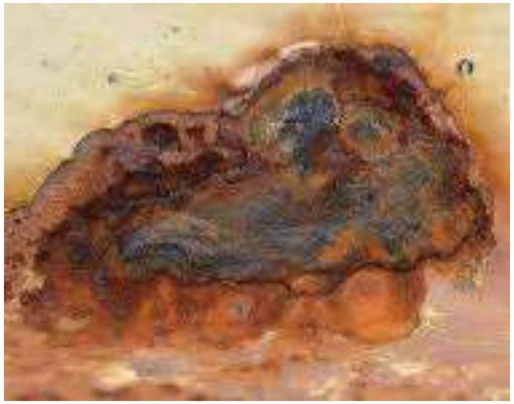
Presentation Outline

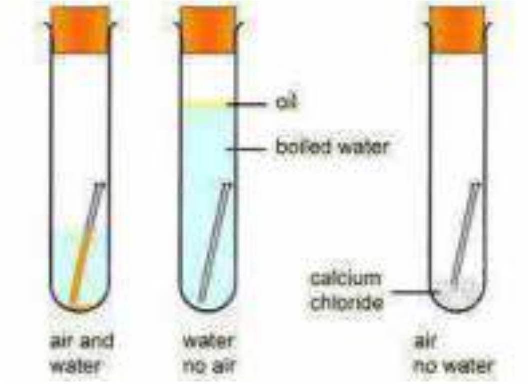
- INTRODUCTION – CORROSION
- COST OF CORROSION
- CORROSION BASICS AND FORMS OF CORROSION
- CORROSION ASSESSMENT AND MONITORING
- CORROSION CONTROL BASICS
- CORROSION ISSUES OF POWER PLANTS
- CORROSION ISSUES OF POWER PLANTS
- ATMOSPHERIC CORROSION
- CORROSION IN RENEWABLES
- CORROSION UNDER INSULATION
- PIPELINE CORROSION
- BOILER SIDE CORROSION
- FLOW ACCELERATED CORROSION
- ACID DEW POINT CORROSION
- TURBINE CORROSION
- COOLING WATER CORROSION RELATED ISSUES
- RCC CORROSION

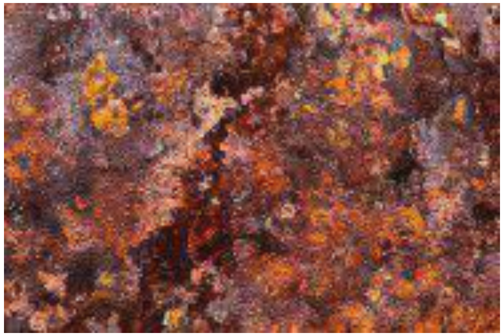
INTRODUCTION – CORROSION

Corrosion – Some Examples

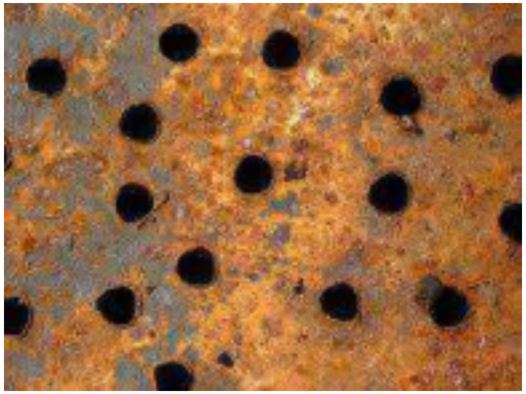
Corrosion – Some Examples







Corrosion – Some Examples



Corrosion – Some Examples

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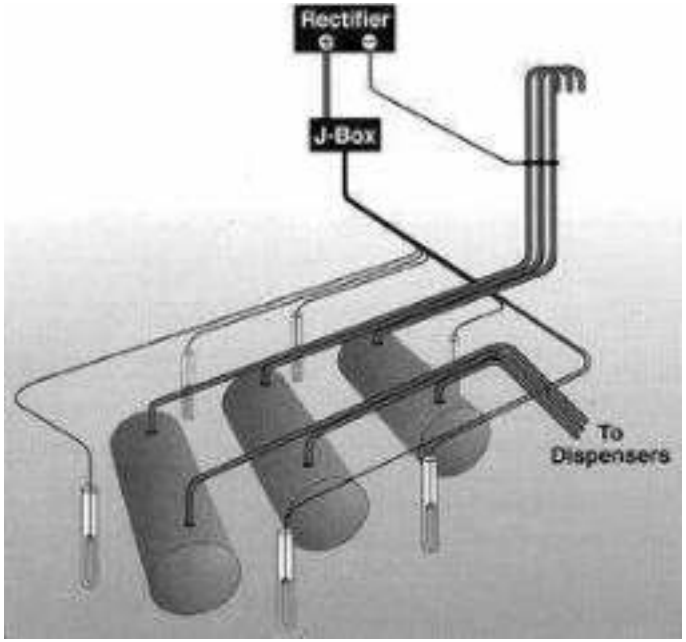

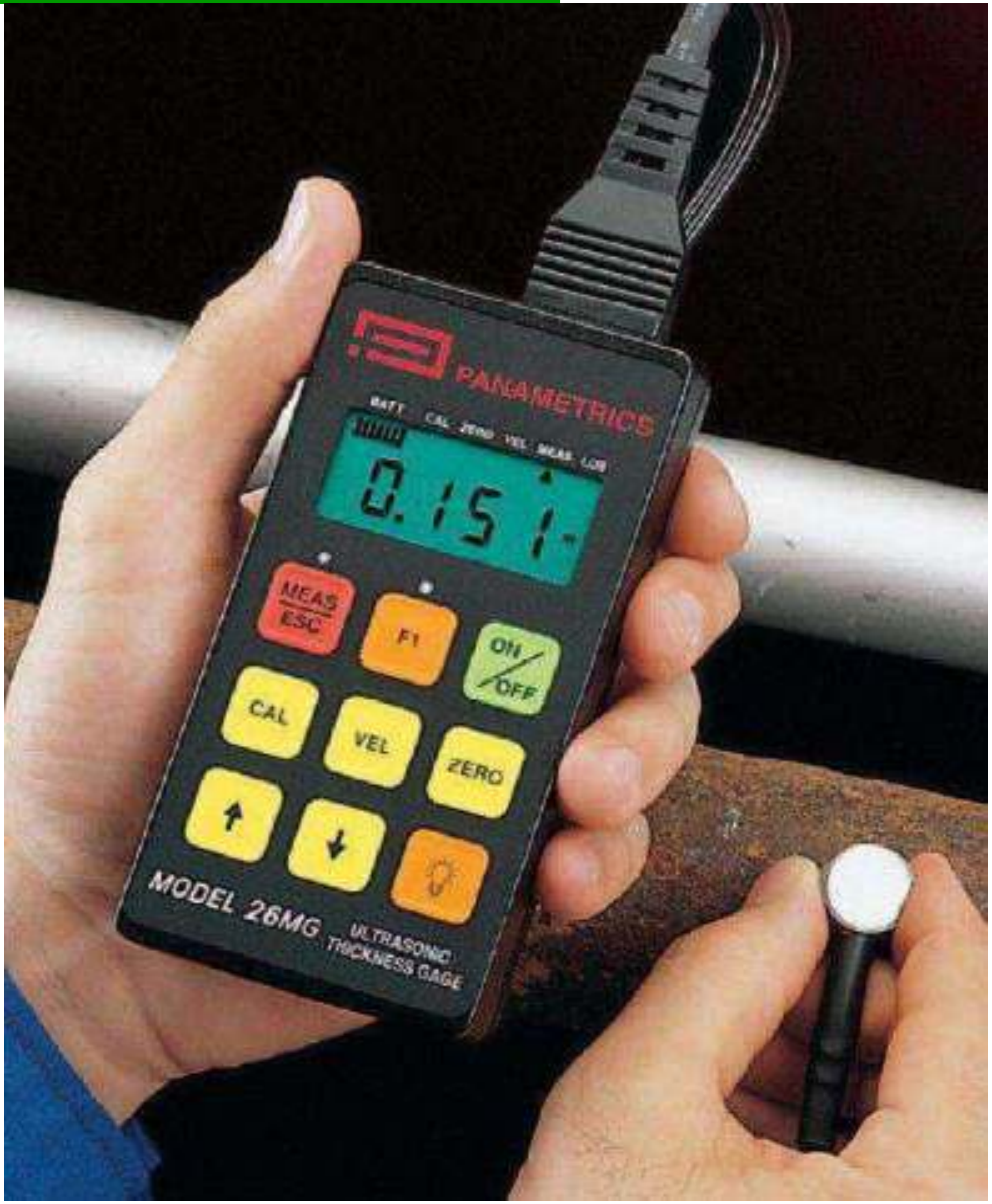

Corrosion – Some Examples

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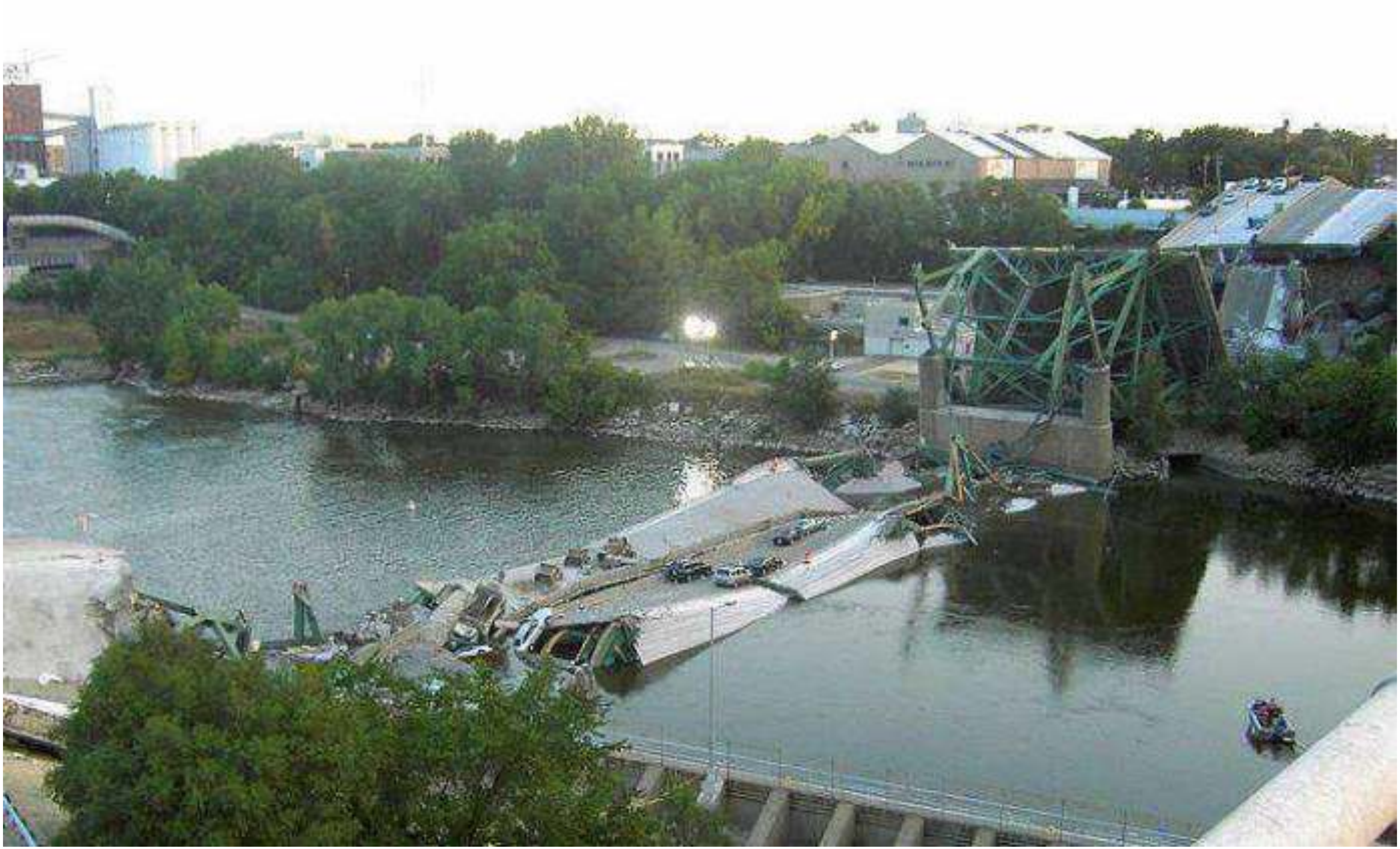

Corrosion – Some Examples

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Corrosion – Some Examples

Piping Rupture Caused by Flow Accelerated Corrosion (FAC):

A piping rupture likely caused by flow accelerated corrosion and/or cavitation-erosion occurred at Mihama-3 at 3:28pm on **August 9, 2004**, **killing four and injuring seven. One of the injured men later died, bringing the total to five fatalities**. The rupture was in the condensate system, upstream of the feedwater pumps, similar to the Surry and Loviisa locations. The AP reports that sections of the failed line were examined in 1996, recommended for additional inspections in 2003, and scheduled for inspection August 14 (five days after the rupture). This story was published Wednesday, August 11th, 2004 By James Brooke, New York Times News Service

On Monday, four days before the scheduled shutdown, superheated steam blew a 2-foot-wide hole in the pipe, fatally scalding four workmen and injuring five others seriously. The steam that escaped had not been in contact with the nuclear reactor, and no nuclear contamination has been reported.

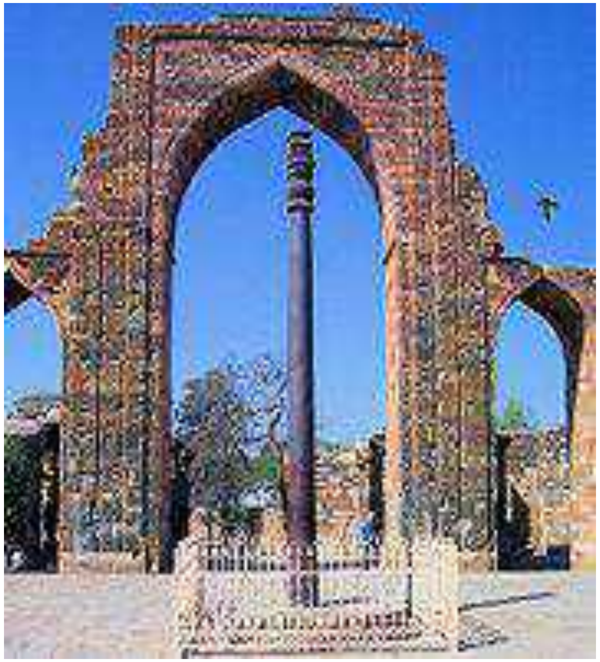
The rupture was 560 mm in size. The pipe wall at the rupture location had thinned from 10mm (394 mils) to 1.5mm.

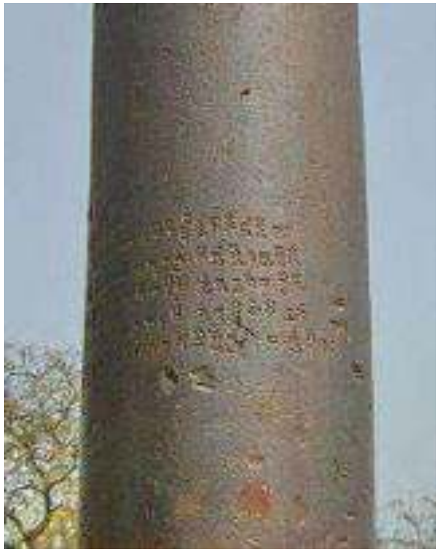
Corrosion – Some Examples

Iron Pillar, Delhi

The **Iron Pillar** located in Delhi, India, is a 7 m (23 ft) column in the Qutub complex, notable for the rust-resistant composition of the metals used in its construction for more than 1600 years.

The pillar has attracted the attention of archaeologists and metallurgists and has been called "a testament to the skill of ancient Indian blacksmiths" because of its high resistance to corrosion. The corrosion resistance results from an even layer of crystalline iron hydrogen phosphate forming on the high phosphorus content iron, which serves to protect it from the effects of the local Delhi climate





Effects of Corrosion in Power Plants

Perhaps most dangerous of all is corrosion that occurs in major industrial plants, such as electrical power plants or chemical processing plants. Plant shutdowns can and do occur as a result of corrosion. This is just one of its many direct and indirect consequences. Some consequences are economic, and cause the following:

- Replacement of corroded equipment
- Overdesign to allow for corrosion
- Preventive maintenance, for example, painting
- Shutdown of equipment due to corrosion failure
- Contamination of a product
- Loss of efficiency—such as when overdesign and corrosion products decrease the heat-transfer rate in heat exchangers

Effects of Corrosion in Power Plants

- Loss of valuable product, for example, from a container that has corroded through
- Inability to use otherwise desirable materials
- Damage of equipment adjacent to that in which corrosion failure occurs

Still other consequences are social. These can involve the following issues:

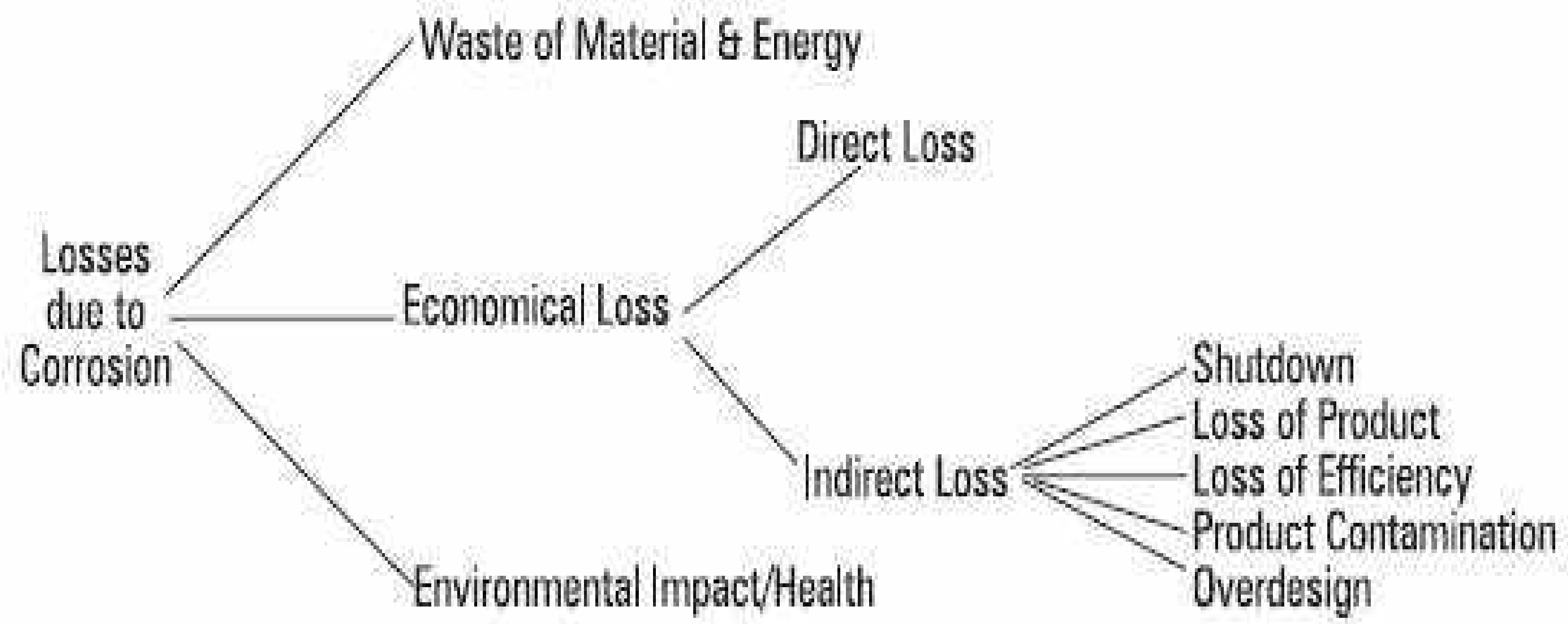
- Safety, for example, sudden failure can cause fire, explosion, release of toxic product, and construction collapse
- Health, for example, pollution due to escaping product from corroded equipment or due to a corrosion product itself
- Depletion of natural resources, including metals and the fuels used to manufacture them
- Appearance as when corroded material is unpleasing to the eye

Effects of Corrosion in Power Plants

- Reduced life of components
- Reduced efficiency of equipment
- Reduced availability of plant equipment
- Reduced reliability of equipment & structures
- Endanger to life of people around
- Enhanced maintenance
- Contaminations in process fluids
- Secondary failures in other associated equipment
- Higher costs of generation

Losses Due to Corrosion

Losses due to Corrosion



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[4] Uhlig, H.H. and R.W. Revie, Corrosion and Corrosion Control. 3rd ed. 1985, New York: John Wiley & Sons.

Losses Due to Corrosion

Low-temperature corrosion problems that occur in the following power plant systems and components:

- Raw water and pretreatment systems
- Cooling water systems,
- Cooling towers,
- Service water systems,
- Auxiliary heat exchangers,
- Fire protection systems,
- Condensers,
- Feedwater piping systems,
- Low-pressure feedwater heaters,
- Deaerators,
- Low-pressure steam turbines,
- Electric generators,
- Air heater and ducts,
- Flue gas desulfurization systems
- Flue gas ducts,
- Stacks.

Introduction

Power Plants are critical for the operation of Industries and for general population for comfortable living. Power plants can be conventional, i.e. Coal, gas based, etc or based on renewable such as Wind, Solar PV, Solar CSP, or hybrids. As a general rule, the power plants are designed for a minimum of 25 years life.

Experience has shown that power plants much attention is not paid on controlling the **damages likely to occur on account of corrosion**. The damages include **corrosion induced damages** on plant equipment due to **processes** involved such as Boilers, Turbines, Balance-of plant, etc. These are generally taken care of by selecting suitable materials and/or suitable treatments/operational procedures.

Other major area of concern is the **Environmentally Induced Corrosion** Damages to different plant components. This issue becomes all the more critical if the plant is located close to some **coastal areas or even off-shore areas**. On tonnage basis **maximum loss is caused by Atmospheric Corrosion**.

Introduction

Generally, to control Atmospheric Corrosion, assessment of Corrosive Conditions of the area are estimated based on environmental parameters.

ISO 9223, ISO 9224, ISO 9226, ISO 12944, etc are employed by many designers to **assess corrosion category** of the area but many times the assessment are far away from the actual corrosive conditions in the area. In many instances, mixed environments are involved where proper assessment is missed and corrosion damages are experienced.

It has been observed that many designers have not taken into account the possible Corrosion Induced damages to various structures, pipelines, tanks, etc exposed to atmosphere. In many cases there is no detailed studies are conducted to assess the corrosiveness of the area except probably distinction between **Coastal and Non-Coastal plants**.

Even Solar PV or Solar CSP or Wind farms are also observed to be affected as they are spread over large areas and are generally close to coastal environments.

COST OF CORROSION

COSTS OF CORROSION

A Supplement to

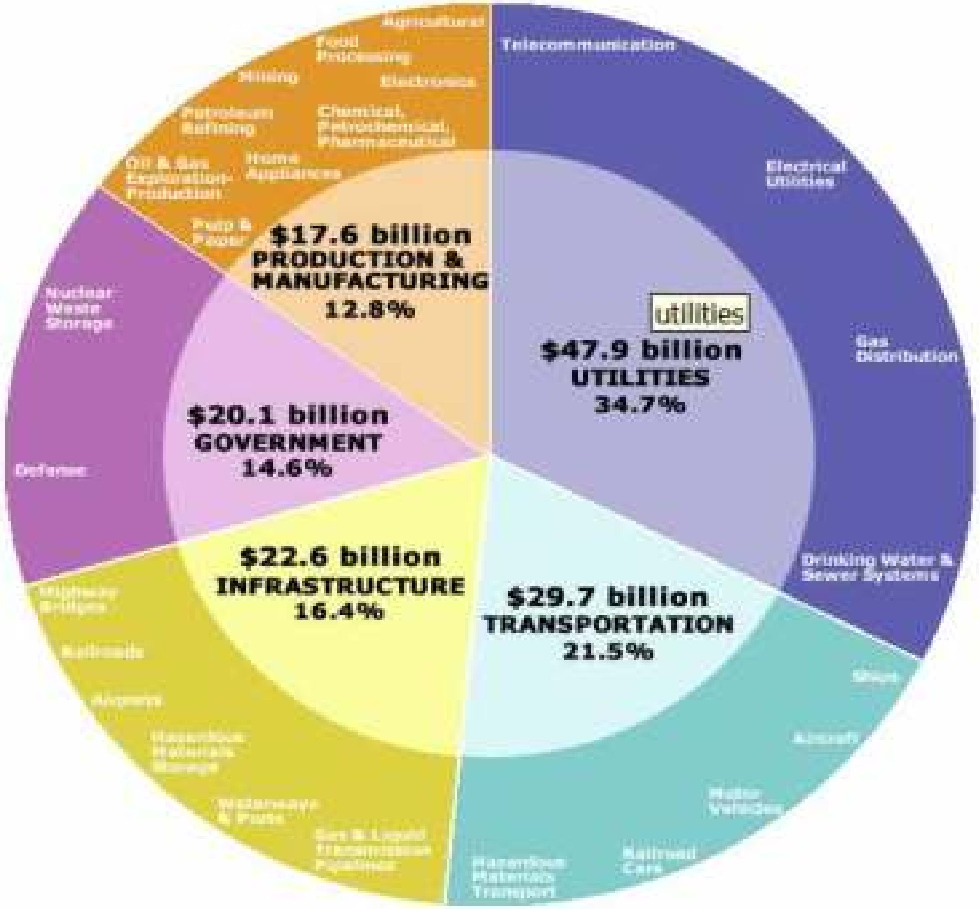
MP

MATERIALS PERFORMANCE

CORROSION PREVENTIO D CONTROL WORLDWIDE

HISTORIC CONGRESSIONAL STUDY:

CORROSION COSTS AND PREVENTIVE STRATEGIES IN THE UNITED STATES



FHWA funds Cost of Corrosion Study.
Total Direct Cost of Corrosion in Analyzed Sectors: $137.9 billion/year (1998).
Extrapolated to U.S. Economy; Cost of Corrosion is $275.7 billion/year (1998).

COSTS OF CORROSION

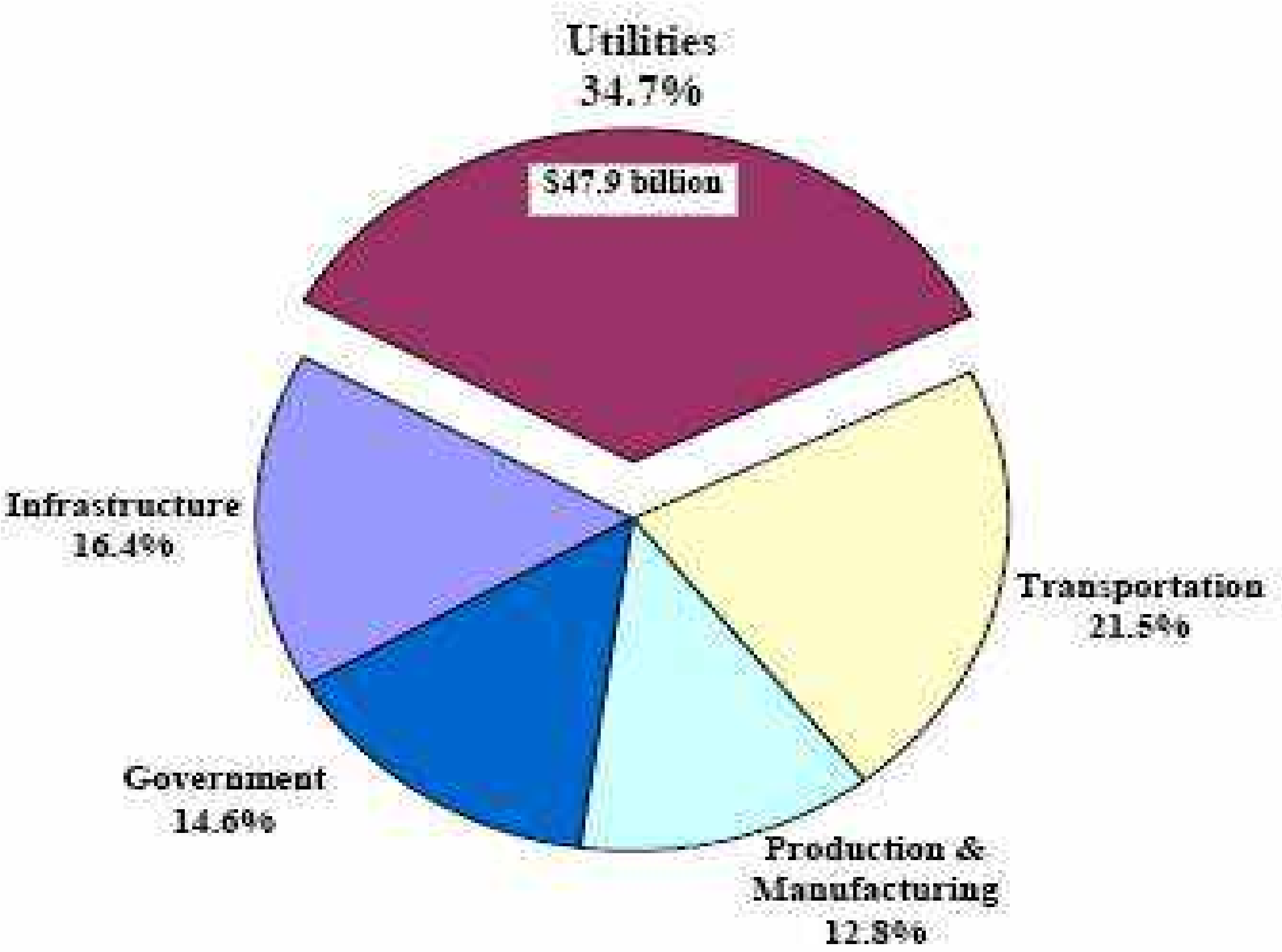


Figure 8. Annual cost of corrosion in the Utilities category.

COSTS OF CORROSION

“EPRI in its research report on the "Cost of Corrosion in the Electric Power Industry" estimated that the cost of corrosion in Electrical Industry of USA was of the order of US $ 34.5 Billion per annum in 2003. Based on the studies various corrosion problems in the Fossil power plants were identified. Around US $ 11 billion was due to boiler tube failures followed by US $ 6 billion due to corrosion problems in turbines”

At present no such studies have been conducted for Indian power sector.

COSTS OF CORROSION

Estimated Corrosion Costs in India:

Direct Cost 4% of GDP

GDP in 2017 – 159015 Billion Rs.

4% of GDP – 6360.6 Billion Rs.

Indirect Cost – Same as Direct Cost

= 6360.6 Billion Rs

Total Costs of Corrosion = 12721.2 Billion Rs.

Opportunities in Corrosion Control

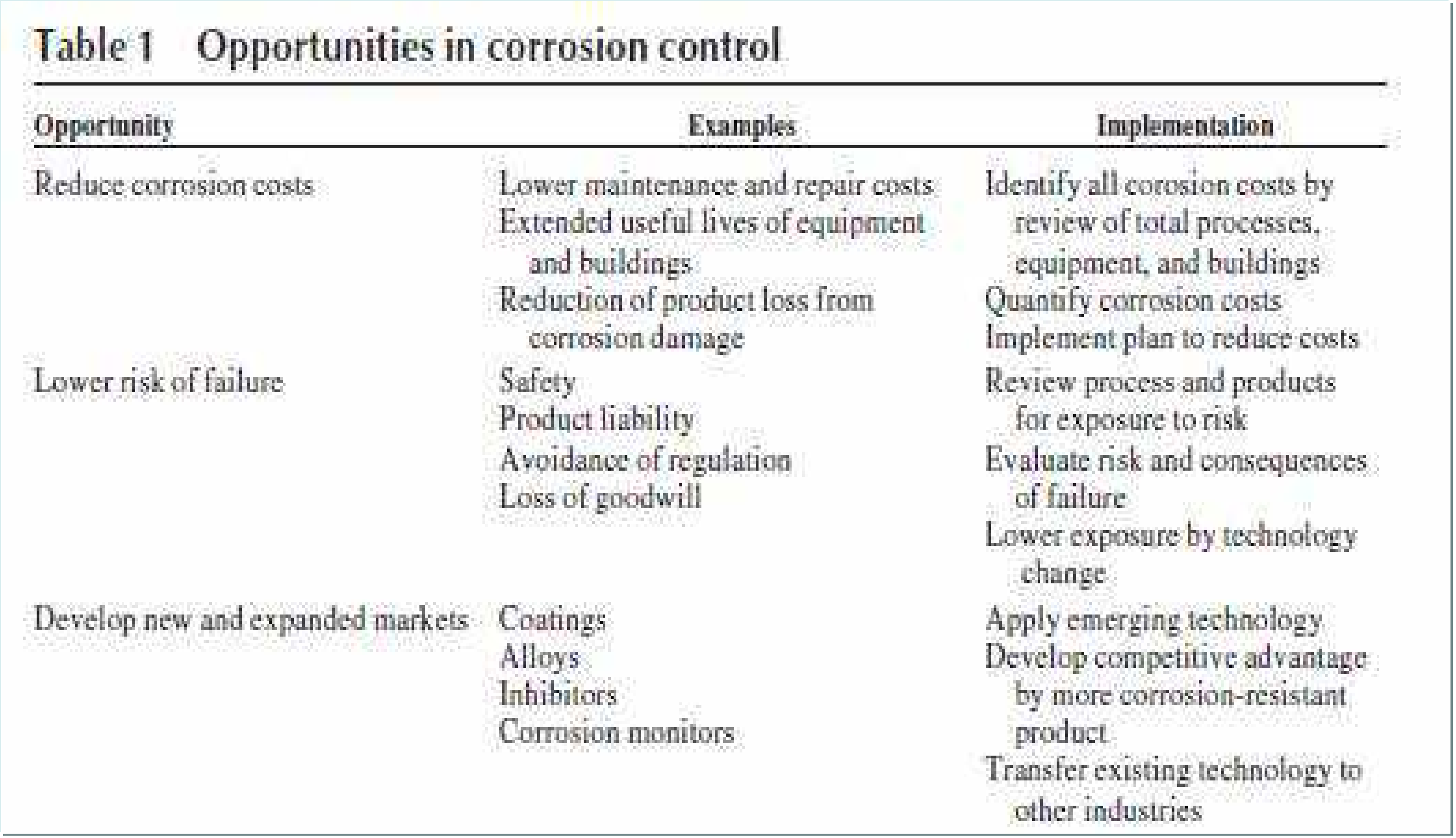


Table 1 Opportunities in corrosion control

Opportunity	Examples	Implementation
Reduce corrosion costs	Lower maintenance and repair costs Extended useful lives of equipment and buildings Reduction of product loss from corrosion damage	Identify all corosion costs by review of total processes, equipment, and buildings Quantify corrosion costs Implement plan to reduce costs
Lower risk of failure	Safety Product liability Avoidance of regulation Loss of goodwill	Review process and products for exposure to risk Evaluate risk and consequences of failure Lower exposure by technology change
Develop new and expanded markets	Coatings Alloys Inhibitors Corrosion monitors	Apply emerging technology Develop competitive advantage by more corrosion-resistant product Transfer existing technology to other industries

COSTS OF CORROSION

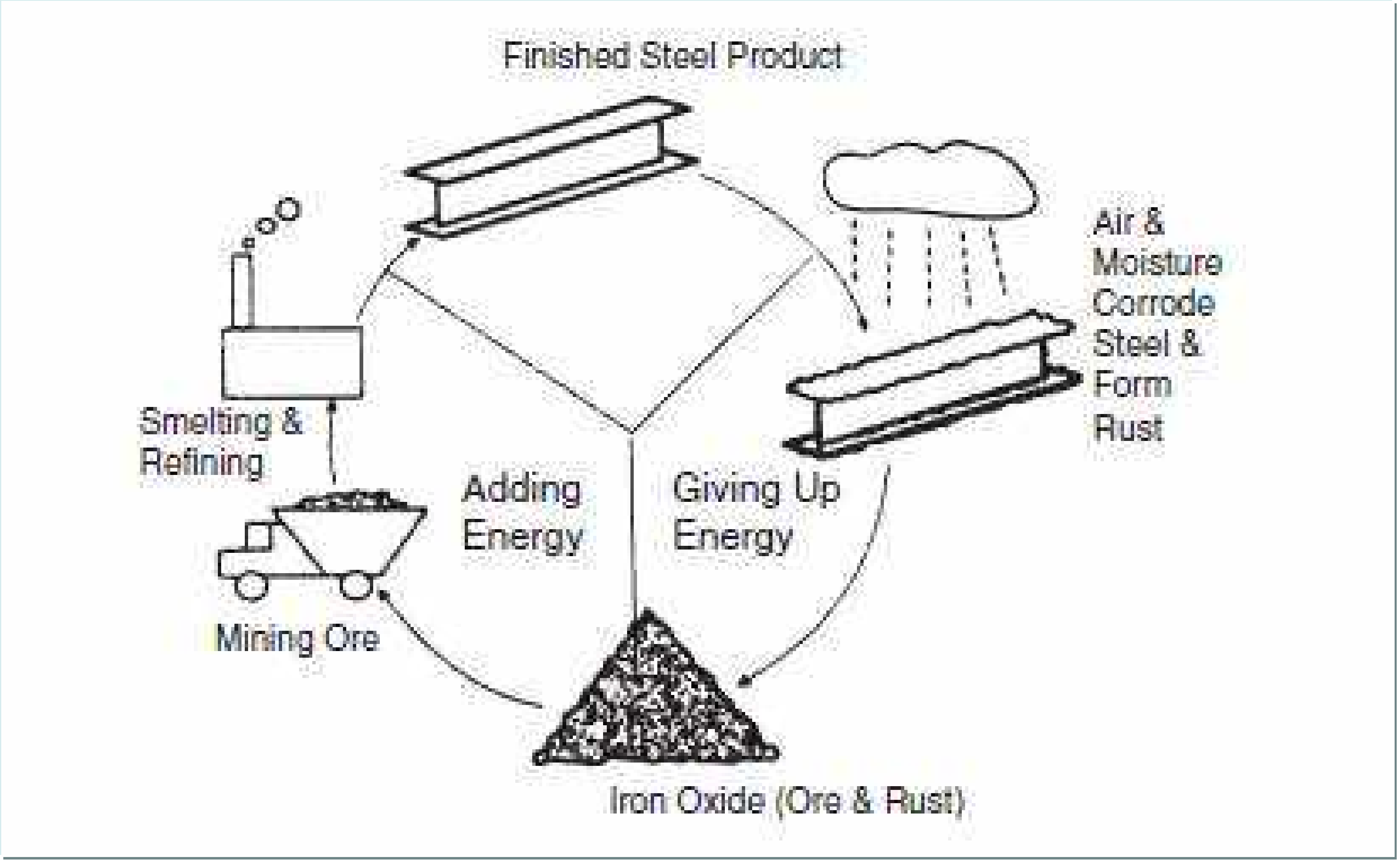
Corrosion Problem	O&M Non- Fuel Related Corrosion Cost US $	Depreciation Corrosion Cost US $	Total Corrosion Cost US $
All Corrosion Problems in Fossil Steam Plants	3,43,50,00,000	1,14,20,00,000	4,57,70,00,000
Waterside/Steam side Corrosion of Boiler Tubes	91,60,00,000	22,84,00,000	1,14,44,00,000
Turbine CF & SCC	45,80,00,000	14,27,50,000	60,07,50,000
Oxide Particle erosion of Turbines	27,48,00,000	8,56,50,000	36,04,50,000
Heat Exchanger Corrosion	27,48,00,000	8,56,50,000	36,04,50,000
Fireside Corrosion of Water wall tubes	18,32,00,000	14,27,50,000	32,59,50,000
Generator clip to strand Corro	18,32,00,000	2,85,50,000	21,17,50,000
Copper deposition in turbines	9,16,00,000	5,71,00,000	14,87,00,000
Fireside Corrosion of SH & RH tubes	9,16,00,000	5,71,00,000	14,87,00,000

COSTS OF CORROSION

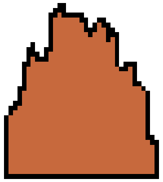
Corrosion Problem	O&M Non- Fuel Related Corrosion Cost US $	Depreciation Corrosion Cost US $	Total Corrosion Cost US $
Corrosion of FGD system	4,58,00,000	8,56,50,000	13,14,50,000
Liquid Slag Corrosion of Cyclone Boilers	9,16,00,000	2,85,50,000	12,01,50,000
Backend dew point corrosion	9,16,00,000	2,85,50,000	12,01,50,000
Generator Cooling water clogging & plugging	9,16,00,000	2,85,50,000	12,01,50,000
FAC of steam plant piping	9,16,00,000	2,85,50,000	12,01,50,000
Corrosion of service water, circulating water and other water systems	9,16,00,000	2,85,50,000	12,01,50,000
All other (Corrosion of structures, ash handling equipment, CHP, oil pipes & tanks, electrical equipment,	45,80,00,000	8,56,50,000	54,36,50,000
Total	3,43,50,00,000	1,14,20,00,000	4,57,70,00,000

CORROSION BASICS AND FORMS OF CORROSION

WHAT IS CORROSION



WHAT IS CORROSION



IRON OXIDE

+

REFINING

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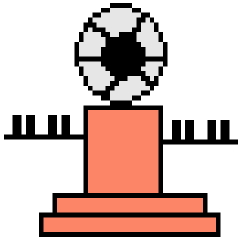

MILLING

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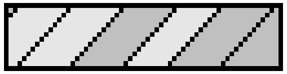
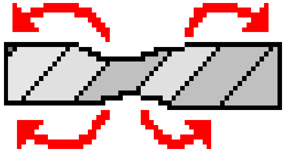


STEEL

+



CORROSION

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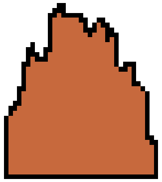
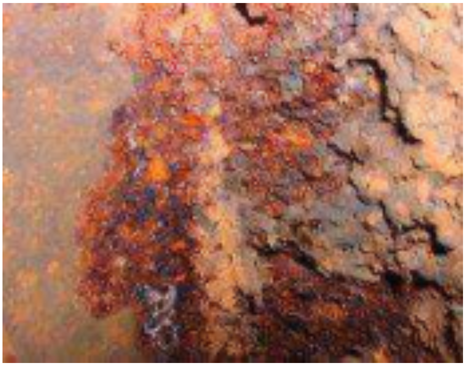


IRON OXIDE

CORROSION

Corrosion is a natural process and is a result of the inherent tendency of metals to revert to their more stable compounds, usually oxides. Most metals are found in nature in the form of various chemical compounds called ores. In the refining process, energy is added to the ore, to produce the metal. It is this same energy that provides the driving force causing the metal to revert back to the more stable compound.

General Corrosion

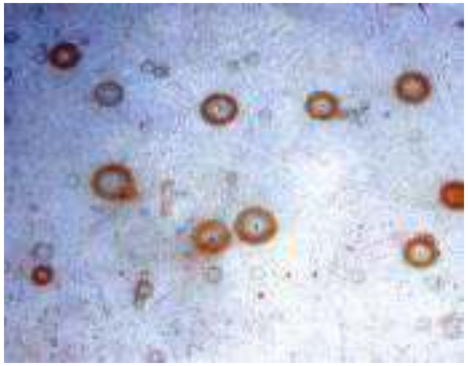


Pitting Corrosion

Under deposit Corrosion

WHAT IS CORROSION

CORROSION IS A NATURAL PROCESS BY VIRTUE OF WHICH THE METALS TEND TO ACHIEVE THE LEAST ENERGY STATE – I.E. COMBINED STATE



MIC

$$M \longrightarrow M^{2+} + 2e^{-}$$

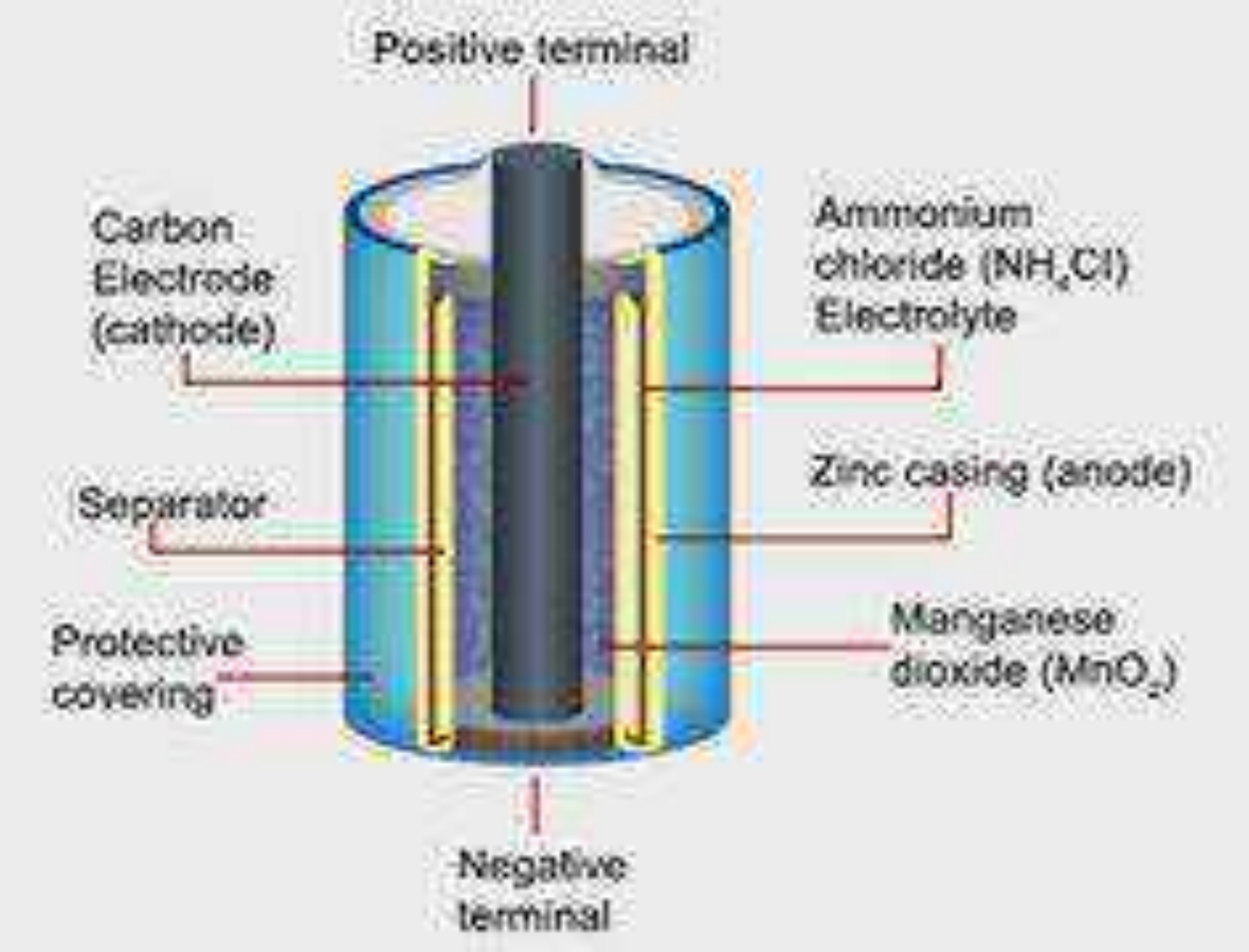
ANODIC REACTION

$$N^{2-} + 2e \longrightarrow N$$

CATHODIC REACTION

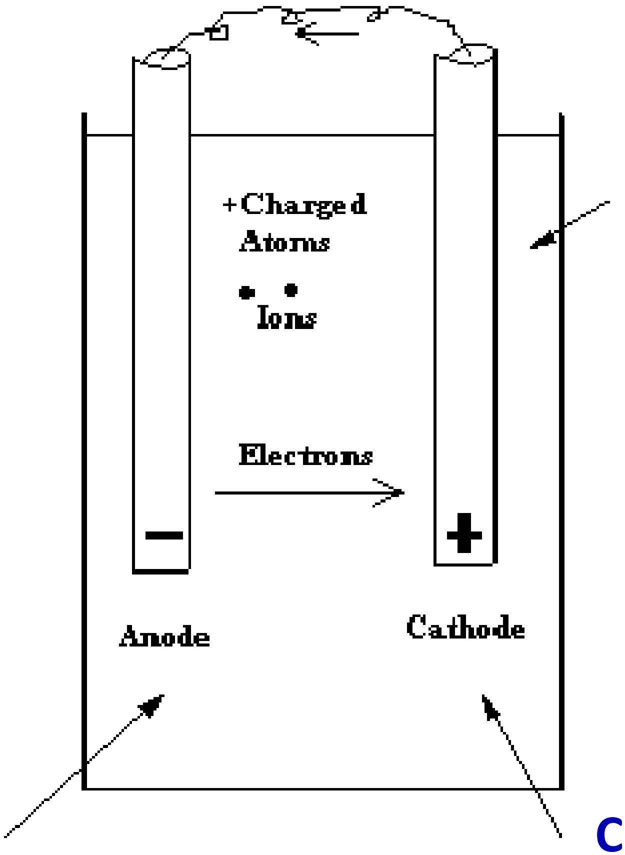
Dezincification

ELECTROCHEMICAL NATURE OF CORROSION



Dry Cell

ELECTROCHEMICAL NATURE OF CORROSION



Electrotype:- solution capable of conducting electricity e.g. fresh/salt water, moisture, alkali's, acids

Anode is the metal which is Corroding

Cathode is the metal which is not Corroding

Corrosion Basics

- Corrosion requires:
  - Oxygen & Water
  - Rusting takes place in presence of Air & Water
  - No rusting will occur if either water or air is removed

Corrosion Basics

- Corrosion is electrochemical
  - Anode (Oxidizing – losing electrons) Electrode
  - Cathode (Reducing – gaining electrons) Electrode
  - Need “Short circuit” for electrons between terminals
  - And need a medium for ion transport

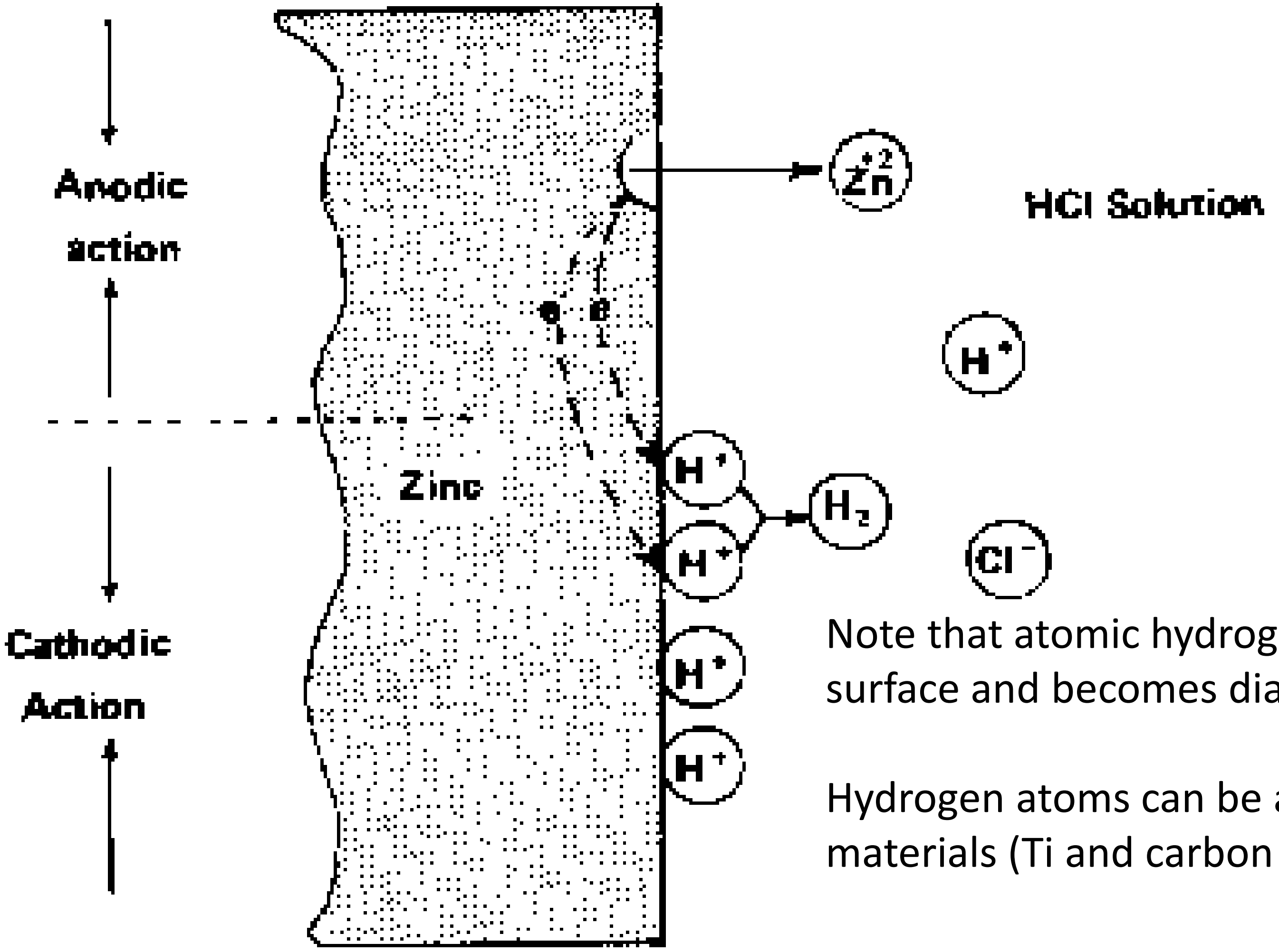
- Electricity and chemicals are main drivers

- Influenced by other factors

Corrosion Basics

- Usual Textbook Equations
  - Chemical: $Zn + 2HCl = ZnCl_2 + 2H$
  - Electrical: $Zn \longrightarrow Zn^{+2} + 2e^-$ (anode)
  - $2H^+ + 2e^- \longrightarrow 2H$ (cathode)
- Note: hydrogen is atomic, not diatomic
  - This can come back to get you
- Generally, the electrical part is not shown
- Oxygen reaction can be inserted as well

Corrosion Basics

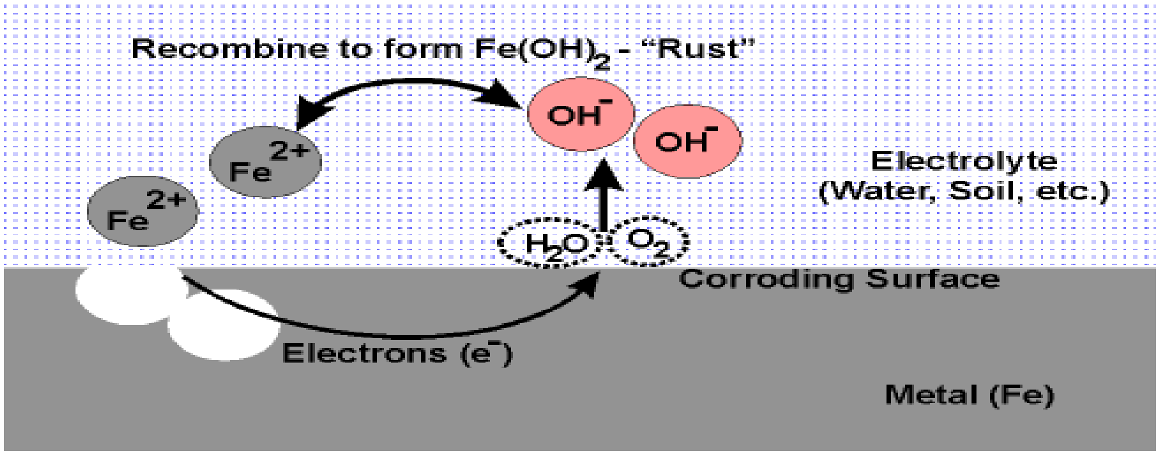


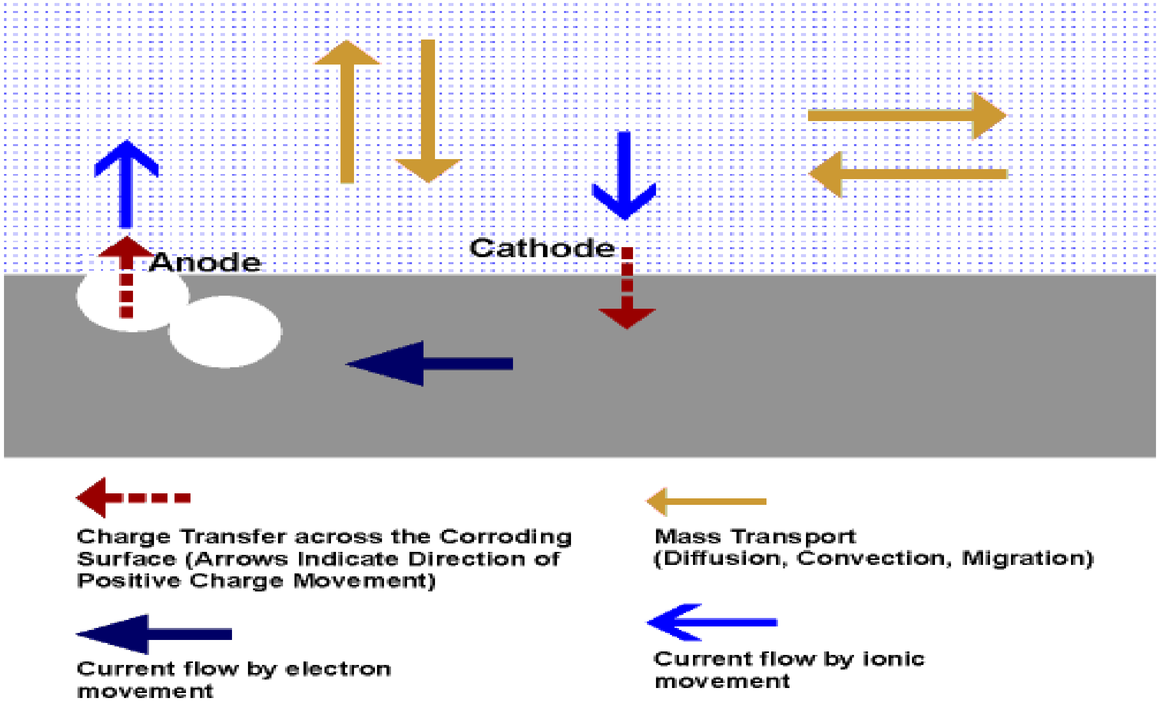
Note that atomic hydrogen forms on surface and becomes diatomic in solution.

Hydrogen atoms can be absorbed into materials (Ti and carbon steel couple)

Figure – Electrochemical reactions occurring during the corrosion of zinc in air-free hydrochloric acid.

Electrochemical Corrosion





- *Oxidation: the loss of electrons by a species, leading to an increase in oxidation number of one or more atoms.* ***loss of electron(s) by a species; increase in oxidation number; increase in oxygen.***
- *Reduction: the gain of electrons by a species, leading to an decrease in oxidation number of one or more atoms.* ***Gain of electron(s); decrease in oxidation number; decrease in oxygen; increase in hydrogen.***
- *Oxidizing agents: the species that is reduced in a redox reaction (or)****Electron acceptor;***
- *Reducing agents: the species that is oxidized in a redox reaction (or)* ***Electron donor;***

CORROSION OF METALS

DRY CORROSION(OR)CHEMICAL CORROSION

1. OXIDATION CORROSION
2. CORROSION BY OTHER GASES
3. LIQUID-METAL CORROSION

WET CORROSION (OR) ELECTROCHEMICAL CORROSION

1. ELECTROCHEMICAL CORROSION BY EVOLUTION OF HYDROGEN AND ABSORPTION OF OXYGEN.
2. GALVANIC CORROSION
3. CONCENTRATION CELL CORROSION

CHEMICAL (OR)DRY CORROSION

THE DIRECT CHEMICAL ATTACK OF THE ATMOSPHERIC GASES LIKE O_2, HALOGENS, H_2S, SO_2 ,ANHYDROUS INORGANIC LIQUID METALS ON METAL SURFACES IN THE ABSENCE OF MOISTURE.

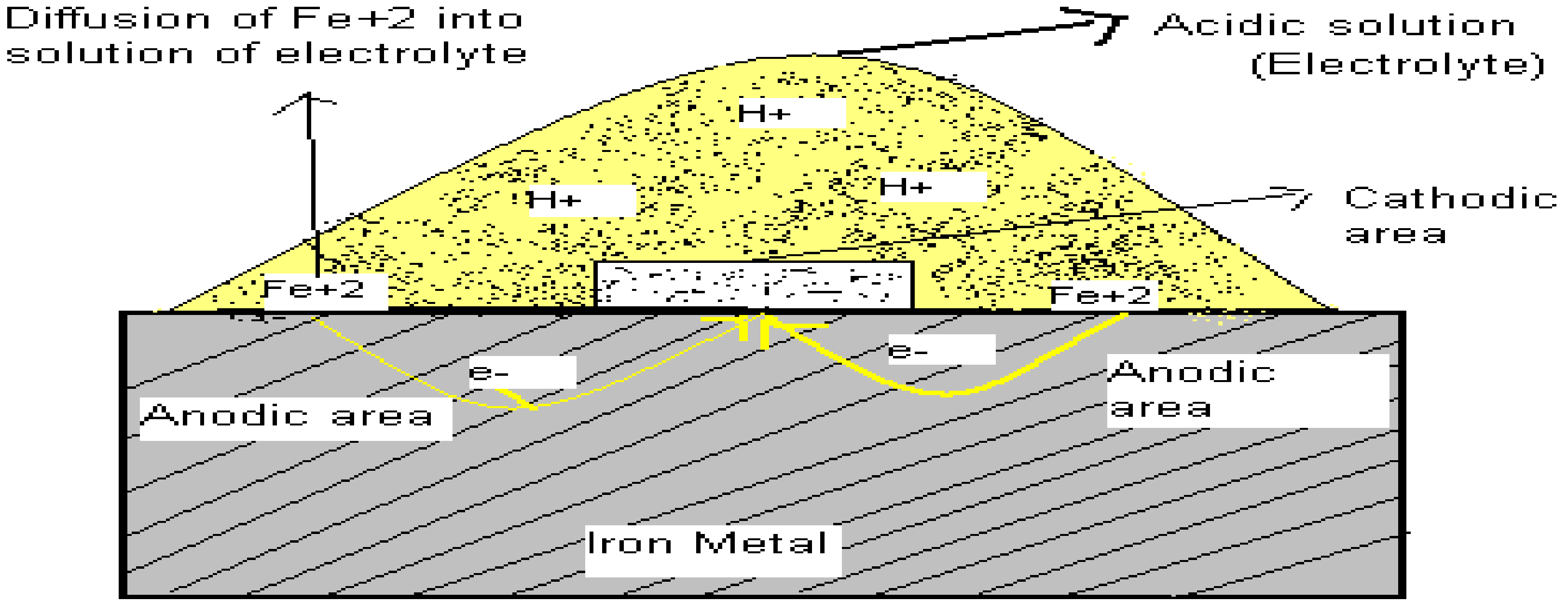
1. **OXIDATION CORROSION:** *DIRECT ACTION OF OXYGEN AT HIGH(OR)LOW TEMPARETURES ON METAL SURFACE.*
2. ***CORROSION BY OTHER GASES:*** *ATTACK OF GASES LIKE SO_2,CO_2,Cl_2,H_2S,F etc ON METAL SURFACE.*
3. ***LIQUID METAL CORROSION:*** *ATTACK OF INORGANIC LIQUID METALS ON SOLID METALLIC SURFACE*

Wet corrosion takes by the following two ways based the medium:

1. Evolution of H2 :

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

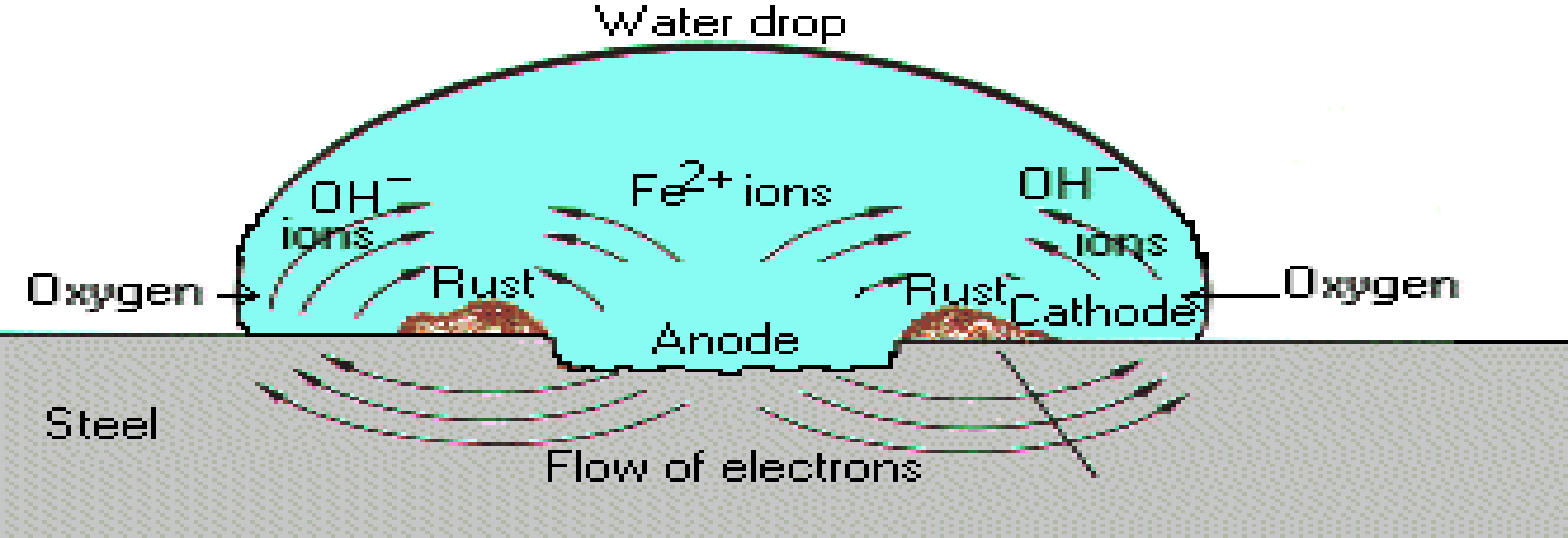
Cathode: $2H^+(aq) + 2e^- \rightarrow H_2$



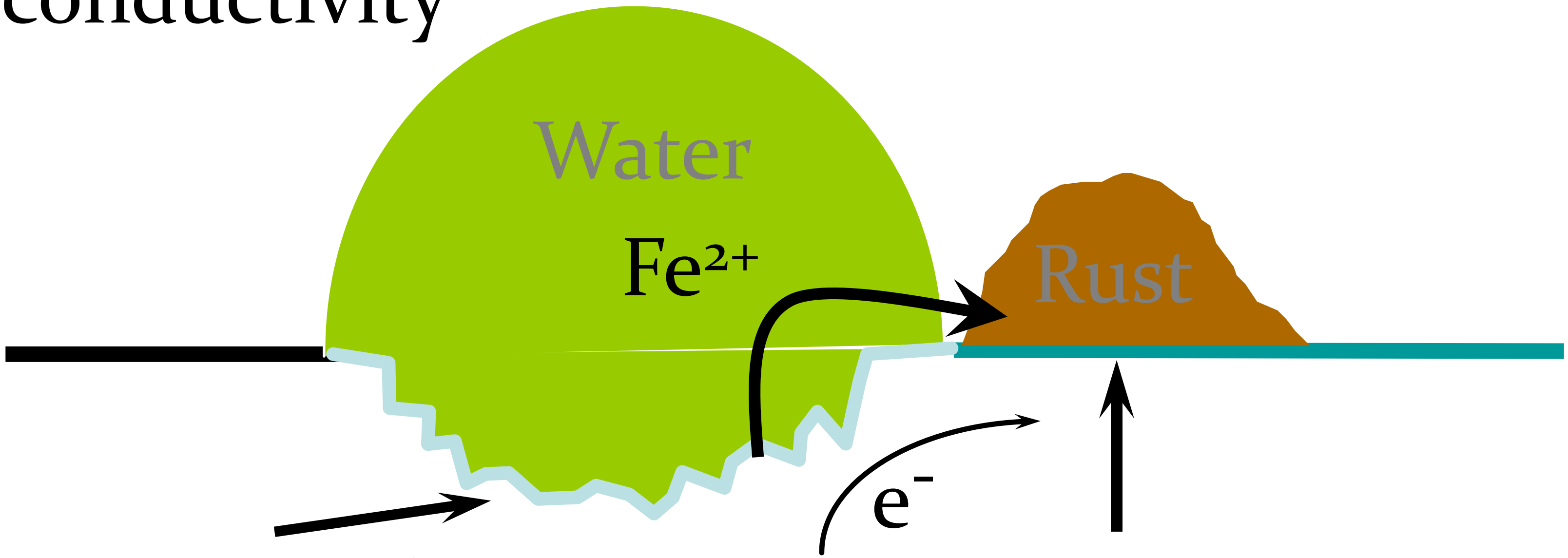
Absorption of O2 :

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

Cathode: $\frac{1}{2} O_2(g) + H_2O\ (aq) + 2\ e^- \rightarrow 2OH^-$



Salt speeds up process by increasing conductivity



Iron Dissolves-
$Fe \rightarrow Fe^{+2}$

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

$Fe^{2+} + O_2 + 2H_2O \rightarrow Fe_2O_3 + 8\ H^+$

The Many Forms of Corrosion

Corrosion occurs in several widely differing forms. Classification is usually based on one of three factors:

- *Nature of the corrodent:* Corrosion can be classified as “wet” or “dry.” A liquid or moisture is necessary for the former, and dry corrosion usually involves reaction with high-temperature gases.
- *Mechanism of corrosion:* This involves either electrochemical or direct chemical reactions.
- *Appearance of the corroded metal:* Corrosion is either uniform and the metal corrodes at the same rate over the entire surface, or it is localized, in which case only small areas are affected.

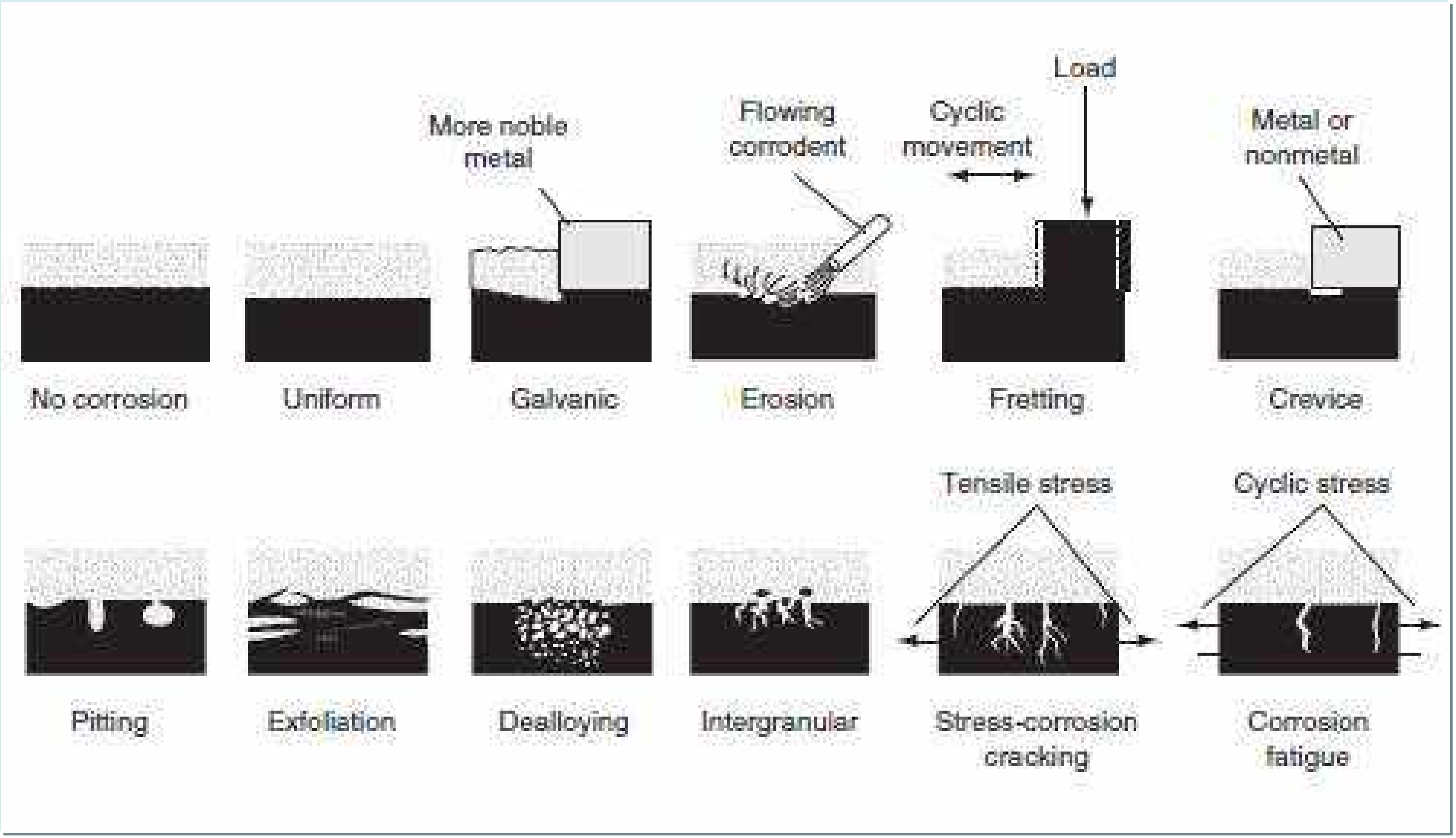
The Many Forms of Corrosion

Eight forms of wet (or aqueous) corrosion can be identified based on appearance of the corroded metal. These are:

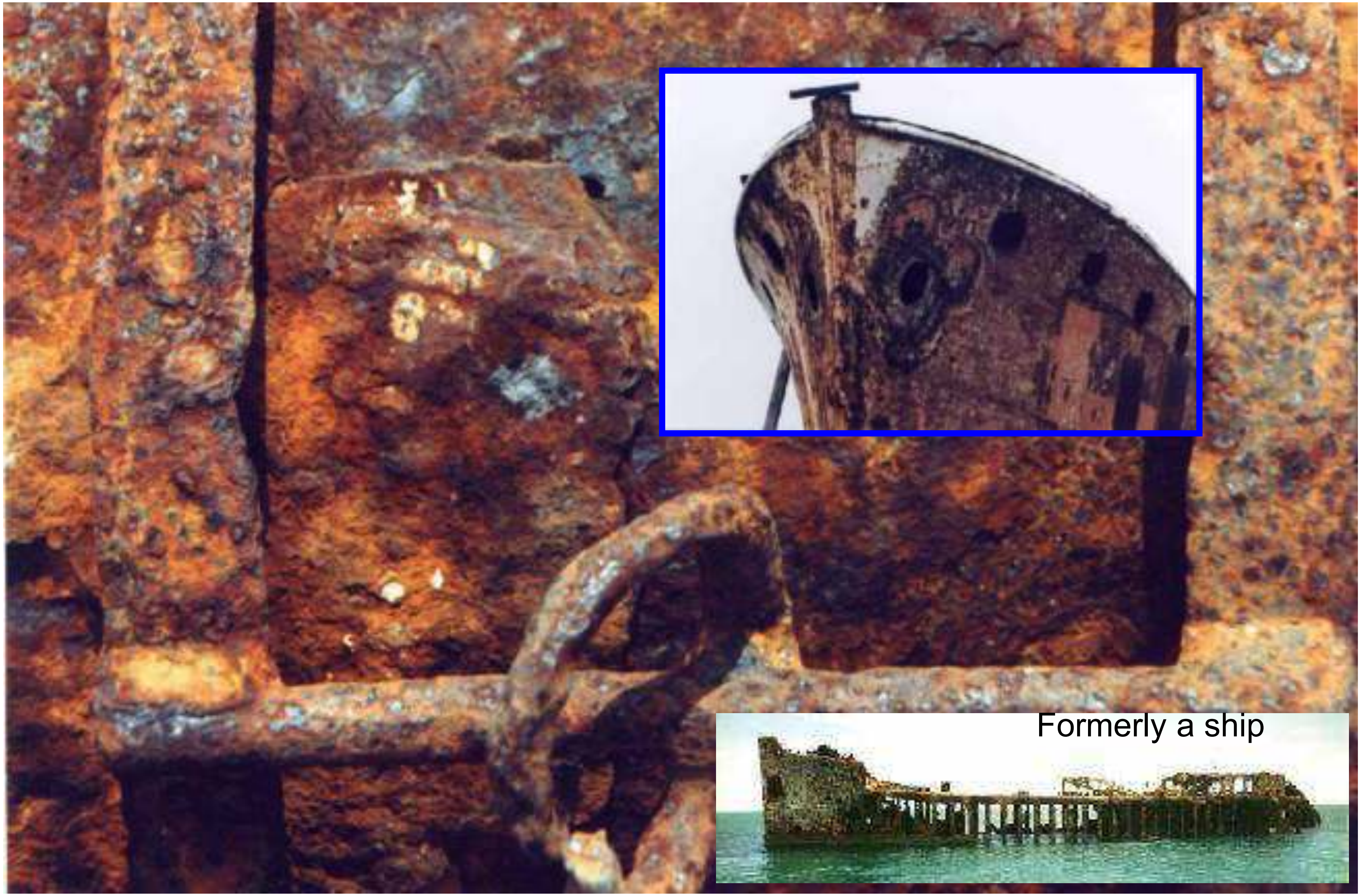
- Uniform or general corrosion
- Pitting corrosion
- Crevice corrosion, including corrosion under tubercles or deposits,
- filiform corrosion, and poultice corrosion
- Galvanic corrosion
- Erosion-corrosion, including cavitation erosion and fretting corrosion
- Intergranular corrosion, including sensitization and exfoliation
- Dealloying, including dezincification and graphitic corrosion
- Environmentally assisted cracking, including stress-corrosion cracking,
- corrosion fatigue, and hydrogen damage

In theory, the eight forms of corrosion are clearly distinct; in practice however, there are corrosion cases that fit in more than one category. Other corrosion cases do not appear to fit well in any of the eight categories. Nevertheless, this classification system is quite helpful in the study.

The Many Forms of Corrosion



Uniform Corrosion



Formerly a ship

Uniform Corrosion

What general corrosion might look like!

Corrosion Top Mechanisms - Pitting

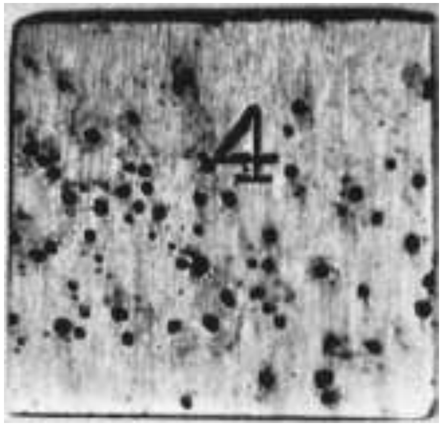
- Most common form of localized attack
- Break down of protective scale
- Localized attack in break
- Pit sets up its own environment
- Draws in chlorides and sulfates
- Can form caps over pits
- Low corrosion rates are deceitful

Corrosion Top Mechanisms - Pitting

Pitting corrosion – small and large

Pitting

Pitting is a localized form of corrosive attack. Pitting corrosion is typified by the formation of holes or pits on the metal surface. Pitting can cause failure, yet the total corrosion, as measured by weight loss, may be minimal.

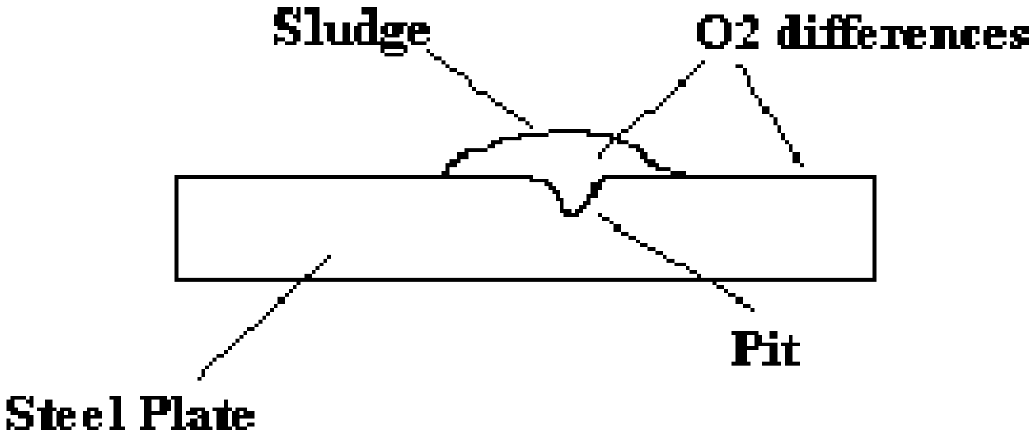


304 stainless steel / acid chloride solution

5th Century sword

Boiler tube

PITTING CORROSION



Corrosion Top Mechanisms - Crevice

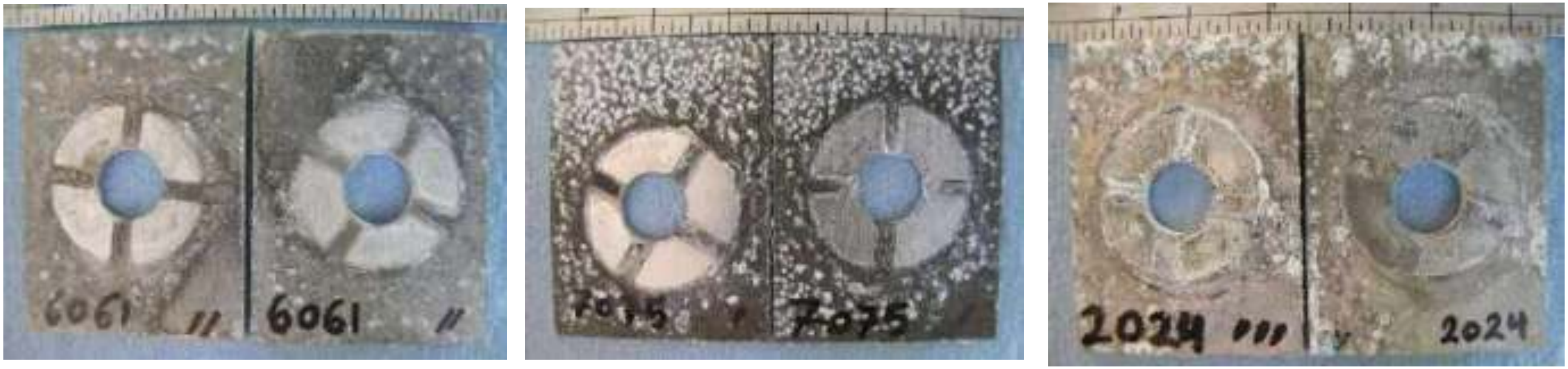
- Much like a large area pit.
- Occurs in cracks or crevices
- Think of flanged connections such as
  - Piping flanges
  - Column body flanges
  - Trays on tray rings
  - Car or truck doors
- It will also set up its own environment

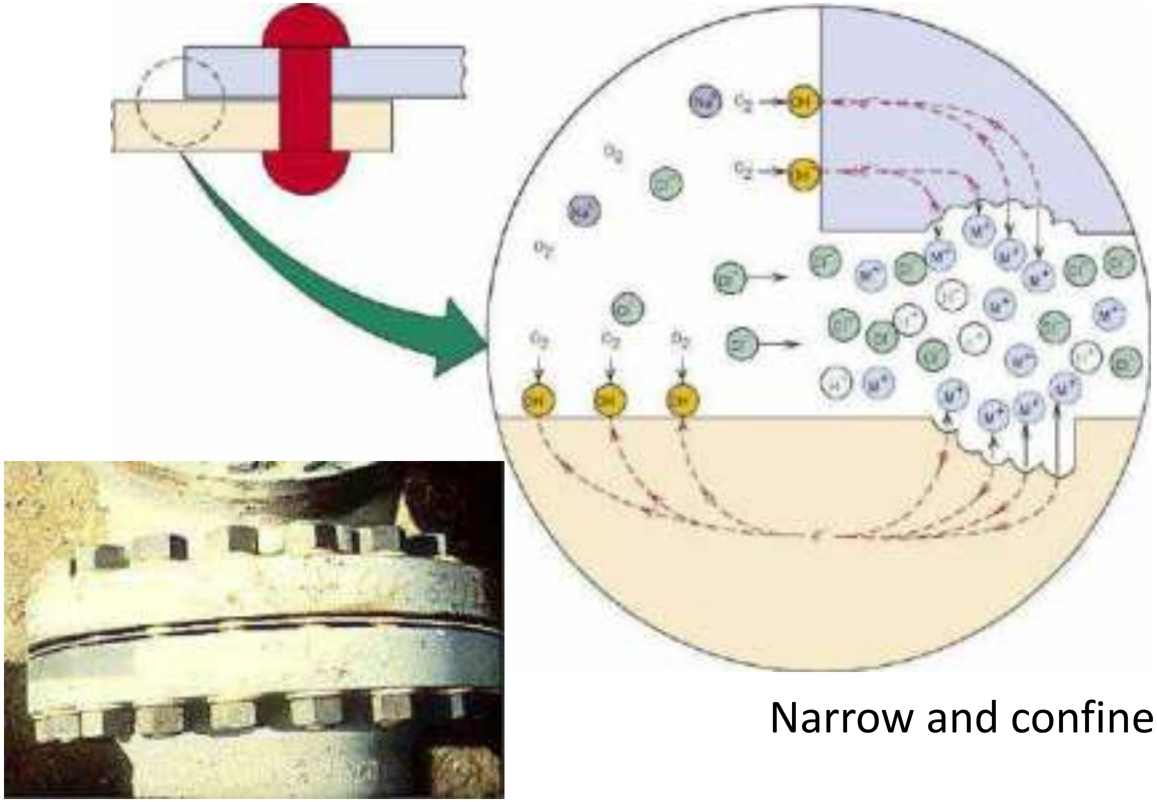
Corrosion Top Mechanisms - Crevice

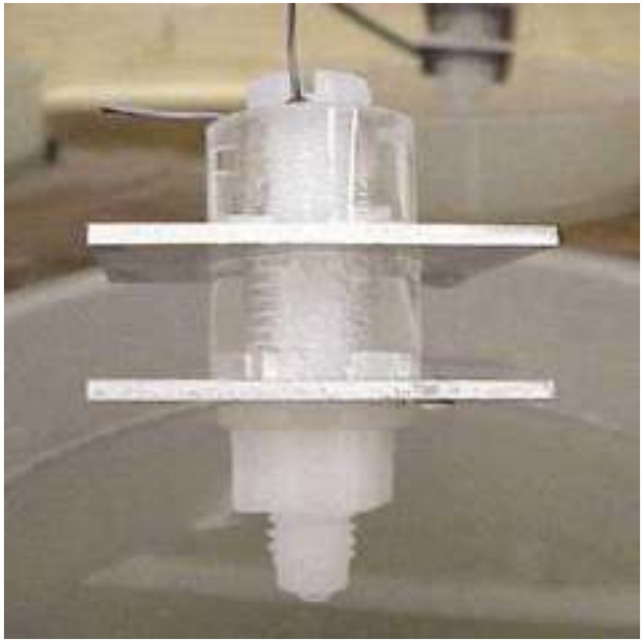
Crevice attack on titanium from fluorinated o-ring

Severe crevice attack as well as general

Crevice Corrosion







Narrow and confined spaces.

Corrosion Top Mechanism - Underdeposit

- Very similar to crevice corrosion but a larger
- Usually an unplanned occurrence
  - Tools left on floor
  - River water silt buildup in bottoms
- Sometimes called poultice corrosion
- Sometimes called oxygen concentration cell

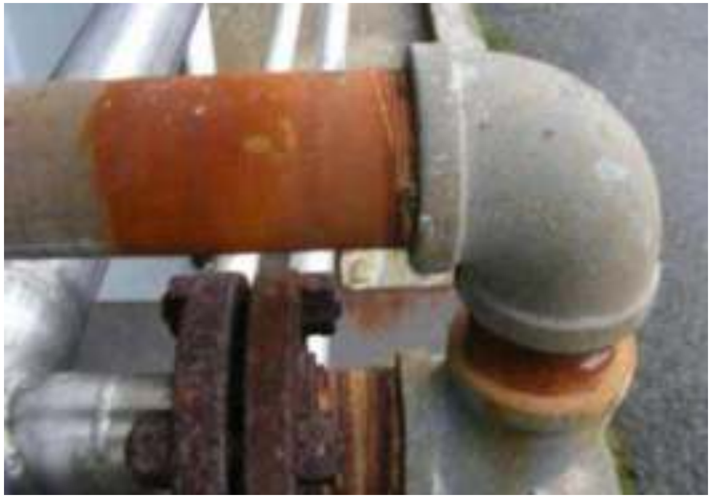
Corrosion Top Mechanism - Dealloying

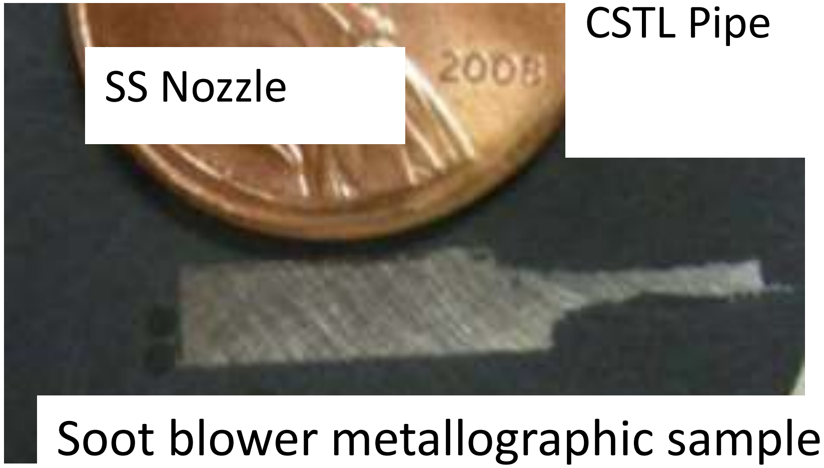
- Copper alloys
  - Brasses with >30% zinc (Dezincification)
  - Copper nickel alloys (nickel removed)
- Cast iron (graphitization)
- Almost any alloy can have the problem
- Two Theories
  - One element is “leached” from solution
  - Both elements corroded but more noble plates back.

Corrosion Top Mechanism - Dealloying

Brass River Water Impellor suffering from dealloying and cavitation

Corrosion Top Mechanism - Dealloying





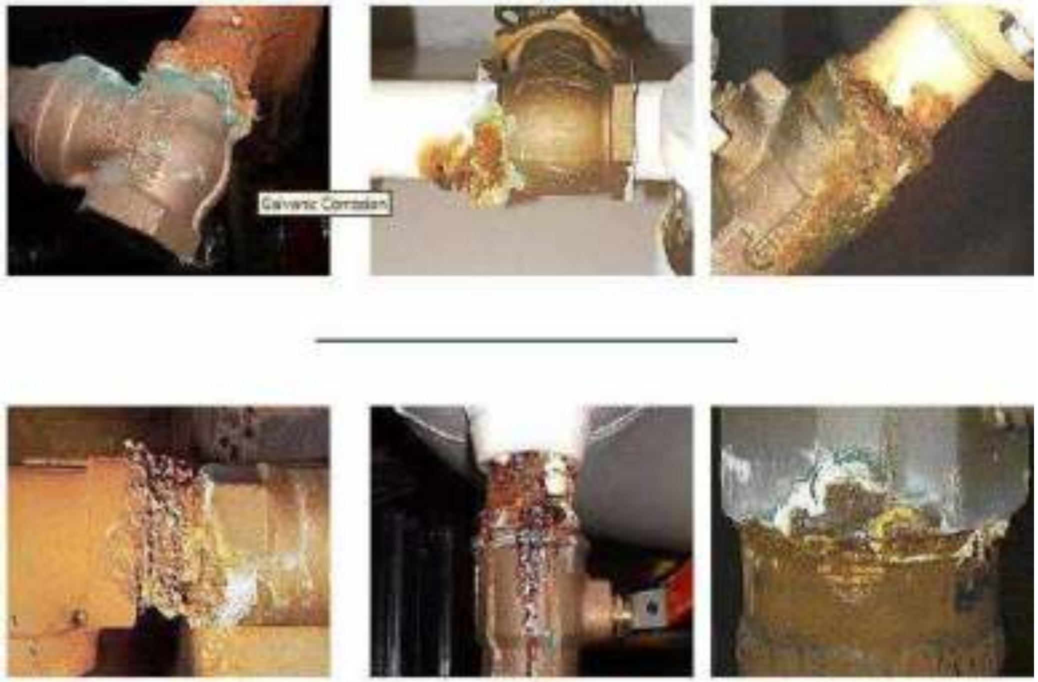
CSTL Pipe

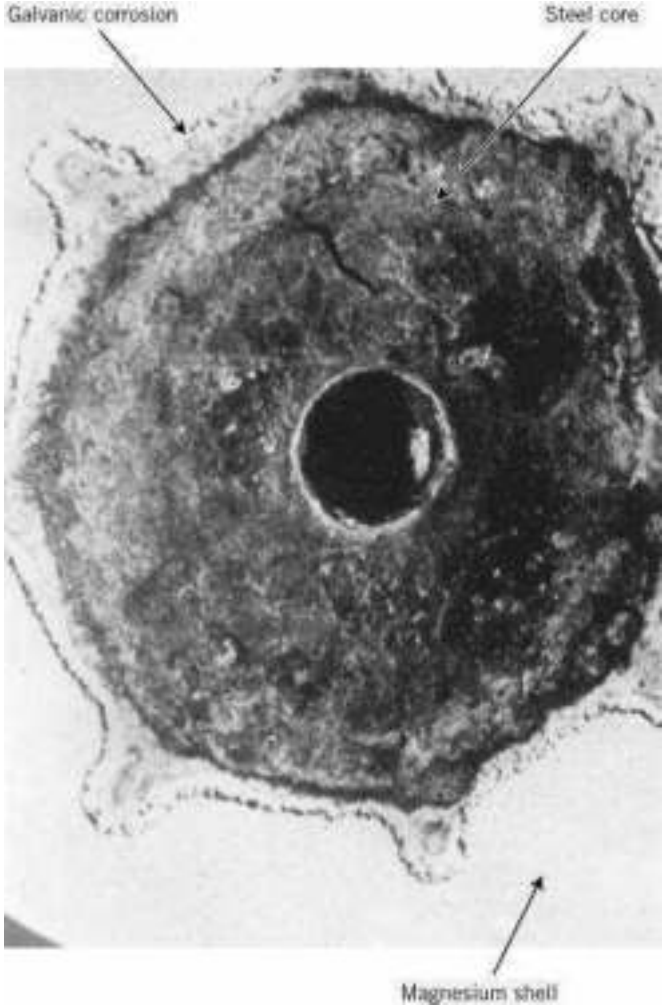
SS Nozzle

Soot blower metallographic sample

Corrosion Top Mechanism - Dealloying

- Dissimilar metals are physically joined in the presence of an electrolyte.
- The more anodic metal corrodes.

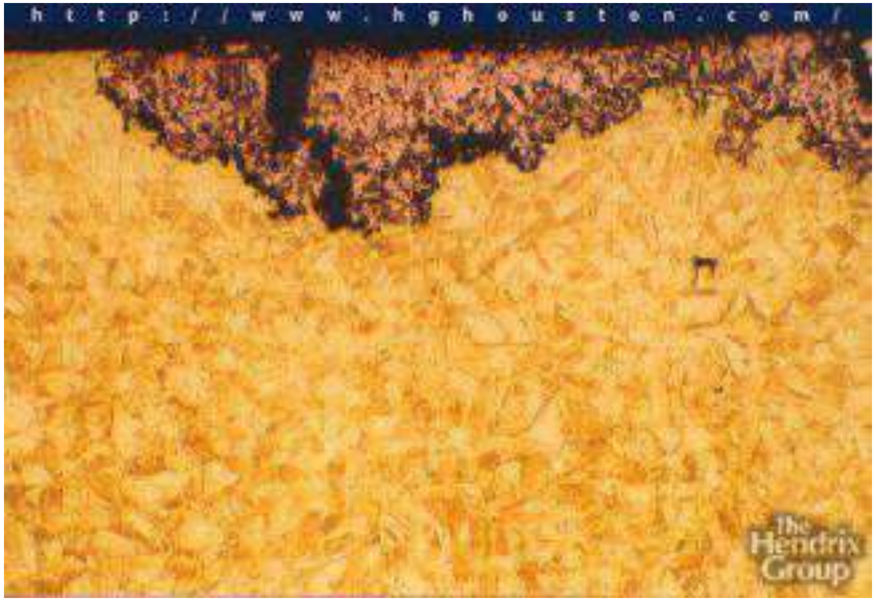


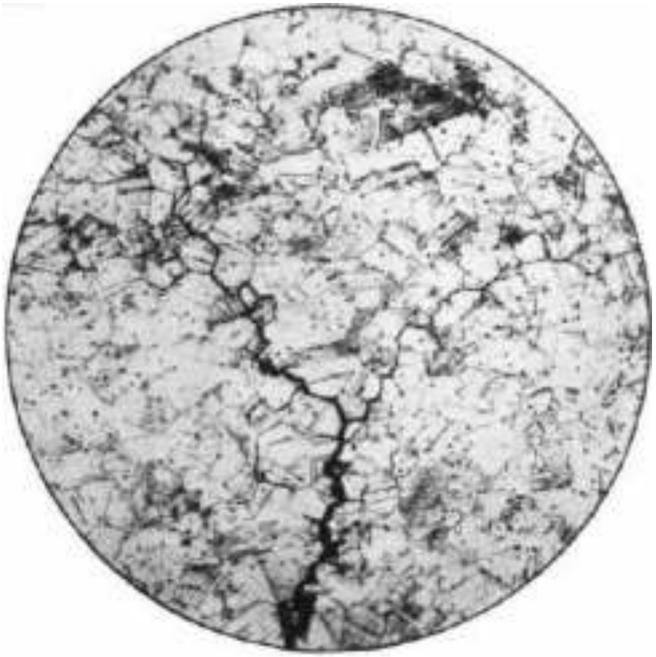


Bilge pump - Magnesium shell cast around a steel core.

Selective Leaching

Preferred corrosion of
one element/constituent
[e.g., Zn from brass (Cu-Zn)].
Dezincification.





Stress Corrosion Cracking (SCC)

(SCC) is the cracking induced from the combined influence of tensile stress and a corrosive environment. The impact of SCC on a material usually falls between dry cracking and the fatigue threshold of that material. The required tensile stresses may be in the form of directly applied stresses or in the form of residual stresses. The problem itself can be quite complex. The situation with buried pipelines is a good example of such complexity. The impact is most commonly catastrophic

Cold deformation and forming, welding, heat treatment, machining and grinding can introduce residual stresses. The magnitude and importance of such stresses is often underestimated. The residual stresses set up as a result of welding operations tend to approach the yield strength.

Stress Corrosion Cracking (SCC)

Chloride SCC

One of the most important forms of stress corrosion that concerns the nuclear industry is chloride stress corrosion. Chloride stress corrosion is a type of intergranular corrosion and occurs in austenitic stainless steel under tensile stress in the presence of oxygen, chloride ions, and high temperature. It is thought to start with chromium carbide deposits along grain boundaries that leave the metal open to corrosion. This form of corrosion is controlled by maintaining low chloride ion and oxygen content in the environment and use of low carbon steels.

Caustic SCC

Despite the extensive qualification of Inconel for specific applications, a number of corrosion problems have arisen with Inconel tubing. Improved resistance to caustic stress corrosion cracking can be given to Inconel by heat treating it at 620°C to 705°C, depending upon prior solution treating temperature. Other problems that have been observed with Inconel include wastage, tube denting, pitting, and intergranular attack.

Stress Corrosion Cracking (SCC)

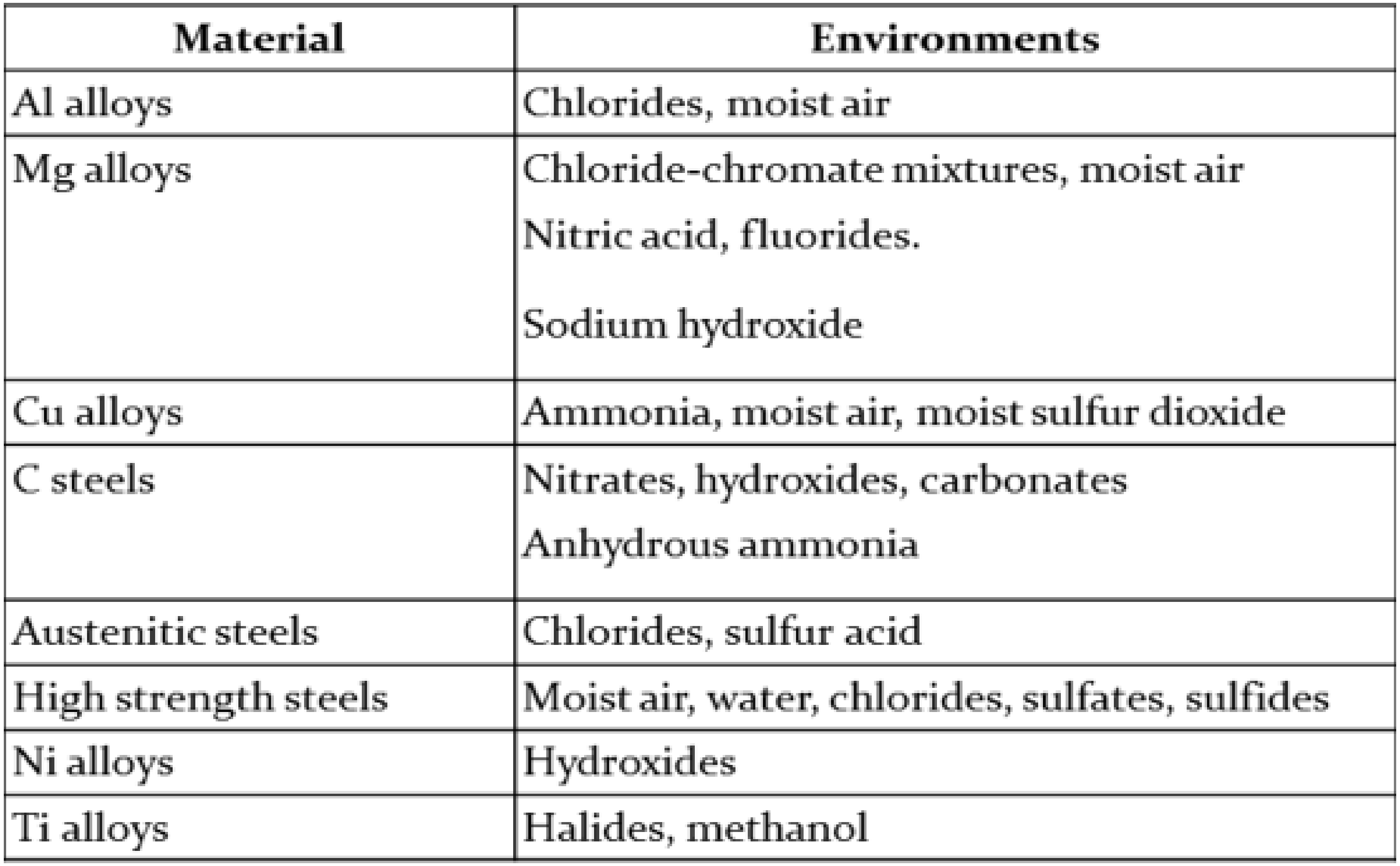
Environments and Stress Corrosion Cracking

The specificity of environments that will promote Stress Corrosion Cracking is significant. It is important to realize that not all corrosive environments promote the formation of stress corrosion cracks. Those that do will usually be those that do not promote widespread corrosion in the sense of the attack being spread fairly uniformly over all exposed surfaces, since, if for no other reason, this is not likely to lead to the geometry of a crack, which requires that the crack sides remain relatively inactive whilst the tip remains active to maintain propagation into the metal.

Consequently those environments, such as sea water, that normally promote general corrosion of mild steel, are not likely to promote stress corrosion, whilst those chemicals sometimes used to control corrosion by addition to an otherwise corrosive environment may result in a borderline condition, between general corrosion and no corrosion, wherein the attack can be localized. Thus, the addition of caustic soda to boiler feed waters to reduce the corrosiveness of the latter towards mild steel can result in the form of stress corrosion frequently referred to as **'caustic cracking'**. The important general point is that those environments that cause stress corrosion are frequently highly specific to the particular alloy involved and a list of some environments that have been shown to promote stress corrosion in various materials is given in the following Table.

Stress Corrosion Cracking (SCC)

Combinations of some alloys and environments that have been shown to promote stress corrosion cracking.



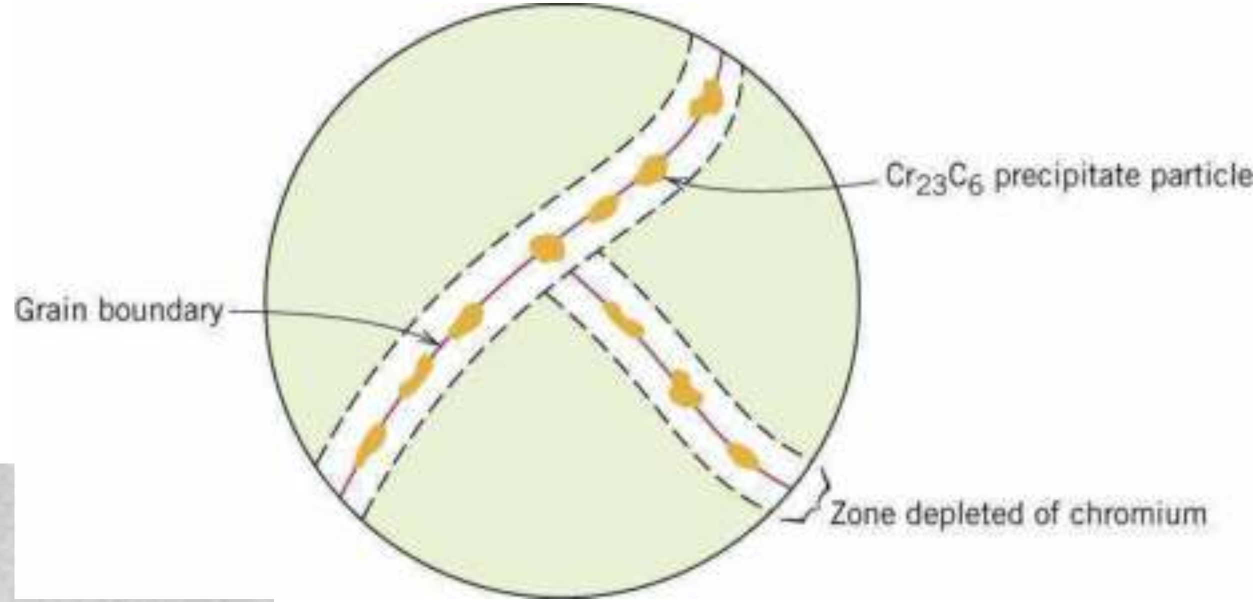
Material	Environments
Al alloys	Chlorides, moist air
Mg alloys	Chloride-chromate mixtures, moist air Nitric acid, fluorides. Sodium hydroxide
Cu alloys	Ammonia, moist air, moist sulfur dioxide
C steels	Nitrates, hydroxides, carbonates Anhydrous ammonia
Austenitic steels	Chlorides, sulfur acid
High strength steels	Moist air, water, chlorides, sulfates, sulfides
Ni alloys	Hydroxides
Ti alloys	Halides, methanol

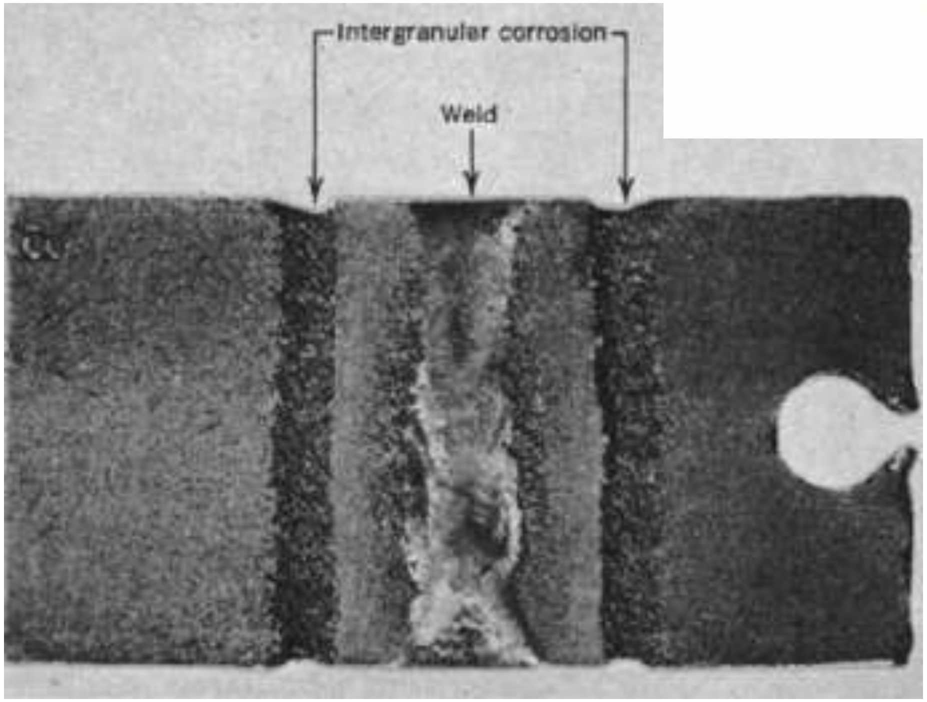
Corrosion Top Mechanisms – Environmental Cracking

- Stress Corrosion Cracking
  - Chlorides (aluminum, 300 series SS)
  - Caustic (cstl, 300 series SS, nickel alloys)
  - Ammonia (brass drain)
- Hydrogen Embrittlement
- Liquid Metal Embrittlement
  - Copper on stainless steel pipe
  - Zinc on stainless steel pipe

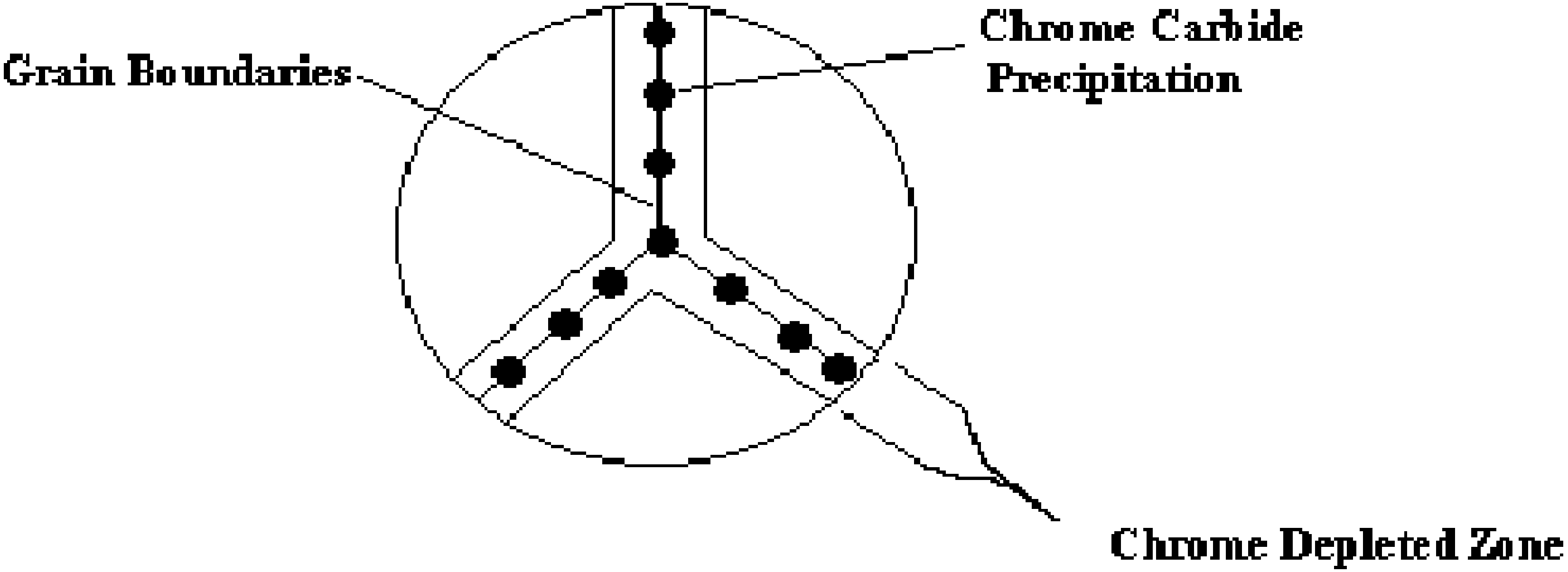
Intergranular

Corrosion along grain boundaries, often where precipitate particles form.





INTERGRANULAR CORROSION



ENVIRONMENT/ALLOY SYSTEMS SUBJECT TO STRESS CORROSION CRACKING

ALLOY	ENVIRONMENT
Aluminium Base	• Air • Seawater • Salt & Chemical Combinations
Magnesium Base	• Nitric Acid • Caustic • HF Solution • Salts • Coastal Atmospheres
Copper Base	• Primarily Ammonia & Ammonium Hydroxide • Amines • Mercury
Carbon Steel	• Caustic • Anhydrous Ammonia • Nitrate Solutions
Martensitic & Precipitation Hardening Stainless Steels	• Seawater • Chlorides • H2S Solutions
Austenitic Stainless Steels	• Chlorides Inorganic & Organic • Sulfurous & Polythionic Acids • Caustic Solutions
Nickel Base	• Caustic Above 600∟_F (315∟ C) • Fused Caustic • Hydrofluoric Acid
Titanium	• Seawater • Salt Atmospheres • Fused Salt

Corrosion Top Mechanism – Corrosion Fatigue

- Starts with an alternating stress state
- Protective oxide breaks open
- Corrosive species attack and form products
- Next cycle repeats:
  - crack growth
  - more corrosion product
  - accelerated fatigue failure
- Seen in rotating shafts

Corrosion Top Mechanism – Corrosion Fatigue

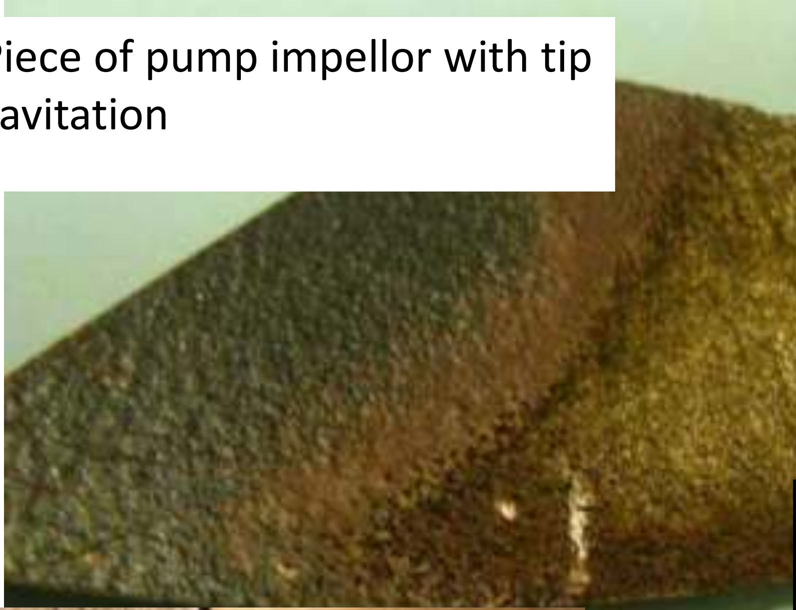
Corrosion fatigue, cracks can be oriented the other direction depending on stress state of shaft.

Corrosion Top Mechanisms – Cavitation

- Mostly found at
    - Pump impellor tips
    - Boat propellers
    - Constriction in fast fluids
- Caused by formation of low pressure bubble
- Bubble is a vacuum
- Collapse of bubble slams the metal
    - Breaking protective oxide
    - Causing great mechanical damage

Corrosion Top Mechanisms – Cavitation

Piece of pump impellor with tip cavitation



Valve trim diffuser with cavitation

Centrifuge feed nozzle

Corrosion Top Mechanism - Erosion

- Can be from
  - Gaseous vapor (steam cuts on flanges)
  - Liquid
  - Solids (Coal slurry)
- Removes the protective oxide layer faster than it can heal

Corrosion Top Mechanism - Erosion

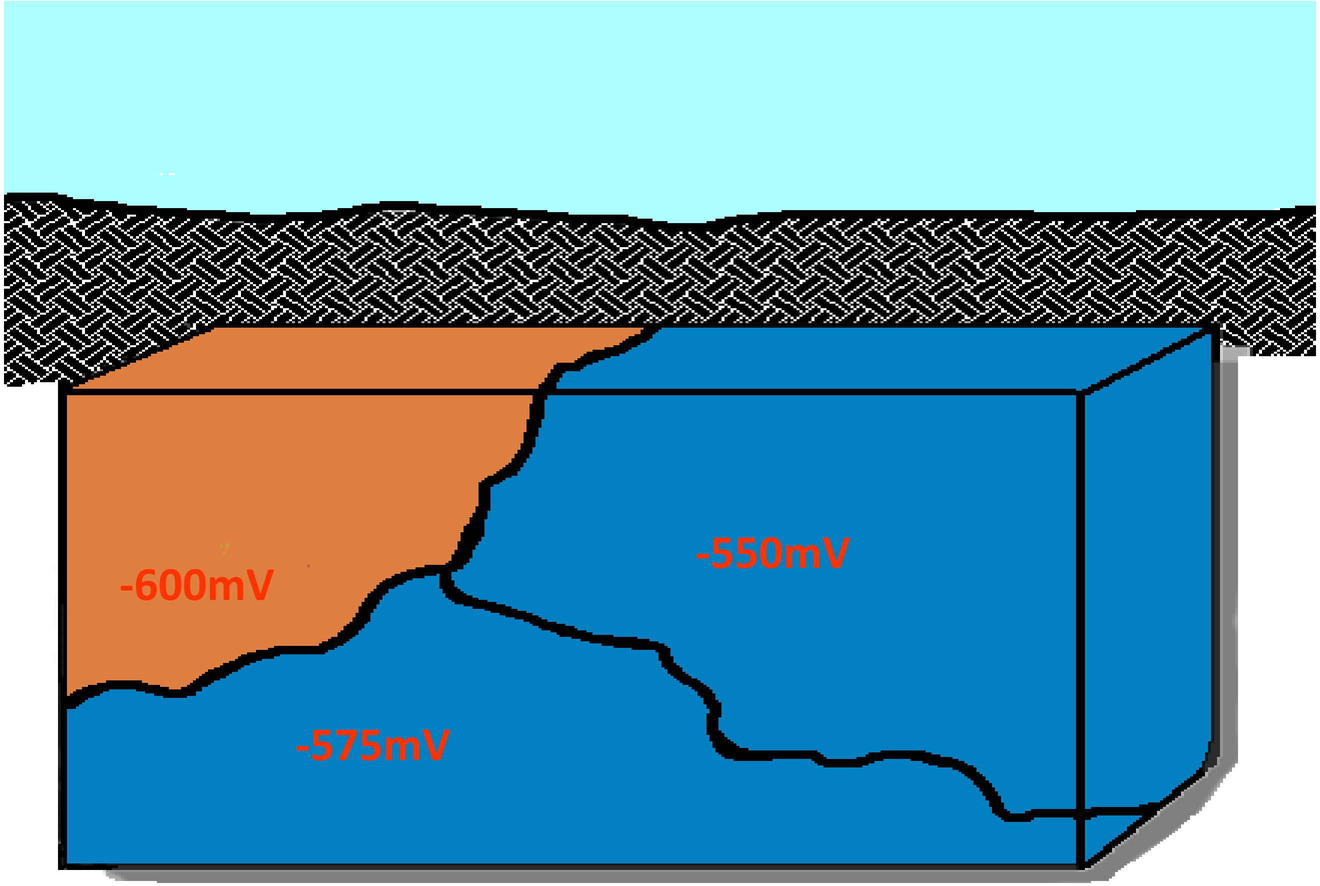
Look for “comet tails”! Water was flowing from right to left in copper water pipe.

Erosion-corrosion

Combined chemical attack and mechanical wear (e.g., pipe elbows).

Brass water pump

ELECTROCHEMICAL NATURE OF CORROSION



Potential Differences on Steel Surface

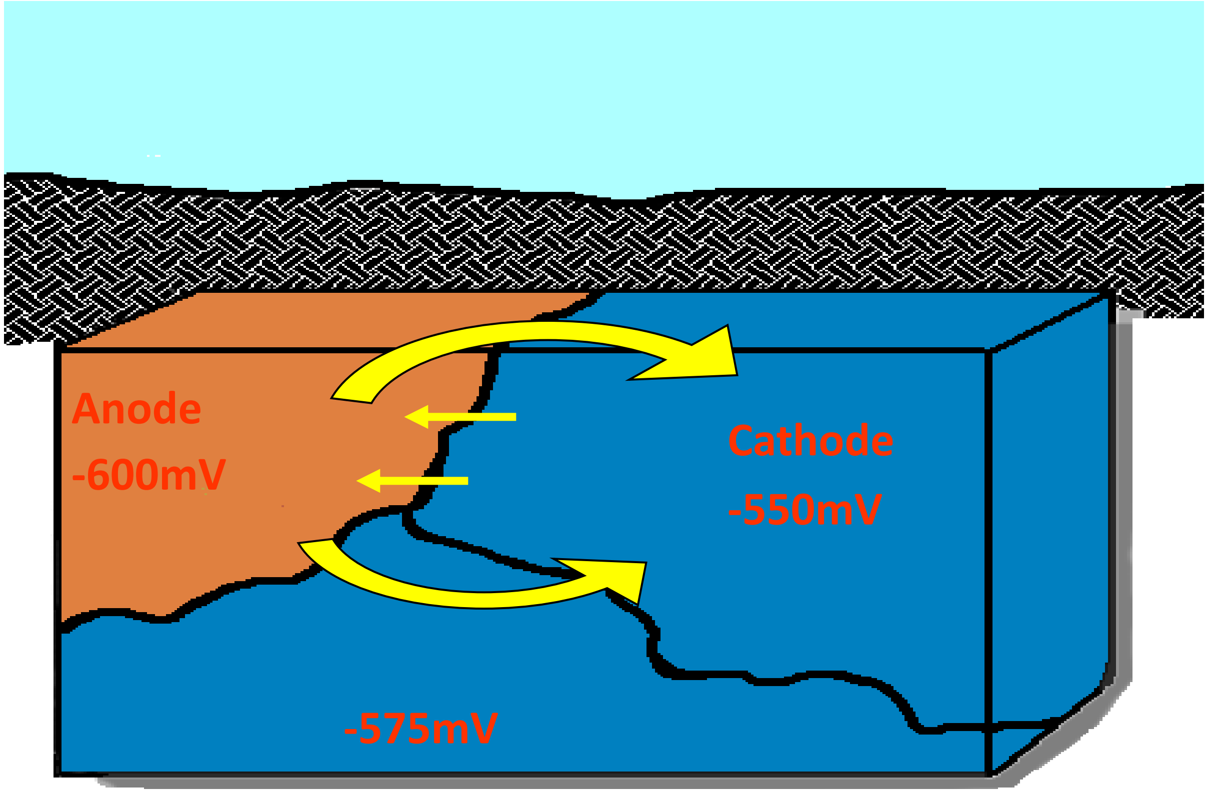
ELECTROCHEMICAL NATURE OF CORROSION

1) ANODE

2) CATHODE

3) ELECTROLYTE

4) ELECTRICAL CONNECTION



Standard EMF Series

- EMF series

more cathodic

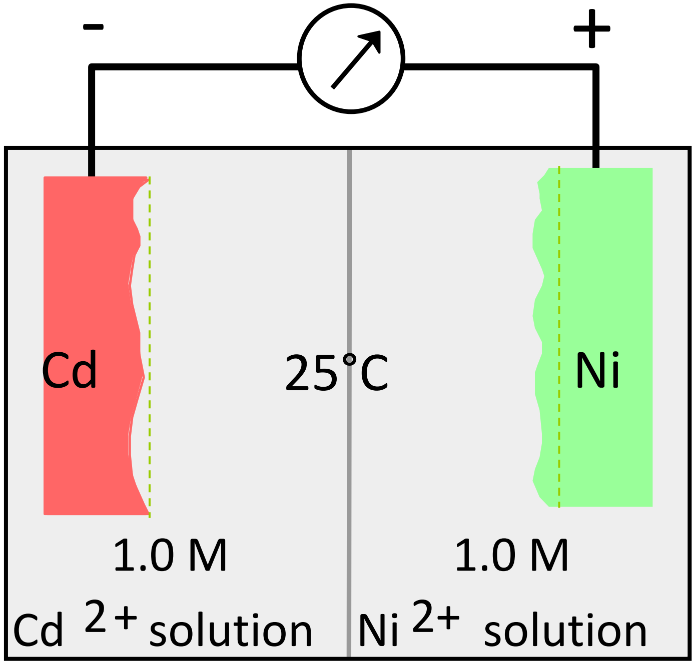
more anodic

metal	V^o_{metal}
Au	+1.420 V
Cu	+0.340
Pb	- 0.126
Sn	- 0.136
Ni	- 0.250
Co	- 0.277
Cd	- 0.403
Fe	- 0.440
Cr	- 0.744
Zn	- 0.763
Al	- 1.662
Mg	- 2.363
Na	- 2.714
K	- 2.924

$\Delta V^o = 0.153V$

- Metal with smaller V^o_{metal} corrodes.
- Ex: Cd-Ni cell

$V^o_{Cd} < V^o_{Ni}$ ∴ Cd corrodes

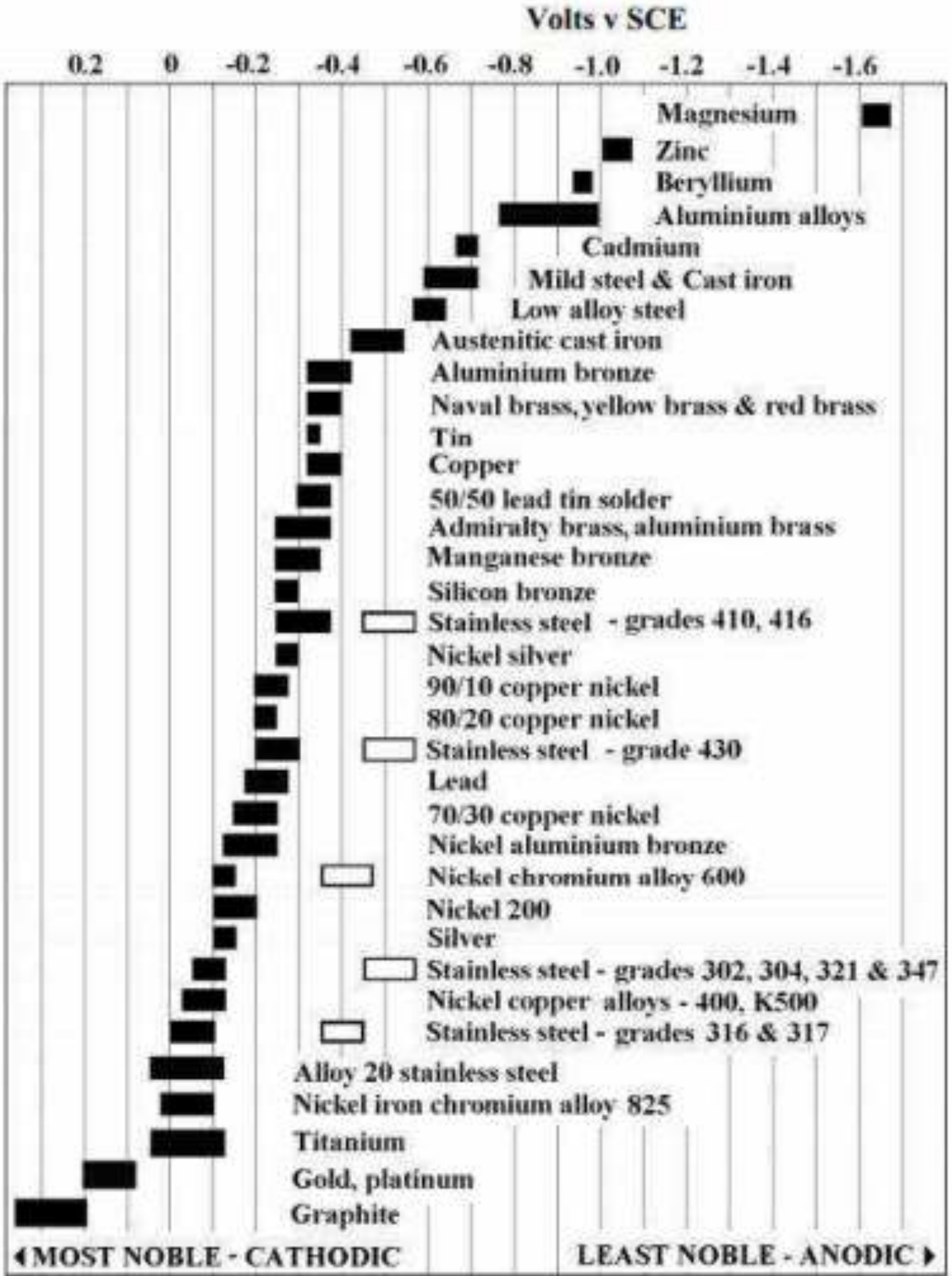


Driving force

- A driving force is necessary for electrons to flow between the anodes and the cathodes.
- The driving force is the difference in potential between the anodic and cathodic sites.
- This difference exists because each oxidation or reduction reaction has associated with it a potential determined by the tendency for the reaction to take place spontaneously. The potential is a measure of this tendency.

Aqueous Corrosion

The Galvanic Series as a Guide to Metal Selection



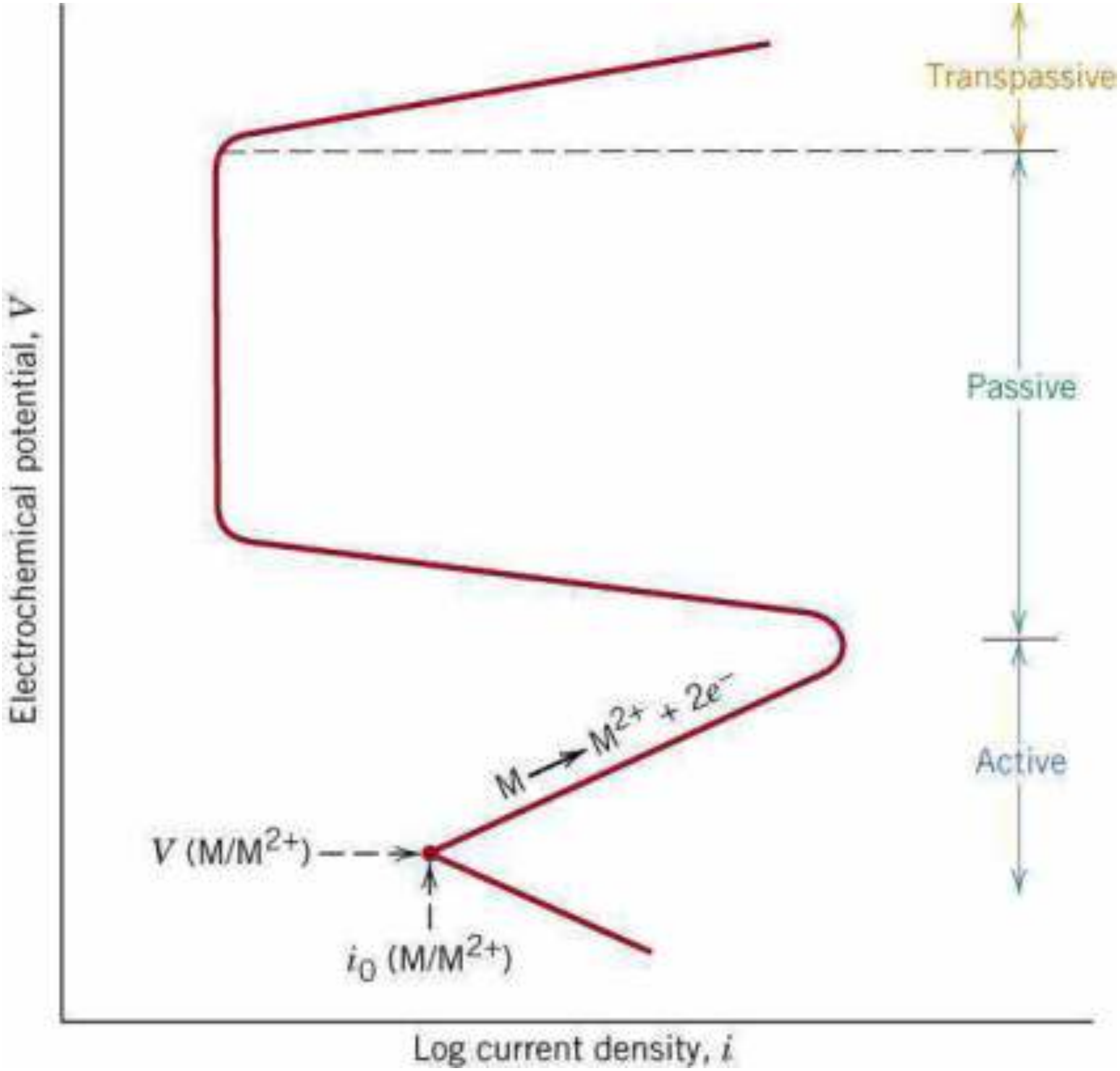
Source: Atlas Steels Technical Note No.7

PRACTICAL GALVANIC SERIES

Material	Potential*
Pure Magnesium	-1.75
Magnesium Alloy	-1.60
Zinc	-1.10
Aluminum Alloy	-1.00
Cadmium	-0.80
Mild Steel (New)	-0.70
Mild Steel (Old)	-0.50
Cast Iron	-0.50
Stainless Steel	-0.50 to + 0.10
Copper, Brass, Bronze	-0.20
Titanium	-0.20
Gold	+0.20
Carbon, Graphite, Coke	+0.30

* Potentials With Respect to Saturated Cu-$CuSO_4$ Electrode

Anodic Polarization Curve -1



- This curve is usually scanned from 20 mV below the E_{oc} (open circuit potential) upward.
- The curve can be used to identify the following corrosion regions:

i_p - passive current density

E_{pp} - primary passivation potential

i_{crit} - critical current density

E_{trans} - transpassive potential

CORROSION ASSESSMENT AND MONITORING

Corrosion Assessment

Without corrosion assessment, mitigating or eliminating corrosion in any industry is almost impossible.

Corrosion testing is one of a corrosion engineer's most important responsibilities. In fact, without corrosion assessment, mitigating or eliminating corrosion in any industry is almost impossible.

There are several reasons for corrosion examination. Sometimes, in a materials selection process for an industrial application, an evaluation of different kinds of materials in a specific environment is required. The assessment of a new type of alloy in different types of environments to compare with conventional commercial alloys; an estimation of inhibitors' efficiency in reducing the corrosion rate of metals; and understanding the mechanism of corrosion are the other reasons.

Corrosion tests are usually divided into two main categories: laboratory tests and field tests, each of which has its merits and demerits. For example, the environmental conditions present in real-world applications are different to those in laboratory situations. Therefore, it is difficult to extrapolate the results of laboratory tests to industry settings. On the other hand, in laboratory tests, it is possible to accelerate the corrosivity of the environment to obtain results more rapidly, something that is impossible in field testing.

Corrosion Assessment

Laboratory Corrosion Tests

Immersion Testing

One of the most common and simplest methods in laboratory tests is the immersion test. In this kind of test, whose procedure is clarified by ASTM and NACE, the weights of dried test specimens are measured by an analytical balance before and after being exposed to a corrosive environment for a specific period of time. Before and after samples are weighed, specific preparation should be carried out to remove any corrosion product or organic contaminants. The corrosion resistance of the samples is generally calculated as the corrosion rate in terms of weight loss or thickness loss in mils (0.001 inch) per year (mpy) or millimeters per year (mm/yr). The results depend on the type of metal (specific weight) being tested, the exposed surface area, and test duration factors.

Visual Examination

Some visual examination is also suggested to evaluate localized corrosion like pitting or exfoliation. Furthermore, optical or scanning electron microscopes; elemental and compositional analyses such as energy dispersive X-ray spectroscopy (EDX); X-ray diffraction (XRD); and energy dispersive X-ray spectroscopy (XPS) are useful techniques to evaluate the corroded surface and corrosion product more precisely.

Corrosion Assessment

Laboratory Corrosion Tests

Immersion Tests

Visual Observations

Corrosion Assessment

Laboratory Corrosion Tests

Visual Examination

There are several ways to evaluate the pitting corrosion of tested samples. Determining the density of pits (number of pits in a specific surface area) or pitting factor (ratio of depth of deepest pit divided by the value of thickness loss due to uniform corrosion) are two important methods to evaluate pitting corrosion. There are different types of practical tools to measure pit depth. A contour gage can be used to achieve a profile of pit depth when it is impossible to use pit gages.

Salt Spray / Fog Testing

Some test samples and procedures are designed to assess specific kinds of corrosion, such as crevice corrosion, stress-corrosion cracking, and erosion corrosion. The atmospheric corrosion of coated samples can be examined by salt spray or fog testing. Here, a 5% NaCl solution is atomized in a chamber at a temperature adjusted to 95°F (35°C). The time that samples can resist against corrosion is the criterion used to understand test sample durability. Although the environment in a salt spray test is a kind of accelerated marine atmosphere, it is accepted that the salt spray results could extrapolate to other atmospheric environments.

Corrosion Assessment

Salt Spray Test Chamber

Weathering Test Chamber

Corrosion Assessment

Laboratory Corrosion Tests

The Weathering Test

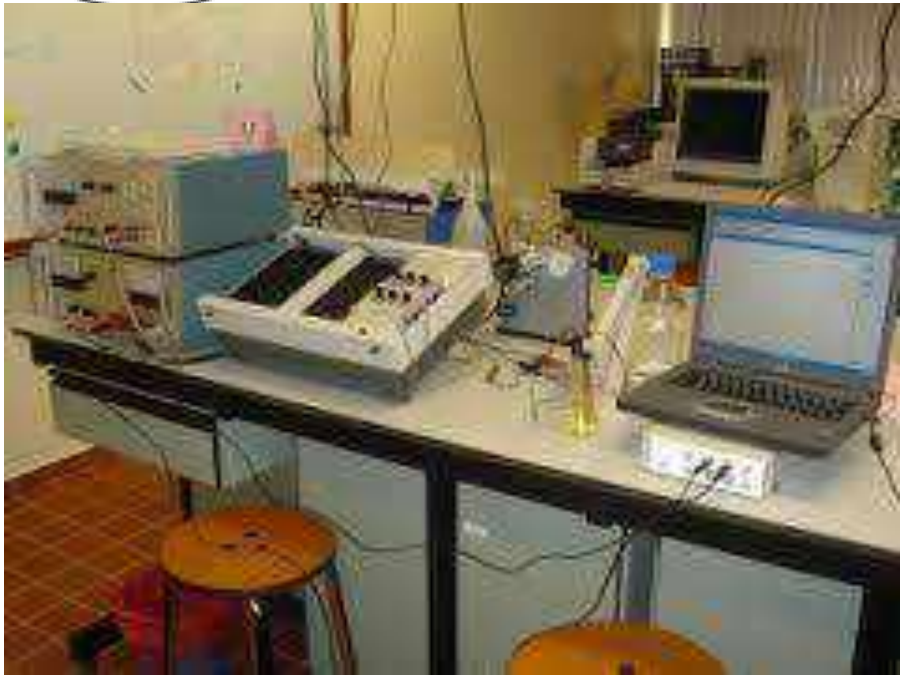
In another atmospheric method called the weathering test, the durability of organic, paint-coated samples is examined by exposing them to UV light and cyclic cooling-heating along with a corrosive environment.

Electrochemical Testing

Electrochemical tests are the other category of laboratory tests that can provide valuable information about corrosion electrochemical reactions and the mechanisms behind them. Apotentiostat instrument is usually used to perform this sort of test. A three-electrode setup, including working electrode, reference electrode, and counter (auxiliary) electrode, are usually used. Potential, current, and time are three important parameters in electrochemical tests. In these tests, an applied potential generally scans in a certain range and the current is measured.

There are various types of electrochemical corrosion tests. Each of them is used for a particular purpose.

Corrosion Assessment



Electrochemical Tests using Potentiostat/Galvanostats

Corrosion Assessment

Laboratory Corrosion Tests

Electrochemical Testing

Linear Polarization Resistance (LPR):

The simplest electrochemical corrosion test islinear polarization resistance, in which current is measured when the applied potential scans in a narrow range (~20 mV) from lower to higher than corrosion potential (E_{corr}). The slope of the current versus the potential curve shows the polarization resistance, which is inversely related to the corrosion rate. This test is very fast and straightforward, and is usually accepted as a kind of non-destructive test. Moreover, this method is very useful to measure extremely low corrosion rates. This is important in some industrial systems such as food processing, nuclear, and pharmaceutical equipment

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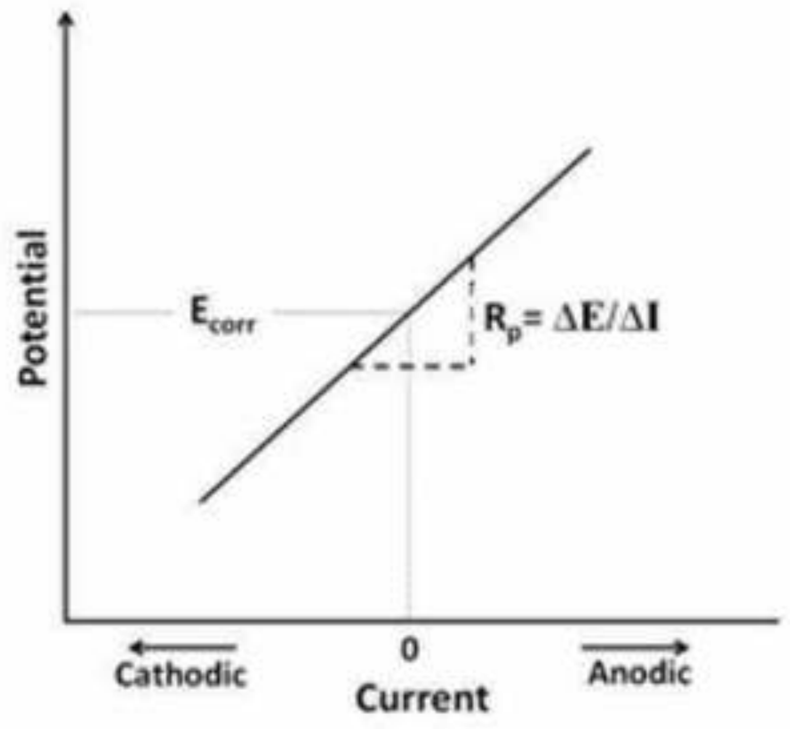
Corrosion Assessment

Laboratory Corrosion Tests

Electrochemical Testing

Linear Polarization Resistance (LPR):



This image shows the LPR curve. The slope of the line shows polarization resistance(Rp).

Corrosion Assessment

Laboratory Corrosion Tests

Electrochemical Testing

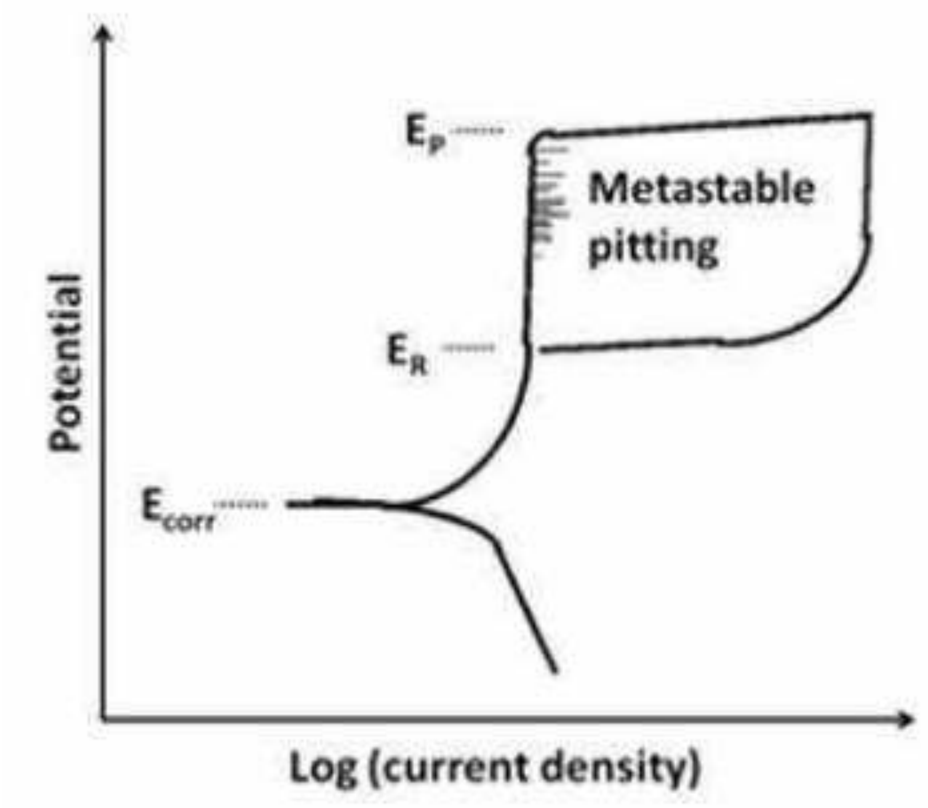
Potentiodynamic Polarization Tests: The passivation behavior of active-passive metals, like stainless steels, can be evaluated by potentiodynamic polarization tests. In this method, the potential scans in a wide range. Critical current density, passive potential, and passive current density can be extracted from this test.

Cyclic Polarization Method: This is the other kind of test that is used to determine the tendency of active-passive metals to localized crevice or pitting corrosion. In this test, the sweeping direction of applied potential is reversed at some potential in the transpassive region. The intersection between forward and backward scans shows the tendency and intensity of localized corrosion.

Corrosion Assessment

Laboratory Corrosion Tests

Electrochemical Testing



This image shows the cyclic polarization curve, which is used to evaluate pitting corrosion. Less E_R and a bigger metastable pitting loop shows more susceptibility to pitting corrosion.

Corrosion Assessment

Laboratory Corrosion Tests

Electrochemical Testing

The Electrochemical Potentiodynamic Reactivation (EPR) Test:
This is the other test that has been suggested to predict the tendency of stainless steels to sensitization or intergranular corrosion. Electrochemical potentiodynamic reactivation is very simple and fast in comparison to other conventional intergranular corrosion tests that are suggested by ASTM A-262, such as Huey or Streicher.

The abovementioned electrochemical tests are conducted under DC conditions. However, understanding the Helmholtz double layer (which can act as a capacitance) or adsorption of inhibitors on the metallic surface (which can act as an inductance) requires alternative currents. This type of test is called Electrochemical Impedance Spectroscopy (EIS), and can reveal valuable information about corrosion mechanisms. Moreover, this technique is very useful when the overall electrical resistance in the electrochemical system is very high, such as when a sample is covered by thick organic coatings or is immersed in organic solutions.

Corrosion Assessment

Field Corrosion Tests

Corrosion Coupons

Installing corrosion coupons is a very simple and common method for monitoring corrosion in pipelines, heat exchangers and storage tanks. The coupons are inserted into a plant or equipment with a coupon holder for a period of time. Although many factors can influence the location of coupon installation, the coupons are usually placed in locations where severe corrosion is expected. The change in weight and size or visual inspection will be considered after retrieving the coupons. The drawback to this method is that it is impossible to accelerate the environmental conditions to achieve faster results.

Ultrasonic Thickness Monitoring

An ultrasonic thickness (UT) gage is one of the instruments used to monitor the internal corrosion of pipelines or storage tanks. The ultrasonic sound wave, which is produced by an ultrasonic transducer, traverses to the back wall and reflects back to the source, making it possible to calculate the thickness of metal by measuring the reflection time and considering the velocity of sound waves in tested material. The UT gage test is useful when there is no access to both sides of a test specimen.

Corrosion Assessment

Corrosion rate meter

Corrosion Coupons

UT Testing for Corrosion

Corrosion Assessment

Field Corrosion Tests

Electrical Resistance Testing

Electrical resistance (ER) probes are used to measure the corrosion rate of coupons, especially when the on-line corrosion rate in required. When a metal corrodes in an environment, its electrical resistance will increase due to a reduction in the thickness or surface area of a cross-section. By measuring the change in electrical resistance of metal over time, the rate of metal dissolution can be determined and the corrosion rate can be calculated in mpy or mm/yr. The ER probes can be used in any kind of environment, including aqueous solutions, oil (hydrocarbons), soil, gas, and atmosphere. The probe can be produced in various geometries depending on the type of metals, system, and environment being tested.

There are many other tests that are used to monitor the structures protected against corrosion by cathodic protection. Most of these tests are based on the measurement of the electrochemical potential of structure versus environment.

Corrosion Assessment

Pipe to soil potential measurement

Electrical Resistance Probes

Corrosion Monitoring

Introduction to Corrosion Monitoring

What is Corrosion Monitoring?

The field of corrosion measurement, control, and prevention covers a very broad spectrum of technical activities. Within the sphere of corrosion control and prevention, there are technical options such as cathodic and anodic protection, materials selection, chemical dosing and the application of internal and external coatings. Corrosion measurement employs a variety of techniques to determine how corrosive the environment is and at what rate metal loss is being experienced. Corrosion measurement is the quantitative method by which the effectiveness of corrosion control and prevention techniques can be evaluated and provides the feedback to enable corrosion control and prevention methods to be optimized.

Corrosion Monitoring

A wide variety of corrosion measurement techniques exists, including:

Non Destructive Testing
- Ultrasonic testing
- Radiography
- Thermography
- Eddy current/magnetic flux
- Intelligent pigs

Operational Data
- pH
- Flow rate (velocity)
- Pressure
- Temperature

Corrosion Monitoring
- Weight loss coupons
- Electrical resistance
- Linear polarization
- Hydrogen penetration
- Galvanic current

Analytical Chemistry
- pH measurement
- Dissolved gas (O_2, CO_2, H_2S)
- Metal ion count (Fe^{2+}, Fe^{3+})
- Microbiological analysis

Fluid Electrochemistry
- Potential measurement
- Potentiostatic measurements
- Potentiodynamic measurements
- A.C. impedance

Corrosion Monitoring

Some corrosion measurement techniques can be used on-line, constantly exposed to the process stream, while others provide off-line measurement, such as that determined in a laboratory analysis. Some techniques give a direct measure of metal loss or corrosion rate, while others are used to infer that a corrosive environment may exist.

Corrosion monitoring is the practice of measuring the corrosivity of process stream conditions by the use of “probes” which are inserted into the process stream and which are continuously exposed to the process stream condition. Corrosion monitoring “probes” can be mechanical, electrical, or electrochemical devices.

Corrosion monitoring techniques alone provide direct and online measurement of metal loss/corrosion rate in industrial process systems.

Typically, a corrosion measurement, inspection and maintenance program used in any industrial facility will incorporate the measurement elements provided by the four combinations of on-line/off-line, direct/indirect measurements.

Corrosion Monitoring

• Corrosion Monitoring	Direct, On-line
• Non Destructive Testing	Direct, Off-line
• Analytical Chemistry	Indirect, Off-line
• Operational Data	Indirect, On-line

Corrosion Monitoring

The Need for Corrosion Monitoring

The rate of corrosion dictates how long any process equipment can be usefully and safely operated. The measurement of corrosion and the action to remedy high corrosion rates permits the most cost effective plant operation to be achieved while reducing the life-cycle costs associated with the operation.

Corrosion monitoring techniques can help in several ways:

(1) by providing an early warning that damaging process conditions exist which may result in a corrosion induced failure.

(2) by studying the correlation of changes in process parameters and their effect on system corrosivity.

(3) by diagnosing a particular corrosion problem, identifying its cause and the rate controlling parameters, such as pressure, temperature, pH, flow rate, etc.

(4) by evaluating the effectiveness of a corrosion control/prevention technique such as chemical inhibition and the determination of optimal applications.

(5) by providing management information relating to the maintenance requirements and ongoing condition of plant.

Corrosion Monitoring

Corrosion Monitoring Techniques

A large number of corrosion monitoring techniques exist. The following list details the most common techniques which are used in industrial applications:

- Corrosion Coupons (weight loss measurements)
- Electrical Resistance (ER)
- Linear Polarization Resistance (LPR)
- Galvanic (ZRA)
- Hydrogen Penetration
- Microbial
- Sand/Erosion

CORROSION CONTROL BASICS

Corrosion Control

Introduction

Corrosion of metals causes damages worth millions, of Rupees both in terms of direct losses and indirect losses due to outage in the industry. Many instances corrosion could lead to severe disasters, which could cause loss of precious lives. The basic aim of all corrosion studies is to minimize losses due to corrosion both to human life and to costly equipment. Corrosion control or prevention methods are employed in various industries to achieve this objective.

The important means of controlling or preventing corrosion are discussed below. The choice of corrosion control method to be employed depends on (not necessarily in order of preference)

- Nature of corrosion
- Criticality of corrosion problem
- Economics of controlling
- Technology available
- Effect on other material/equipment in the system/industry
- Nature of effluents likely to be discharged.
- Effect of control measure on the process etc.

Corrosion Control

Selection of Alloy/Material:

The most common method of preventing corrosion is the selection of the proper metal or alloy for a particular corrosive service. One of the most popular misconceptions to those not familiar with metallurgy or corrosion engineering, concerns the uses and characteristics of stainless steel. Stainless steel is the generic name for a series of different alloys containing 11.5 to 30% chromium and 0 to 22% nickel together with other alloy additions. Though highly corrosion resistant in most of the common environments in service, they are more susceptible to localized corrosion such as intergranular corrosion attack than the ordinary steels.

In alloy selection, there are several "natural" metal corrosive combinations. These combinations of metal and corrosives usually represent the maximum amount of corrosion resistance for the least amount of money..

There are some general but usually accurate rules, which may be applied to the resistance of metals and alloys. For reducing or non-oxidizing environments such as air-free acids and aqueous solutions, nickels, copper and their alloys are frequently employed. For oxidizing condition, chromium-containing alloys are used, for extremely powerful oxidizing conditions, titanium and its alloys have shown superior resistance.

Corrosion Control

Alteration of Environments:

Changing Mediums

Altering the environment provides a versatile means for reducing corrosion. Typical changes in the medium that are often employed are (1) Lowering temperature (2) decreasing velocity (3) removing oxygen or oxidizers and (4) changing concentration. In many cases, these changes can significantly reduce corrosion, but they must be done with care.

Lowering temperature

This usually causes a pronounced decrease in corrosion rate. However, under some conditions, temperature changes have little effect on corrosion rate. In other cases, increasing temperature decreases attack. This phenomenon occurs as hot fresh or salt water is raised to the boiling point and is the result of the decrease in oxygen solubility with temperature.

Decreasing Velocity

This is often used as practical method of corrosion control. Velocity generally increases corrosive attack, although there are some important exceptions. Metals and alloys that passivate such as stainless steels generally have better resistance to flowing mediums than stagnant solutions. Very high velocities should be always avoided where possible, because of erosion-corrosion effects.

Corrosion Control

Alteration of Environments:

Removing Oxygen or oxidizers:

This is a very old corrosion-control technique. Boiler feed water was de-aerated by passing it through a large mass of scrap steel. In modern practice this is accomplished by vacuum treatment, inert gas purging, or through the use of oxygen scavengers. Hydrochloric acid containing iron ($Fe\ Cl_3$), as impurity is highly corrosive to nickel molybdenum alloys (hastalloy B, Chlorimet 2) which is otherwise highly corrosion resistant to pure hydrochloric acid. Although Dearation finds vide spread application, it is not recommended for active-passive metals or alloys. These materials require oxidizers to form and maintain their protective films and usually possess poor resistance to reducing or non- oxidizing environments.

Changing concentration:

Decreasing corrosive concentration is usually effective. In many processes, the presence of corrosive is an accidental. Many acids, such as sulphuric and phosphoric are virtually inert at high concentrations at moderate temperatures. In these cases, increasing acid concentration can reduce corrosion.

Corrosion Control

Alteration of Environments:

Inhibitors:

An inhibitor is a substance which, when added in small concentration to an environment, decreases the corrosion rate. In a sense, an inhibitor can be considered as a retarding catalyst. There are numerous inhibitor types and compositions. The broad classification of inhibitors is as follows:

Adsorption type inhibitors :

These represent the largest class of inhibiting substances. In general, these are organic compounds that adsorb on the metal surface and suppress metal dissolution and reduction reactions. In most cases it appears that adsorption inhibitors affect both the anodic and cathodic processes, although in many cases the effect is unequal. Typical examples of this type are the organic amines.

Hydrogen-evolution reaction :

These substances such as arsenic and antimony ions specifically retard the hydrogen evaluation reaction. As a consequence, these substances are very effective in acid solutions but are in effective in environments where other reduction processes such as oxygen reduction are the controlling cathodic reactions.

Corrosion Control

Alteration of Environments:

Scavengers:

These substance act by removing corrosive reagents from solution. Example of this type of inhibitor are sodium sulfite and hydrazine which remove dissolved oxygen from aqueous solutions as indicated in following equations:

$$2\,Na_2SO_3 + O_2 \longrightarrow 2\,Na_2SO_4$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

It is apparent that such inhibitors will work very effectively in solutions where oxygen reduction is the controlling corrosion cathodic reaction but will not be effective in strong acid solutions.

Oxidizers:

Such substances as chromate, nitrate and ferric salts also act as inhibitors in many systems. In general, they are primarily used to inhibit the corrosion of metals and alloys, which demonstrate active-passive transitions. Such as iron and its alloys and stainless steels.

Corrosion Control

Alteration of Environments:

Vapour Phase Inhibitors:

These are very similar to the organic adsorption type inhibitors and possess a very high vapour pressure. As a consequence, these materials can be used to inhibit atmospheric corrosion of metals without being placed in direct contact with the metal surface. In use, such inhibitors are placed in the vicinity of the metal to be protected, and sublimation and condensation transfer them to the metal surface. The vapour phase inhibitors are usually only effective if used in closed spaces such as inside packages or on the interior of machinery during shipment. These are also known as temporary rust preventives, though there are other substances also which act as temporary rust preventives to metals and alloys under shipment and storage.

Design:

The design of a structure is frequently as important as the choice of materials of construction. Design should consider mechanical and strength requirements together with an allowance for corrosion. In all cases, the mechanical design of a component should be based on the material of construction. This is important to recognize, since materials of construction used for corrosion resistance very in their mechanical characteristics.

Corrosion Control

Design:

Wall thickness:

Since corrosion is a penetrating action, it is necessary to make allowances for this reduction in thickness in designing pipes tanks and other components. In general, wall thickness is usually made twice the thickness that would give the desired life. Such a design factor allows for some variation in the depth of penetration during uniform corrosion. Which in most cases is not completely uniform.

Design rules:

Some important design rules for best corrosion resistance are as follows:

- Weld rather than rivet tanks and other containers riveted joints provide sites for crevice corrosion,
- Design tanks and other containers for easy draining and easy cleaning. Tank bottom should be sloped toward drain holes so that liquids cannot collect after the tank is emptied.
- Design systems for the easy replacement of components that are expected to fail rapidly in service.
- Avoid excessive mechanical stresses and stress concentrations in components exposed to corrosive mediums. Mechanical or residual stresses are one of the requirements for stress corrosion cracking.

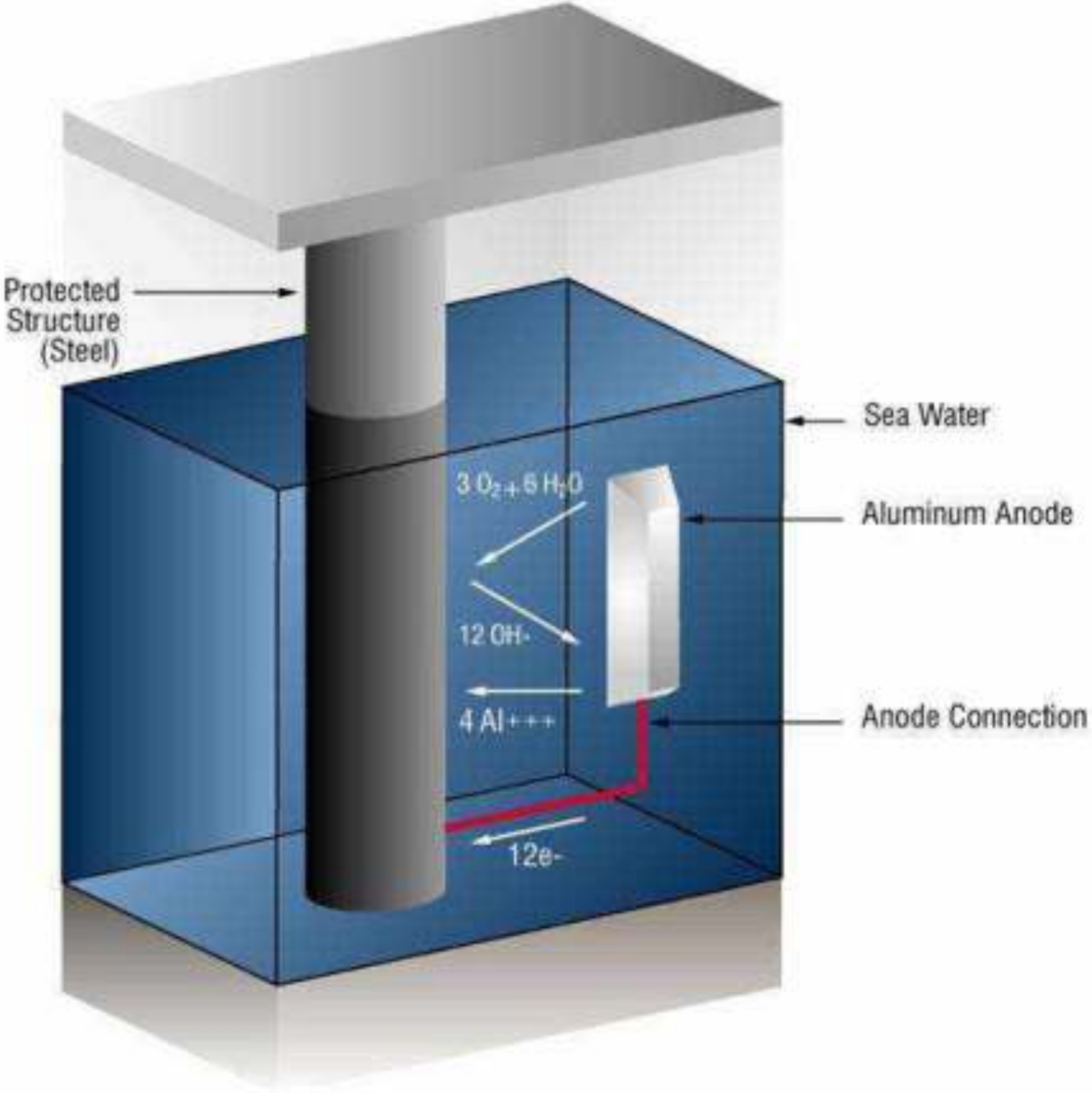
Corrosion Control

Design:

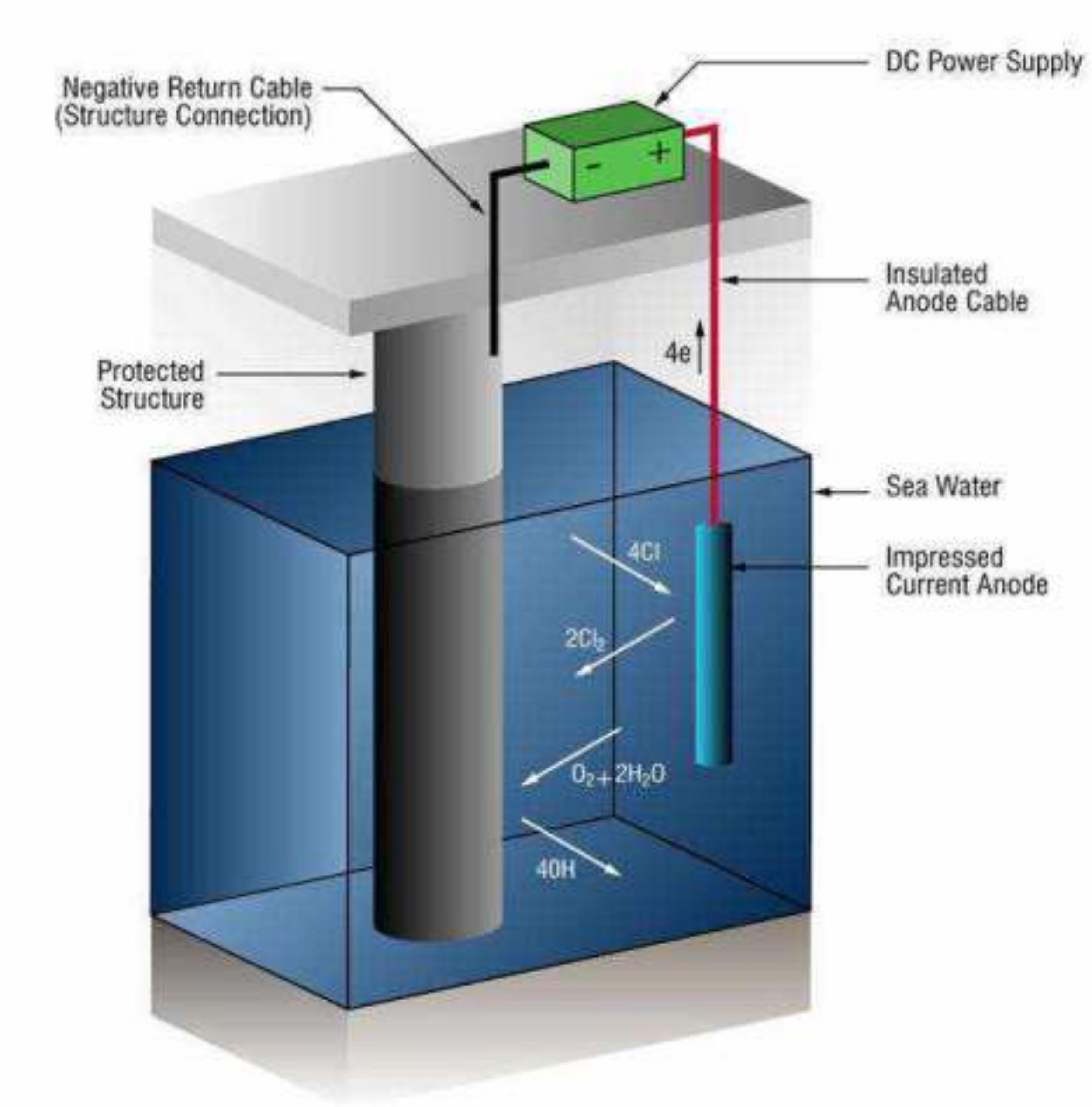
Design rules:

- Avoid electric contact between dissimilar metals to prevent galvanic corrosion. If possible, use similar materials through out the entire structure, or insulate difference materials from one another
- Avoid sharp bends in piping systems. Sharp bends and other areas where fluid direction changes rapidly tend to promote erosion-corrosion. This is particularly important in systems susceptible to erosion-corrosion such as lead, copper and their alloys.
- Avoid hot spots during heat transfer operations, uneven temperatures distribution leads to local heating and high corrosion rates. Further, hot spots tend to produce stresses that may produce stress corrosion cracking failures.
- Design to exclude air. Oxygen reduction is one of the most common cathodic reactions during corrosion and if oxygen is eliminated, corrosion can often be reduced or prevented, and active passive metals are exception.
- The most general rule for design is to avoid heterogeneity. Dissimilar metals, Vapour spaces, uneven heat and stress distributions, and other differences between point in the system lead to corrosion damage. Hence in design attempt to make all conditions as uniform as possible throughout the entire system.

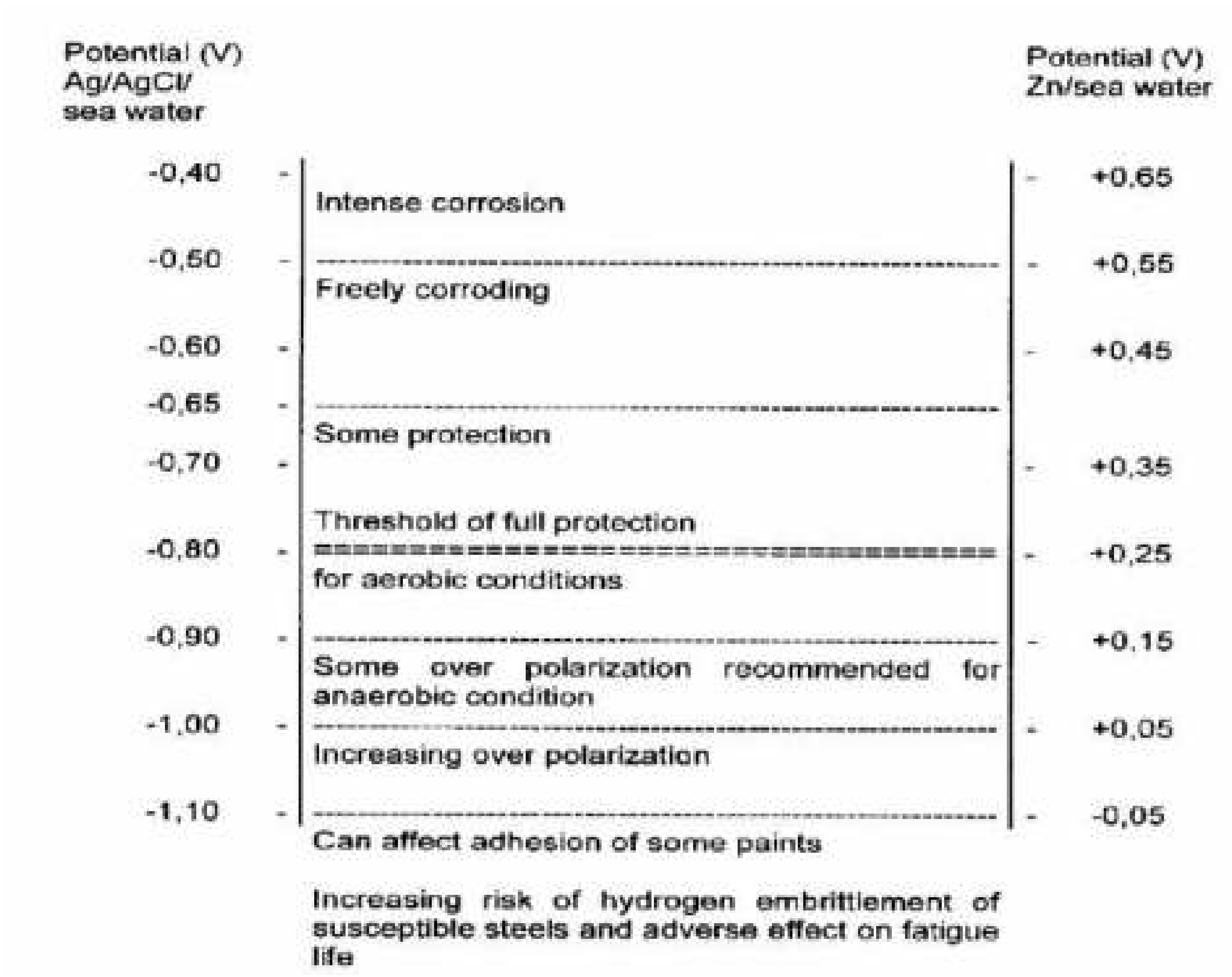
FUNDAMENTALS OF CATHODIC PROTECTION



FUNDAMENTALS OF CATHODIC PROTECTION



FUNDAMENTALS OF CATHODIC PROTECTION



Potential (V) Ag/AgCl/ sea water		Potential (V) Zn/sea water
-0,40	Intense corrosion	+0,65
-0,50	Freely corroding	+0,55
-0,60		+0,45
-0,65	Some protection	
-0,70		+0,35
-0,80	Threshold of full protection for aerobic conditions	+0,25
-0,90	Some over polarization recommended for anaerobic condition	+0,15
-1,00	Increasing over polarization	+0,05
-1,10	Can affect adhesion of some paints	-0,05
	Increasing risk of hydrogen embrittlement of susceptible steels and adverse effect on fatigue life	

Corrosion & Electrode Potential (Source: BS EN 12473 – General Principles of Cathodic Protection in Seawater)

FUNDAMENTALS OF CATHODIC PROTECTION

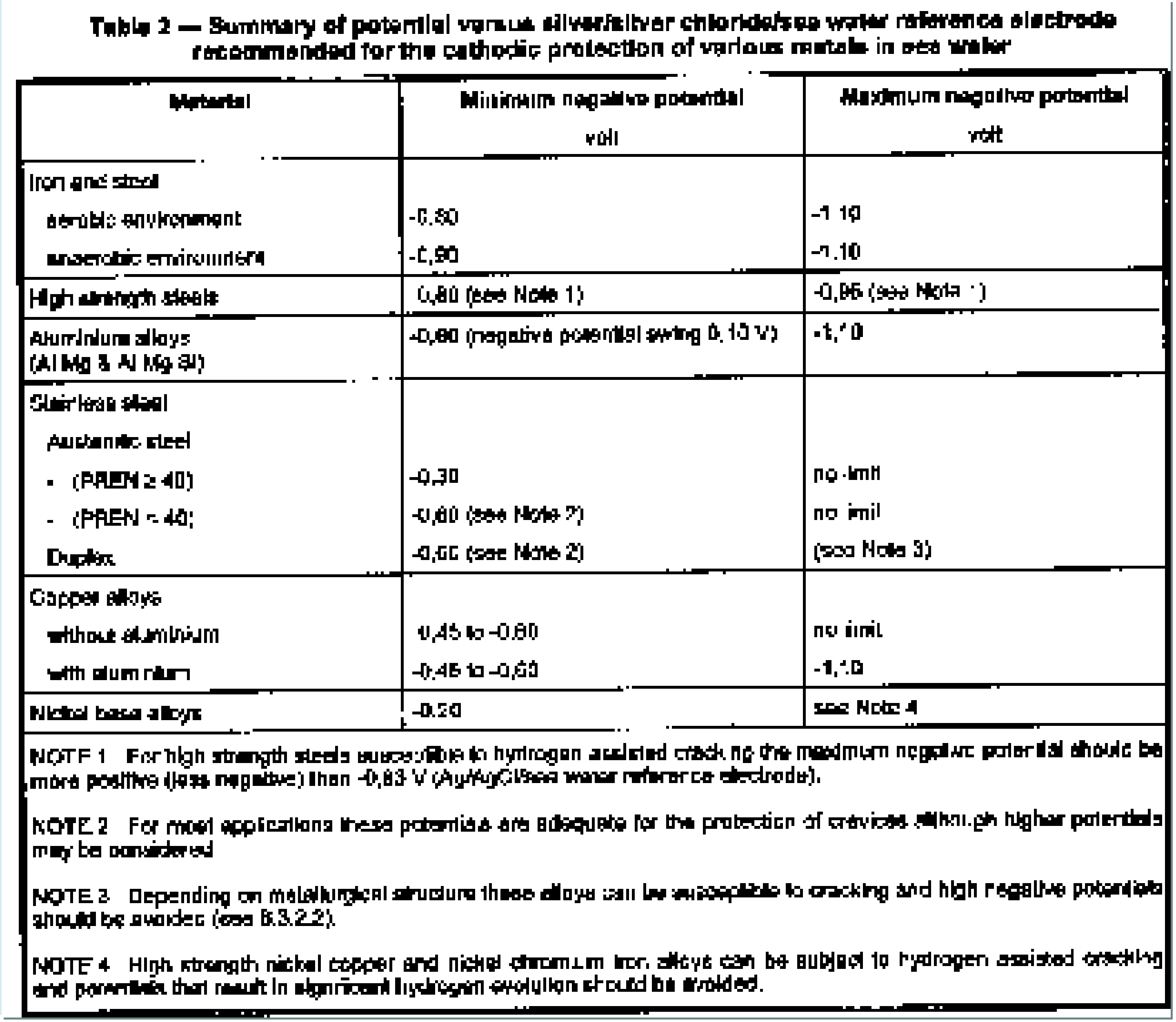


Table 2 — Summary of potential versus silver/silver chloride/sea water reference electrode recommended for the cathodic protection of various metals in sea water

Material	Minimum negative potential volt	Maximum negative potential volt
Iron and steel		
aerobic environment	-0,80	-1,10
anaerobic environment	-0,90	-1,10
High strength steels	-0,80 (see Note 1)	-0,95 (see Note 1)
Aluminium alloys (Al Mg & Al Mg Si)	-0,80 (negative potential swing 0,10 V)	-1,10
Stainless steel		
Austenitic steel		
- (PREN ≥ 40)	-0,30	no limit
- (PREN < 40)	-0,60 (see Note 2)	no limit
Duplex	-0,60 (see Note 2)	(see Note 3)
Copper alloys		
without aluminium	-0,45 to -0,60	no limit
with aluminium	-0,45 to -0,60	-1,10
Nickel base alloys	-0,20	see Note 4

NOTE 1 For high strength steels susceptible to hydrogen assisted cracking the maximum negative potential should be more positive (less negative) than -0,83 V (Ag/AgCl/Sea water reference electrode).

NOTE 2 For most applications these potentials are adequate for the protection of crevices although higher potentials may be considered.

NOTE 3 Depending on metallurgical structure these alloys can be susceptible to cracking and high negative potentials should be avoided (see 6.3.2.2).

NOTE 4 High strength nickel copper and nickel chromium iron alloys can be subject to hydrogen assisted cracking and potentials that result in significant hydrogen evolution should be avoided.

Corrosion & Electrode Potential (Source: BS EN 12473 – General Principles of Cathodic Protection in Seawater)

Corrosion Control

Electrochemical Protection:

Anodic Protection:

Anodic protection is based on the principle of formation of a protective film on metals by externally applied-anodic currents. Considering equations given under cathodic protection, it appears that the application of anodic current to a structure should tend to increase the dissolution rate of a metal and decrease the rate of hydrogen evolution. This usually does occur except for metals with active-passive transitions such as nickel, iron chromium titanium and their alloys. If carefully controlled. Anodic currents are applied to these materials, they are passivated and the rate of metal dissolution is decreased. To anodically protect a structure, a device called a Potentiostat is required. A Potentiostat is an electronic device, which maintains a metal at a constant potential with respect to a reference electrode. The Potentiostat has three terminals, one is connected to the structure to be protected, another to an auxiliary cathode (a platinum or platinum clad electrode) and the third to a reference electrode (e.g. saturated calomel electrode). In operation, the Potentiostat maintains a constant potential between the structure and the reference electrode. The optimum potential for protection is determined by electrochemical measurements.

Although anodic protection is limited to passive metals and alloys, most structural materials contain these elements. The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low current requirements.

Corrosion Control

COATINGS:

Surface preparation:

Surface preparation is a critical part of the coatings operation and must provide a surface that is compatible with the coating material to be applied. The major considerations concern the cleanliness of the surface required and the surface area to be obtained.

Material Selection:

A coating combination must be specified after testing that will provide proper stability during the life of the project. The number of coats to be applied, the compatibility of the various coats, and the requirements for their maintenance must be considered.

Application:

The coating material must have application characteristics that would allow its proper application under all conditions existing during the coating process. Proper identification of the physical or other properties of the film expected from the application must be specified.

Corrosion Control

COATINGS:

Metallic Coatings:

Metal coatings are applied by Electro-deposition, flame spraying, cladding, hot dipping and vapour deposition.

Electrodeposition:

This process, also called electroplating, consists of immersing a part to be coated in a solution of the metal to be plated and passing a direct current between the part and another electrode. The character of the deposit depends on many factors including temperature, current density, time and composition of the both. These variables can be adjusted to produce coatings that are thick or thin, dull or bright, soft or hard and ductile or brittle. Hard platings are utilized to combat erosion-corrosion. The electroplate can be a single metal, layers of several metals or even an alloy composition.

Corrosion Control

COATINGS:

Flame Spraying:

This process, also called Metallizing, consists of feeding metal wire or powder through a melting flame so the metal, in finally divided liquid particles, is blown on to the surface to be protected. Oxygen and acetylene or propylene is commonly used for the melting flame. The coatings are usually porous and are not protective under severe wet corrosive conditions. Generally the porosity decreases with the melting point of the metal. The surface to be sprayed must be roughened (sand blasted) to obtain a mechanical bond. Sometimes paint coating is applied over the sprayed metal to fill the voids and provide a better barrier.

High melting metals may be deposited by plasma jet spraying. These are used for special applications such as for coating composite materials, alloys etc. for Erosion, Corrosion resistance. Examples are Alumina, Zirconia, Stainless Steels, Gas turbine coatings, cavitation resistant coatings etc.

Corrosion Control

COATINGS:

Vapour Deposition:

This is accomplished in a high vacuum chamber. Heating it electrically, and the vapour deposits on the parts to be coated vaporize the coating metal. This method is more expensive than others and generally limited to "critical" parts such as high strength parts for missiles and rockets. More recently Chromium deposition over steel is done for making automobile headlight reflectors.

Diffusion:

Diffusion coatings involve heat treatment to cause alloy formation by diffusion of one metal into the other. For this reason the process is also termed "surface alloying". Parts to be coated are packed in solid materials or exposed to gaseous environments, which contain the metal that forms the coating. Sherardizing (zinc coating), chromizing (chromium) and anodizing (Aluminium) are examples. Calorizing and chromizing are utilized mainly for resistance to high temperature oxidation.

Corrosion Control

COATINGS:

Chemical Conversion:

“Corroding” the metal surface to form an adherent and protective corrosion product produces coatings from chemical conversion. Anodizing consists of anodic oxidation in an acid both to build up oxide layer. Aluminium is one such example. Sufficient corrosion resistance is not obtained, so anodized Aluminium should not be used where untreated Aluminium would show rapid attack. The surface layer is porous and provides good adherence for paints. The anodized surface can be “sealed” by exposing to boiling water.

Additional example are bondorizing and parkerizing (phosphatizing) in a phosphoric acid both), chromatizing (exposure to chromic acid and di-3chromates) and oxide or heat coatings for steel. Phosphating provides a good base for painting and also provides for some corrosion resistance to the steel before rusting can take place in the event of failure of the paint finish.

Corrosion Control

COATINGS:

Organic Coatings:

These involve a relatively thin barrier between substrate material and the environments. Paints, varnishes lacquers and similar coatings protect more metal on a tonnage basis than any other method for combating corrosion. Extension surfaces are most familiar, but inner coatings or linings are also widely utilized. As a general rule, these coatings should not be used where the environment would rapidly attack the substrate material.

Aside from proper application, the three main factors to be considered for organic coatings are (1) surface preparation (2) selection of primer or priming coat and (3) selection of coat. If the metal surface is not properly prepared, the paint may peel off because of poor bonding. If the primer does not have good adherence or is not compatible with the topcoat, early failure occurs. Poor performance is, in most cases due to poor application and surface preparation.

Surface preparation involves surface roughening to obtain mechanical bonding as well as removal of dirt, rust mill scale, oil, grease, welding flux, crayon marks, and other impurities. In other words a clean rough surface is needed.

Corrosion Control

COATINGS:

Organic Coatings:

Best method is to grit blast or sand blast the steel surface. Other methods are pickling and other types of chemical treatments, scrapping wire brushing, flame cleaning, chiseling and clipping. In addition to economic considerations, the selection of surface preparation method depends upon the metal to be painted the shape, size and accessibility of the structure, the coating system and the service conditions.

Primers can contain rust-inhibitive pigments such as zinc chromate and zinc dust and there by provide another function in addition to acting as barriers. Wet-ability is needed so that crevices and other surface defects will be filled rather than bridged short drying times, are advantageous to preclude contamination before top coats are applied, particularly in field applications.

Topcoat selection is important. Many times paint is applied primarily for appearance. Good appearance and good corrosion resistance in severe atmospheres can be obtained at a justifiable cost by selecting a good topcoat material.

Corrosion Control

COATINGS:

Organic Coatings:

The coating thickness must be such that bare metal is not exposed. It is almost impossible, to apply one coat of paint and have it completely free of fine holes or other defects. Thickness is important also because paint deteriorates or weathers with time.

A large number of paints are available. Asphalt and bituminous paints are often used on pipelines. Sometimes a cloth wrapping is used with the coating for reinforcement. Alkyds, glyptals, concrete, red lead, iron oxide, phenolics, lithopanes, titanium dioxide paints and chlorinated rubber are just a few examples. Vinyl and epoxy paints have been widely adopted for corrosion applications.

Many methods of applying a coating are available. The familiar techniques involve brushing, rolling, dipping, and painting of coatings of acrylic, acrylic latex or varnish bases. The important techniques are:

Corrosion Control

COATINGS:

Organic Coatings:

(1) Brushing and rolling (2) palming (3) dipping (4) air spraying (5) airless spraying (6) electrostatic spraying (7) electro-phoratic painting (8) fluidized bed (9) Powder spraying (10) flame spraying (11) Trowelling (12) vacuum deposition (13) calandered or chat lining.

These are broad indications of different Corrosion Control Techniques that are used in Industries. More details of these Control techniques would be discussed in subsequent presentations.

Materials Selection

- **Basic Groups**
  - Metals
  - Plastics
  - Ceramics
  - Elastomers
  - Coatings
  - Linings

- **Balance of “+”s and “-”s**
  - Corrosion Resistance
  - Availability
  - Mechanical Properties
  - Cost
  - Code Compliance
  - Fabricability
  - Repair options

Materials Selection – Metals

- Carbon steels
- Aluminum (3000, 5000 and 6000 series)
- Coppers, brasses, and bronzes
- Stainless steels
  - Austenitic (200 and 300 series)
  - Martensitic (400 series)
  - Precipitation hardening (17-4 PH)
  - Duplex (2101, 2205, 255, and 2507)
- Nickel Alloys (600 series, C, B, X, Inconel®, Hastelloy®)
- Titanium alloys (common grades 2, 5, 7, and 11)
- Zirconium

Materials Selection - Plastics

- HDPE and Polypropylene (low end)
- PVC and CPVC
- Resins – epoxy, vinyl esters
- Fluoropolymers
  - PTFE, PFA, FEP, ETFE, PVDF
- PEEK (high end)
- Can be used as monolithic or composite pieces in equipment

Material Selection - Coatings

- Coatings (thin or thick films)
  - Many different technologies
  - Always have holidays
  - With or without reinforcement?
- Linings (how to anchor)
  - What’s your permeation rate?
  - Differences in thermal expansion rates
  - How do you clean?

Materials Selection - Ceramics

- Concrete
- Acid proof bricks and mortar
- Refractory
- Glass lined steel
- Alumina
- Silicon carbide
- Silicon nitride

Materials Selection -Elastomers

- Natural Rubbers
- Nitriles
- Neoprenes
- Polyurethanes
- EPDM
- Silicones
- Viton®
- Kalrez® or Chemraz®

- Compatibility
- Temperature limit
- Mechanical properties
- Availability
- Supply Chain
- Identification
- Specifications

Gaskets & Sealing

- Gasketing has many options
    - CNA Fiber sheet gaskets (250°F limit)
    - Rubber sheet goods (250°F to 350°F limits)
    - PTFE sheets and composites (350°F limit)
    - Expanded PTFE products (600°F limit)
    - Graphite gaskets (600°F limit)
    - Spiral wounds (rings, windings and fillers)
    - Ring joints (for high T & P)
    - Specialty materials (Thermiculite®, Cogebi®)

CORROSION ISSUES OF POWER PLANTS

Power Plant Corrosion

Chemistry-Related Damage Of Components In Fossil Plant Units

Component	Type Of Damage
Boiler Tubes, Drums And Headers	**Hydrogen Damage, Acid Phosphate Corrosion, Caustic Gouging, Corrosion Fatigue, Scale Or Deposit, Induced Overheating, Pitting**
Superheater Tubes	**Corrosion Fatigue, Overheating, Pitting, Stress Corrosion Cracking**
Reheater Tubes	**Corrosion Fatigue, Exfoliation, Pitting**
Economizer Tubes	**Corrosion Fatigue, Hydrogen Damage, Pitting, Flow Accelerated Corrosion**
Turbines	**Corrosion Fatigue, Galvanic Corrosion, Erosion And Erosion/Corrosion, Fouling, Stress Corrosion Cracking, Deposition, Crevice Corrosion, Pitting**
Feedwater Heater And Condenser Tubes And Shells	**Corrosion Fatigue, Galvanic Corrosion, Erosion/Corrosion, Condensate Grooving, Stress Corrosion Cracking, Dealloying, Intergranular Corrosion, Exfoliation, Pitting, Cavitation**
Deaerators	**Corrosion Fatigue, Stress Corrosion, Pitting**
Storage Tanks	**General Corrosion, Pitting**

Conclusions

- Corrosion is a Natural Process, it cannot be stopped completely and can only be controlled to suit our requirements.

- Corrosion of plant components is a costly affair as it impairs availability, reliability, performance and loss of materials putting a lot of financial burden on plant management.

- Putting Corrosion Control Measures at design stage is always desirable as retrofitting such measures is not always feasible nor provide adequate results.

- Regular Corrosion Monitoring and assessment is essential for safety and performance of the power plants.

- Corrosion assessment, monitoring and control measures should be inherent strategy of Plant O&M.

- **Remember, we need to consider life cycle cost of corrosion management against the possible losses accruing on damages to plant components.**

Conserve Resources

Thank You