# Corrosion & Corrosion Control снэ

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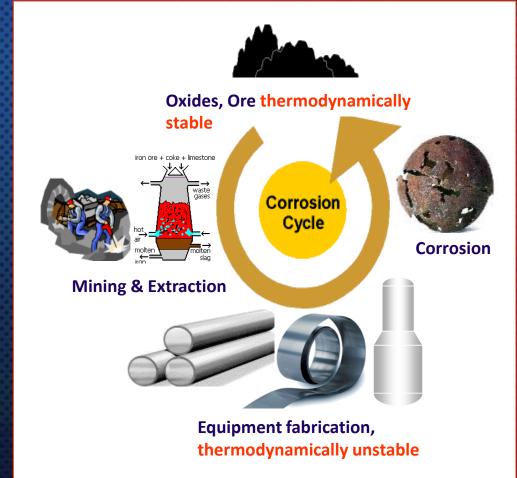
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# I. Basics of Corrosion

## What is Corrosion?

- Corrosion is defined as the degradation of a material due to its reaction with the environment.
- In case of metallic corrosion, corrosion is related to the law of conservation of energy.

CRE (Smelting) METAL (Corrosion)



#### Why we study Corrosion?

- In some countries corrosion damage reaches 5% of the total yearly GDP.
- Economic losses are attributed to; loss of production, replacement of equipment, maintenance of equipment, environmental pollution, etc.
- Recent studies revealed that 2/3 of such corrosion damage could have been avoided if a proper corrosion control technique was applied.
- Corrosion damage can extend far from economic losses, where it could cause loss of life in some circumstances.
   Loss of life was reported in many incidents and reason was directly attributed to corrosion.

## **Cost Of Corrosion**



CORRODED ROTOR LEADING TO EQUIPMENT FAILURE

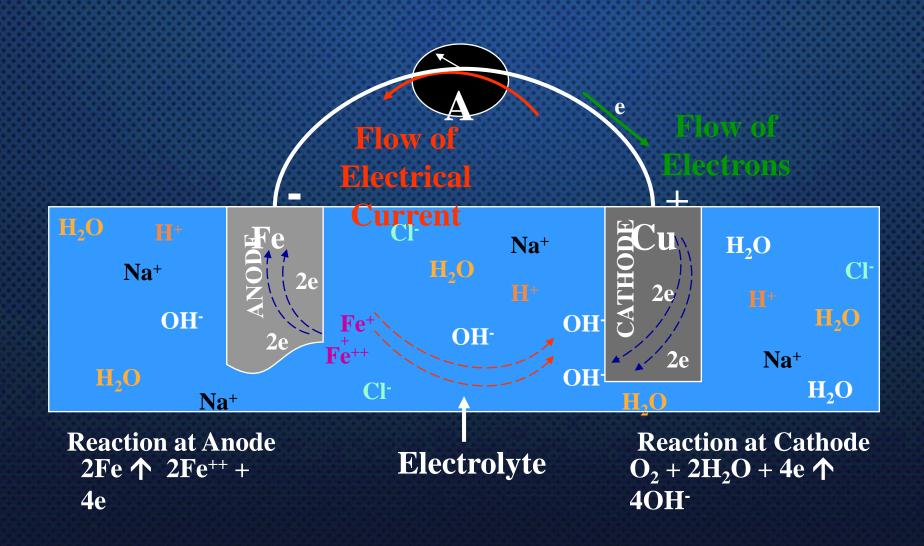
LEAKAGE LEADING TO ENVIRONMENTAL POLLUTION

**CATASTROPHIC FAILURE** 

#### **Corrosion Mechanism**

- In most cases corrosion is an electrochemical phenomenon.
- For corrosion to take place, the following are required:
  - An anode at which the metal goes into solution (corrodes)
  - A cathode at which electrons from the anode are consumed
  - An electrical continuity between anode and cathode (the internal conductor)
  - A common continuous electrolyte (the external conductor) across both anode and cathode.

#### **Corrosion Mechanism**



#### **Corrosion Mechanism**

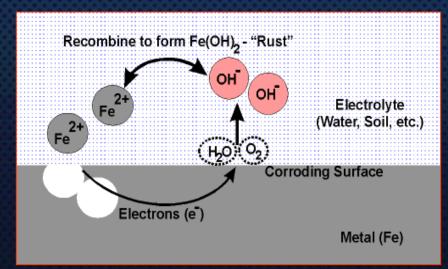
At anode, metal dissolves producing electrons
 4M = 4M<sup>++</sup> + 8e

#### At cathode electrons are consumed

 $4H_2O + 2O_2 + 8e = 8OH^-$ 

- The faster that electrons are consumed at the cathode, the faster will the metal go into solution at the anode (corrode).
- This keeps the reaction in equilibrium.
- Overall reaction is:

 $4M + 4H_2O + 2O_2 = 4M(OH)_2$ 



#### **Standard EMF Series**

Standard EMF series represents a ranking of metals in terms of its natural potential reference to a hydrogen electrode.

Element		Potential (Volts)
Magnesium	Mg $\rightarrow$ Mg <sup>++</sup> + 2e	-2.34
Aluminum	Al $\rightarrow$ Al <sup>+++</sup> + 3e	-1.67
Zinc	$Zn \rightarrow Zn^{++} + 2e$	-0.76
Iron	$Fe \rightarrow Fe^{++} + 2e$	-0.44
Nickel	$Ni \rightarrow Ni^{++} + 2e$	-0.25
Tin	$Su \rightarrow Su^{++} + 2e$	-0.14
Lead	$Pb \rightarrow Pb^{++} + 2e$	-0.13
Hydrogen	$2H \rightarrow 2H^+ + 2e$	0.00
Copper	$Cu \rightarrow Cu^{++} + 2e$	0.34
Silver	$Ag \rightarrow Ag^{++} + 2e$	0.79
Platinum	$Pt \rightarrow Pt^{++} + 2e$	1.20
Gold	$Au \rightarrow Au^{+++} + 3e$	1.42

**Reconvert to** 

**Readiness to (** 

**Ease of Smelting** 

### **Standard Galvanic Series**

Standard galvanic series represents a realistic ranking for metals. Ranking is made in seawater reference to a Cu/CuSO<sub>4</sub> electrode.

Potential Cathodic Platinum east Active Gold Carbon (graphite) ЧġН Titanium Type 316 or 304 stainless steel (passive) Monel metal (70% nickel, 30% copper) Silver. Nickel Lead Bronze, Copper, Brass Tin Lead/Tin solder Type 316 or 304 stainless steel (active) Low Potentia Cast Iron/Mild Steel Most Active Cadmium Anodic Aluminium Zinc Magnesium

### THE GALVANIC SERIES OF METALS IN SEA WATER

Couple Mildly Corrosive for Iron Magnesium Zinc Aluminum Iron Lead Tin Nickel (Active) **Brass** Copper Nickel (Passive) **410 Stainless** Titanium **304 Stainless** Silver Gold **Platinum** 

#### ACTIVE

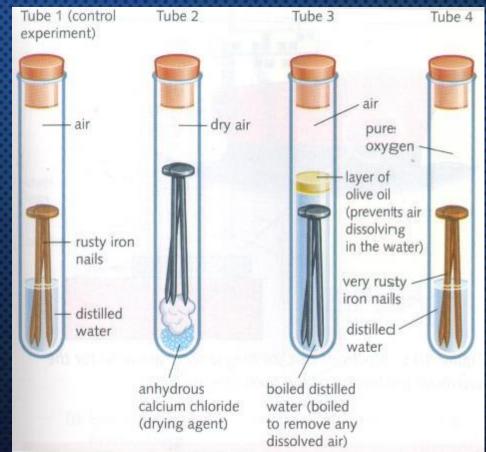
**Couple Severely Corrosive for Iron** 

NOBLE

# **Factors Affecting Corrosion**

There are numerous factors that affect the corrosion process these are:

- pH of environment
- Concentration of corrosive species
- Stream Velocity
- Oxygen Content
- Temperature



# **Forms of Corrosion**

There are two major forms of corrosion and these are: <u>UNIFORM</u> and <u>LOCALIZED</u> corrosion forms

# Forms of Corrosion Uniform Corrosion

- Is called general corrosion
- Is of little engineering importance
- Can be easily controlled
- Can be easily monitored
- Is caused by natural environments and acids



**Uniform Corrosion** 

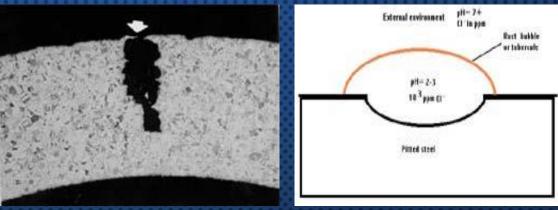
## Forms of Corrosion Localized Corrosion

Takes place on specific locations:

- Is hard to predict
- Is hard to monitor
- Can lead to catastrophic failures
- Has numerous forms the most important are:
  - Pitting
  - Crevice
  - Stress Corrosion Cracking
  - Erosion Corrosion
  - Galvanic

#### **Forms of Corrosion** Uniform Corrosion – Pitting Corrosion

Pitting is another form of much localized corrosion attack in which small pits or holes form. This type of corrosion is very dangerous where it is undetected and with very little material loss until failure occurs.



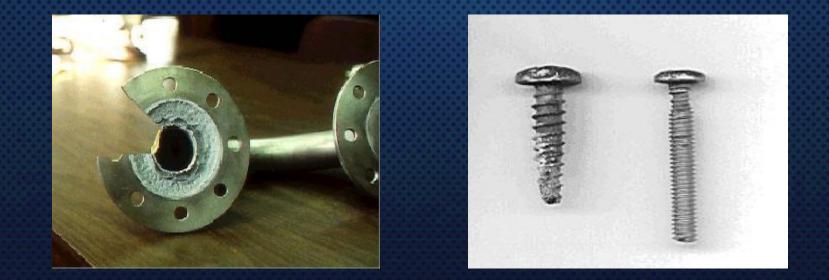


Pitting corrosion of SS

#### **Forms of Corrosion** Uniform Corrosion – Crevice Corrosion

Crevice or contact corrosion is the corrosion produced at the region of contact of metals with metals or metals with nonmetals.

Stainless steels are susceptible to this kind of corrosion.



Crevice corrosion of SS

#### **Forms of Corrosion** Uniform Corrosion – Galvanic Corrosion

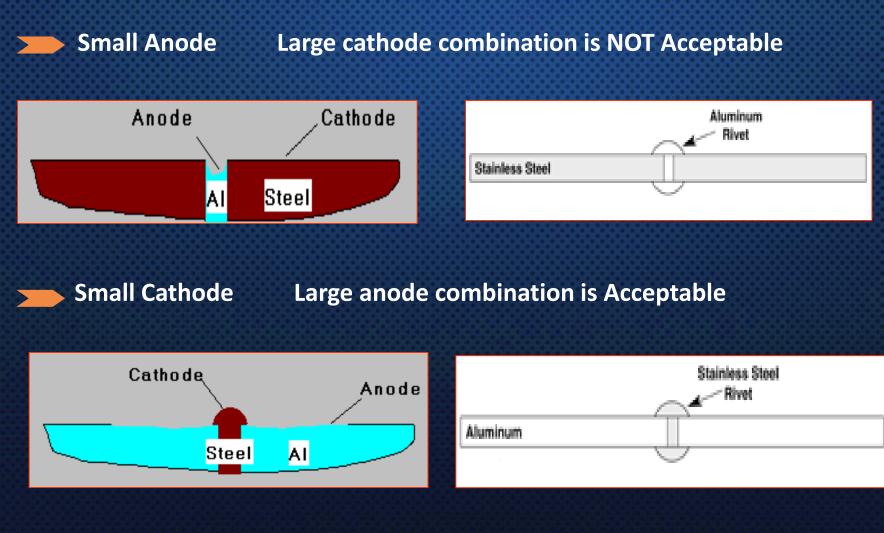
- Galvanic corrosion occurs when two metals or alloys having different compositions are electrically coupled while exposed to an electrolyte.
- Rate of galvanic attack depends on the relative anode to cathode surface areas that are exposed to the electrolyte



Galvanic corrosion of a helicopter rotor blade

#### Forms of Corrosion Uniform Corrosion – Galvanic Corrosion

#### **Surface Area Effect in Galvanic Corrosion**



#### **Forms of Corrosion** Uniform Corrosion – Galvanic Corrosion

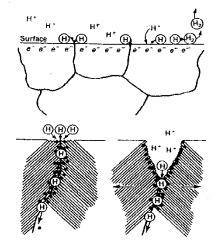


Galvanic corrosion of painted steel body in contact with SS wheel opening molding

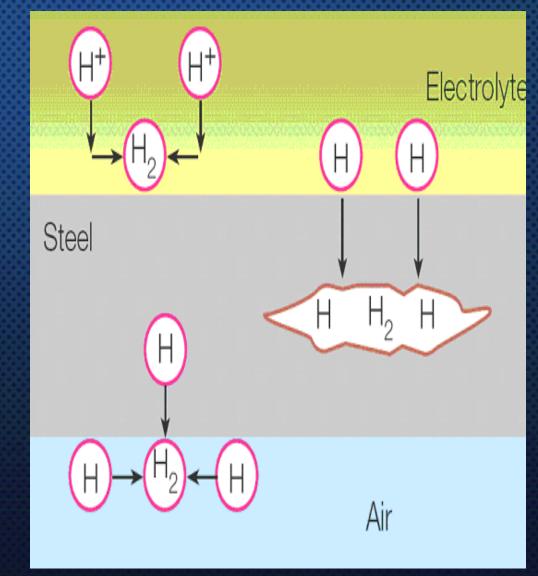
Galvanic corrosion of steel pipe at brass fitting in humid marine atmosphere

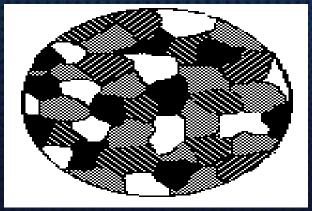


# **Hydrogen Blistering**



Schematic showing effect of some impurities on mechanism by which intergranular embrittlement of nickel is presumed to occur at cathodic potentials



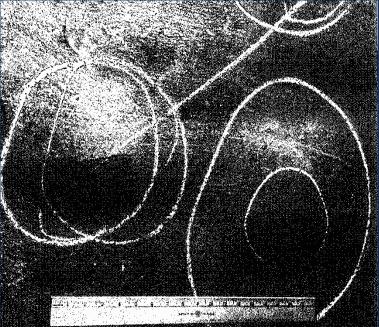


**Grain Boundaries** 

# Hydrogen Blistering



Cross-section of a carbon steel plate showing a large hydrogen blister



Hydrogen blistering of a carbon steel plate

# Hydrogen Embrittlement



#### **Intergranular Corrosion**

 Intergranular corrosion occurs preferentially along grain boundaries for some alloys and in specific environments



Intergranular corrosion attack of stainless steel in the heat affected zone of welding

#### **Erosion Corrosion**

 Erosion Corrosion arises from the combined action of chemical attack and mechanical abrasion or wear as a consequence of fluid motion.



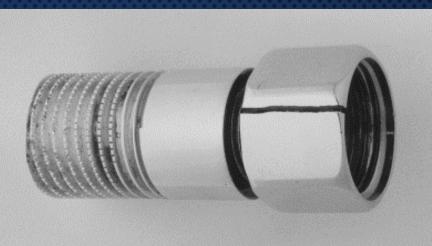
Erosion corrosion for: Check valve (left) and ship rotor blade (right)

#### **Stress Corrosion Cracking**

 Stress corrosion cracking (SCC) is caused by the simultaneous effects of tensile stress and a specific corrosive environment. Stresses may be due to applied loads, residual stresses from the manufacturing process, or a combination of both.



Stress corrosion cracking of stainless steel



Stress corrosion cracking of brass

# **II. Engineering Material**

### ENGINEERING MATERIALS

Materials are classified into two groups; metals and non metals

Metals are divided into ferrous and non-ferrous metals : • Ferrous:

e.g. Carbon Steel, Cast Iron, Stainless Steel
•Non-ferrous:

e.g. Monel, Inconel, Hastelloy

Non metals contain several categories like:Polymer:

e.g. PTFE, PF, PP, Epoxies

•Ceramics:

e.g. Silicon Carbide

#### **Materials Standards and Specifications**

Materials International codes and standards aim at issuing standard procedures for testing of materials and at specifying the grades and properties of standard materials.

#### INTERNATIONAL MATERIAL STANDARD SPECIFICATION

GERMANY	D.I.N.
FRANCE	A.F. N O R.
ENGLAND	B.S.
JAPAN	J.I.S.
SWEDEN	S.I.S.
RUSSIA	GOST
USA	A.S.T.M. A.P.I. A.N.S.I. A.W.S. A.W.W.A.

#### INTERNATIONAL CODES

GERMANY	T.Ü.V. D.I.N.
FRANCE	S.N.C.T.
USA	A.S.M.E. A.P.I. N.A.C.E. A.N.S.I. T.E.M.A.

# International materials standards and codes

### **Material Properties**

#### Physical Properties

- Density
- Thermal Expansion
- Thermal Conductivity

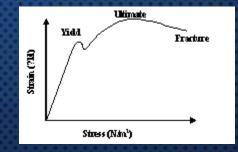
😫 Mechanical Properties

- Strength (ultimate, yield)
- Ductility
- Elasticity
- Hardness
- Toughness (Impact resistance)
- Wear Resistance
- Creep resistance & rupture

#### Yield Strength

Material resistance to yield (start of plastic deformation)

#### Ultimate Strength Maximum strength prior to fracture





#### 👱 Hardness

Material resistance to notch formation, however, more hard materials are more susceptible to cracking during processing, forming, or welding

#### **Hardness Test Methods**

- Brinell Method (HB)
- Rockwell Methods (HRC, HRB)
- Vickers Method (HV)

#### Toughness

Toughness is defined as a materials capacity to absorb energy, which, is dependent upon strength as well as ductility

**Test Methods** 

- Charpy V-notch -Most applicable method

- Drop weight nil-ductility -Used for brittle materials

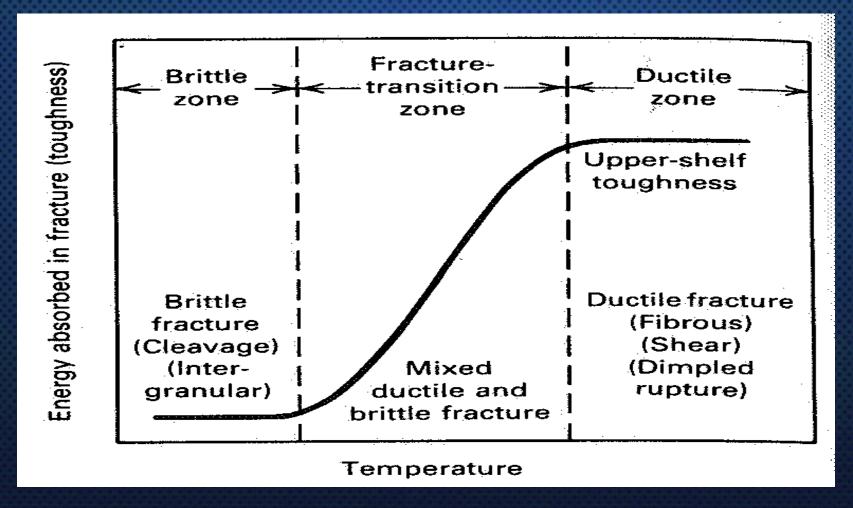
- Crack tip opening displacement -Used for measuring flaw size

#### Factors affecting material toughness

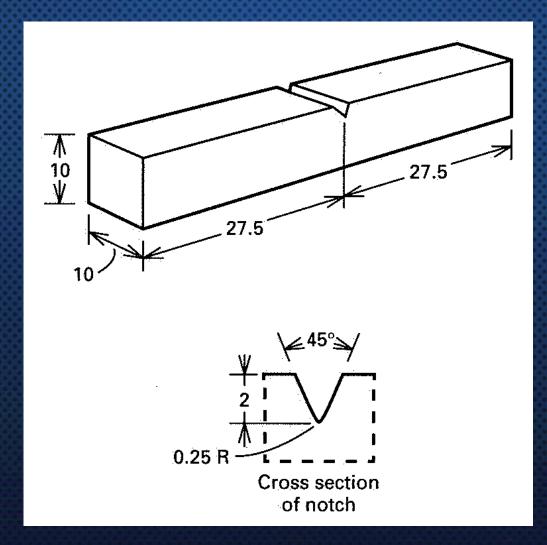
- Chemical composition
- Materials processing
- Heat treatment

#### **Ductile-to-Brittle Transition**

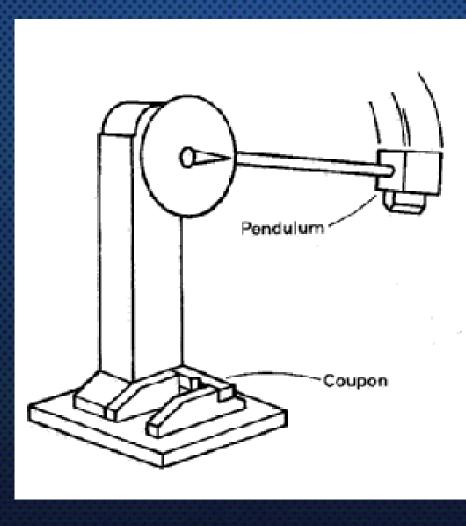
This characteristics is accompanying solid-state phase transformation changing fracture characteristics from ductile to brittle whenever metal temperature is decreased to lower levels (-29 deg. C for carbon steel materials)



**Ductile-to-Brittle Transition** 



V-Charpy Impact Test Specimen



V-Charpy Impact Test Set-up

#### Wear Resistance

Wear of metal is defined as plastic displacement of surface or near-surface material by contact with other metals, non-metallic solids, flowing liquids, solid particles contained in flowing liquids

#### **Classification of Wear**

Metallic against non-metallic abrasive (erosion)
 Erosion of impellers by sands contained in flowing liquid
 Erosion of earth removing devices by abrasives in dry sand

#### - Metal against metal

-Sliding

-Rolling
e.g. wear of shaft in bearing

Liquid or vapor impingement on metal

e.g. cavitation, turbulent, high-velocity flo

#### Creep

Creep is defined as a very slow plastic strain increased by time and temperature (time and temperature dependant) for stressed materials.



#### Rupture

Rupture is material failure due to creep

## I. Families of Alloys

#### **Materials Categories**

For the sake of materials selection, materials fall in two categories;

- **1.** Degradable materials (e.g. Carbon Steel)
- 2. Corrosion Resistant Alloys (CRA), such as stainless steels, nickel alloys, copper alloys and titanium alloys

#### 6. Carbon Steel

- Is the most common material used today
- Known of is excellent mechanical properties
- High availability
- Economic
- Has poor corrosion resistance properties
- Usually requires corrosion control techniques

#### **Carbon Steel Materials**

#### Carbon Steels

Iron-Base alloys contain certain percentage of carbon as a main alloying element, however, some elements may be contained as residuals.

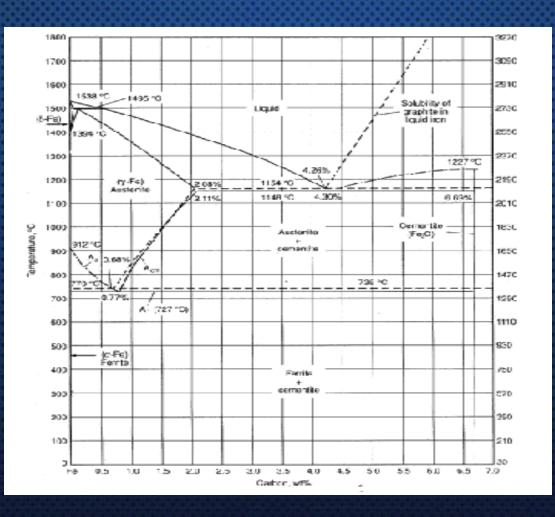
**Classification of Carbon Steels** (according to Carbon content)

- Low-carbon steels Contain upto 0.3% C

- Medium-carbon steels Contain 0.3 to 0.6% C

- High-carbon steels Contain 0.6 to 1.0 % C

#### **Carbon Steel Materials**



**Iron-Carbon Diagram** 

#### **Carbon Steel**

- Is the most common material used today
- Known of is excellent mechanical properties
- High availability
- Economic
- Has poor corrosion resistance properties
- Usually requires corrosion control techniques

#### 7. Stainless Steel



Experimental car made from a stainless steel body, photo taken after 30 years of manufacturing

## 7. Stainless Steel (Cont.)



Stainless Steel is defined as a ferrous alloy containing a minimum of 11% of Cr content.

Is known of its superior resistance against corrosion

Is known of its good mechanical properties

Is divided into five families according to their crystallographic structure

#### 7. Stainless Steel (Cont.)

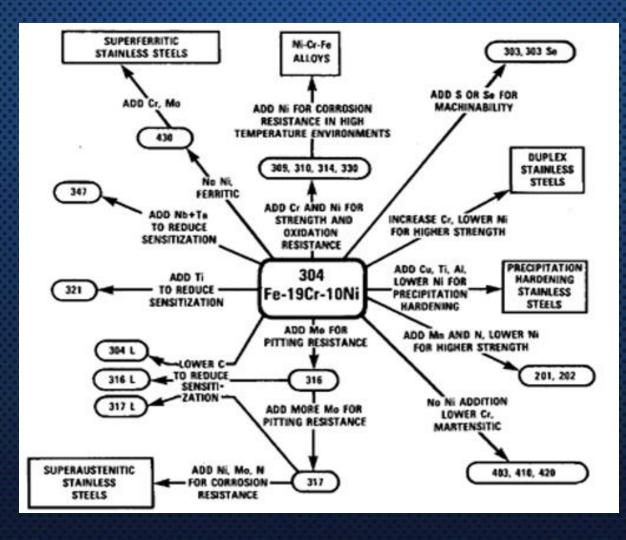
**Stainless Steel families are:** 

- Austenitic Stainless Steel
- Ferritic Stainless Steel
- Martensitic Stainless Steel
- Super Stainless Steel
- Duplex Stainless Steel

## 7.1 Austenitic Stainless Steel

- Is of an austenite FCC (face centered cube structure)
- Non-Magnetic
- Non-hardenable by Heat-treatment
- Hardenable by cold-working
- Have high corrosion resistance properties
- High temperature strength
- Good weldability
- Contains a min. of 18%CR and 8%Ni as the main alloying elements
- Is recognized by the AISI (American Iron and Steel Institute) as the 3xx series, e.g. 304, 316, etc.

## 7.1 Austenitic Stainless Steel (Cont.)



**Austenitic SS Grades** 

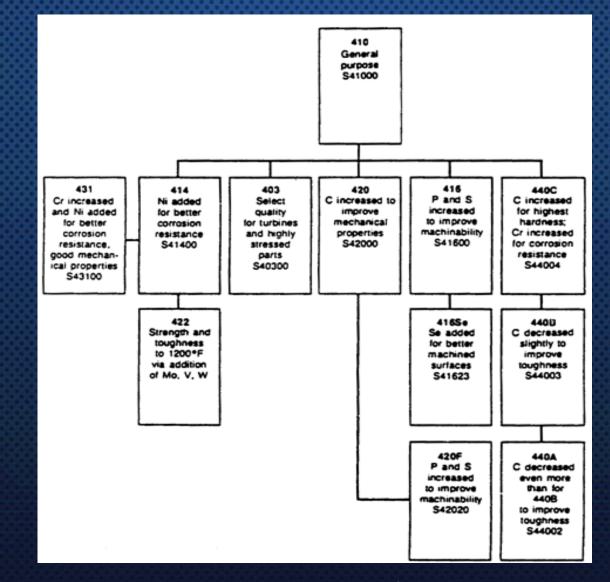
#### 7.2 Ferritic Stainless Steel

- Is included within the AISI 400 series
- Cr is 11-30%
- Ferro-magnetic
- Not hardened by heat treatment
- Used for nitric acid services, water, food processing, automobile trims and architectural applications.
- Their impact resistance is poor
- Their weldability is poor
- The general-purpose grade of this stainless steel family is grade 430 which contains 17% Cr.
- Contains Cr and Mo as the major alloying elements

#### 7.3 Martensitic Stainless Steel

- Martensitic SS are hardenable grades
- Resist high temperatures, used in turbine blades
- Have a fair corrosion resistance and are only used in mild environments
- The most common grade is grade 410
- These grades are difficult to weld
- Their low temperature impact resistance is also poor
- Contains mainly Cr as the major alloying element
- Is the cheapest stainless steel

#### 7.3 Martensitic stainless steel(Cont.)



**Martensitic SS Grades** 

## 7.4 Super Stainless Steel

- The most famous super stainless steel is the 6 moly SS
- Super stainless steel have been developed to cover some weakness in corrosion resistance
- Mainly developed to combat chloride stress corrosion cracking that occurs to all austenitic grades
- The other famous SS type is the AISI 904 which is considered to be a non ferrous alloy due to its high Ni content

## 7.5 Duplex Stainless Steel

- Approximately they have 50% Austenite and 50% Ferrite
- Ferrite forming alloys such as Mo and Cr are present as well as Ni
- Duplex contains Mo for more resistance Chloride pitting
- Ferrite/Austenite mixture is not a blessing where any of the two phases can be selectively attacked or even galvanically corroded
- Welding of duplex should be controlled and monitored closely where the austenite phase could turn to ferrite

#### 8. NICKEL AND NICKEL ALLOYS



Is a noble metal, this is why it is known of it superior resistance to corrosion

Ni forms a protection layer of nickel oxide

Ni and Ni alloys are being used extensively in industry

Its relatively high cost relative to the carbon steel or to the conventional stainless steel grades, resembles the only problem

#### 8. NICKEL AND NICKEL ALLOYS (Cont.)

Ni and its alloys are found as :

- Ni (Alloys 200 & 201)
- Ni-Cu alloys (Alloys 400,K500, Cupronickel alloys 90/10 &70/30)
- Nickel-Molybdenum alloys (Alloy B-2)
- Nickel-Chromium-Iron alloys (Alloys 600 & 800)
- Nickel-Chromium-Molybdenum alloys (C-276, C-4 & alloy 625)

### 8.1 Ni (alloys 200 & 201)

- Corrosion rates in waters contaminated or aerated is less than 0.1 mm/yr
- Not resistant to stagnant seawater
- Is resistant to all salt solutions at all concentrations
- Resistant to of oxidizing and reducing acids

## 8.2 Ni-Cu alloys (alloys 400, K-500, Cupro-Nickels 90/10 & 70-30)

- Alloy 400 (Monel) si 65% Ni, 30% Cu, is resistant to HCl, to alkaline and neutral salts.
- Most famous application of Monel, is its use in the overhead section in crude distillation units.
- Cupro-nickel alloys 90/10 & 70/30 were mainly developed to be used as piping for the marine atmospheres

#### 8.3 Nickel-Molybdenum alloys (Alloy B-2)

Addition of molybdenum ensures good resistance to chloride pitting and to reducing acids in general. Also alloy B-2 is known of its immunity against stress corrosion cracking.

## 8.4 Nickel-Chromium-Iron alloys (Alloys 600 & 800)

Due to the high Chromium content, these two alloys were developed to be used in corrosive gases at extremely high temperatures under oxidizing conditions.

## 8.5 Nickel-Chromium-Molybdenum alloys (C-276, C-4 & alloy 625)

Nickel-Chromium-Molybdenum alloys combine the good resistance properties of the last two families they considered like the super-nickel alloys where they are resistant to nearly every single environment and hence their cost is considerably higher than the other Ni alloys.

## 9. TITANIUM AND TITANIUM ALLOYS

 $\checkmark$ 

Is widely used in aerospace, medical and petroleum industries

Is known of its excellent corrosion resistance properties

Used in seawater cooling, seawater valves and fittings, data logging systems, cathodic protection anodes, pumps and valves as well as underwater operations.

# III. Corrosion Monitoring & Control

#### How we control Corrosion?

- **1.** Anodic : by blocking the anodic reaction
- 2. Cathodic : by blocking the cathodic reaction
- **3.** Mixed : by blocking both anodic & cathodic reactions

# The army of corrosion control techniques is deployed to fulfill this goal

#### **Corrosion Control Techniques**

Corrosion control techniques are based on the mechanisms of the eight forms of corrosion: These techniques are:

- **1- Proper Materials Selection.**
- 2- Improved design.
- **3- Environmental Process Control.**
- 4- Utilization of Corrosion Inhibitors.
- **5- Application of Coatings and Paints.**
- 6- Cathodic Protection.

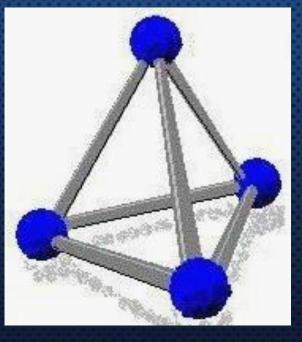
# I. MATERIALS SELECTION

#### **Corrosion Control Techniques** Materials Selection

**Materials Selection Factors:** 

#### **Corrosion Resistance**

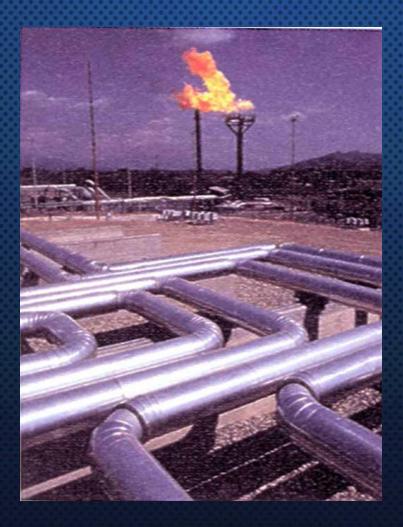
#### Mechanical Properties



Availability

Cost Effectiveness

## Corrosion Control Techniques Materials Selection



#### INTRODUCTION

Materials play an important role in our lives.

 Historical ages have been defined in conjunction with development of materials.

#### 1- Materials Selection Introduction



Is considered as the first line of defense towards corrosion control.



Is made to ensure proper resistance against the intended service environment.



Materials are selected also against mechanical properties as well as cost viability.

Materials selection is made either using a degradable material (carbon steel) with the addition of a "corrosion allowance" with or without the addition of a corrosion control technique (e.g. coating, cathodic protection, etc.)

Or using a corrosion resistant alloy (a material that doesn't readily corrode in the environment) such as the use of stainless steel or nickel alloys.

The decision either to go for a CS or for CRA depends mainly on economics as well as other factors such as replacement capabilities, maintainability, criticality of service, etc.

Materials selection for corrosion control depends upon

- 1. Knowledge of materials properties and corrosion control
- 2. Knowledge of corrosion process, mechanism and theory
- 3. Knowledge of service (environment, its operating conditions)
- 4. Knowledge of materials behavior with the environment
- 5. Knowledge of lifetime required
- 6. Knowledge of economics
- 7. Knowledge of corrosion control techniques
- 8. Case histories in same application

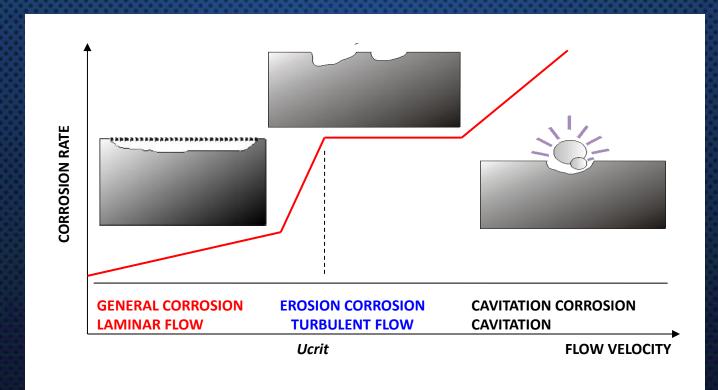
#### A. Information needs

Process flow diagrams (PFD) showing design/ operating/ upset conditions of:

- Temperature (min. & max.)
- Pressure
- Stream chemical analyses showing the corrosive constituents and their concentrations:
  - H<sub>2</sub>O
  - Dissolved gases (O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S)
  - Cl<sup>-</sup>
  - TDS (total dissolved salts)
  - pH
  - TAN (total acid number ) for crude oil
  - Total Sulfur Content

#### 3. Stream Velocity

Corrosion rate and corrosion type are function of flow velocity



B. <u>Issuance of materials selection diagram (MSD) and materials</u> <u>selection philosophy report (MSPR)</u>

<u>MSG</u> = PFD with designated material of construction for each equipment

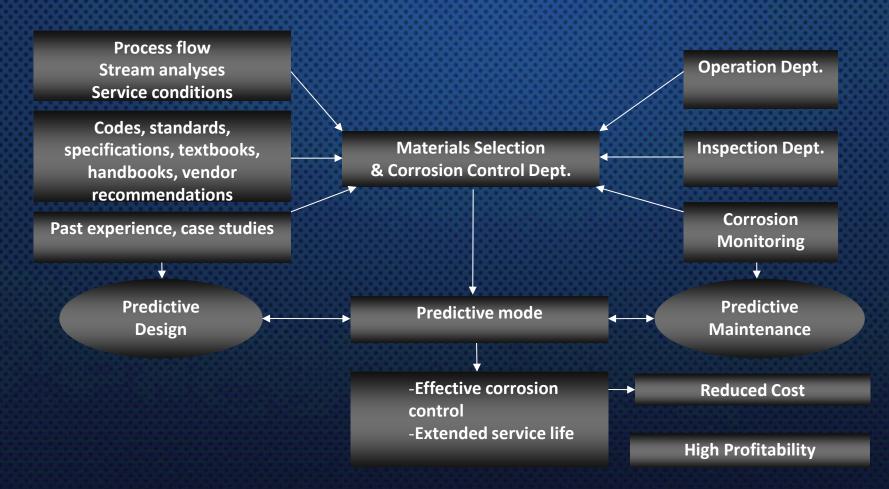
**MSPR** = highlights:

- expected corrosion mechanism
- predicted corrosion rates
- material of construction of each stream and equipment.

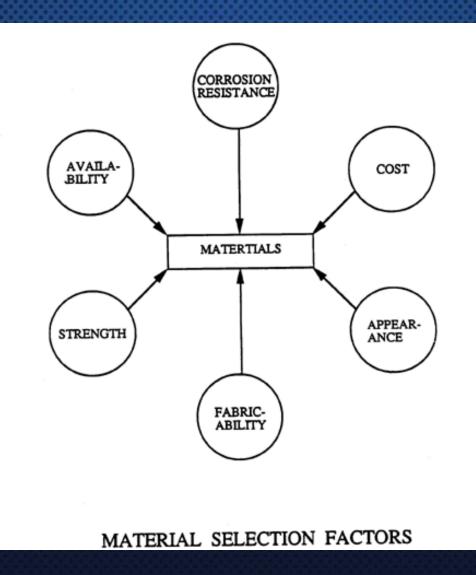
## **Effect of temperature on material selection**

	Design Temperature, °F	Material	Plate	Pipe	Forgings	Fittings	Boiting
Cryogenic	- 425 to - 321	Stainless steel	SA-240- 304, 304L, 347,	SA-312- 304, 304L, 347,	SA-182- 304, 304L, 347,	SA-403 304, 304L, 347,	SA-320-88
			316, 316L	316, 316L	316, 8 <b>16L</b>	316, 316L	with SA-194-6
	- 320 to - 151	9 nickel	SA-353	SA-333-8	SA-5224	SA-420-WPL8	
Low temperature	- 150 to - 76	3½ nickel	SA-203-D	04,000,0			
	- 75 to - 51	2½ nickel	· SA-203-A	SA-333-3	SA-350-LF63	5A-420-WPL3	SA-320-1.7 with SA-194-4
	-50 to -21		SA-516-55, 60 10 SA-20	SA-333-6	SA-3504 F2	5A-420-WPL6	. <u></u>
	-20 to 4		SA-516-AM	SA-333-1 or 6	0A-0004.52	SA-420-MPLO	
ليو 	5 to 32	Carbon steel	SA-285-C				
ate			SA-516-All	SA-53-B	SA-105		
Intermediate	33 to 60		SA-515-All SA-455-II	SA-106-B	SA-181-60,70	SA-234-WPB	SA-19 <b>3-87</b> with SA-1 <b>94-2</b> #
Ē	61 to 775						-
ated Temperature	776 to 875	C-1/2Mo	SA-204-B	SA-335-P1	SA-182-F1	SA-234-WP1	
	876 to 1000	1Cr-1/2Mo	SA-387-12-1	'SA-335-P12	SA-182-F12	SA-234-WP12	
		11/4Cr-1/2Mo	SA-387-11-2	SA-335-P11	SA-182-F11	SA-234-WP11	
	1001 to 1100	21/4Cr-1Mo	SA-387-22-1	SA-335-P22	SA-162-F22	SA-234-WP22	with SA-193-85 SA-194-3
	1101 to 1500	Stainless steel	SA-240-347H	SA-312-347H	SA-182-347H	SA-403-347H	
		Incoloy	SB-424	\$ <b>6</b> 423	\$8-4?5	SB-366	SA-193-B8
Elevated	Above 1500	Inconei	SB-443	S <del>B-444</del>	SB-446	SB-366	with SA-194-8

## **MATERIALS SELECTION**



# Materials Selection (cont.)



# Materials Selection (cont.)

Materials selection for corrosion control requires knowledge of corrosion theory and dynamics as well as materials behavior in corrosive environments, factors are summarized as follows:

- 1. Corrosion Theory
- **2.** Corrosion Forms
- 3. Criticality of Service
- 4. Lifetime Required
- **5. Corrosion Control Techniques**
- 6. Corrosion Resistance of Materials

### 2. Corrosion Allowance

Carbon steel is the classical material that is used in construction, its performance in any atmosphere shall be determined and hence we have to determine the quantity of metal to be lost by corrosion and then account for during design

## **Corrosion Allowance (Cont.)**

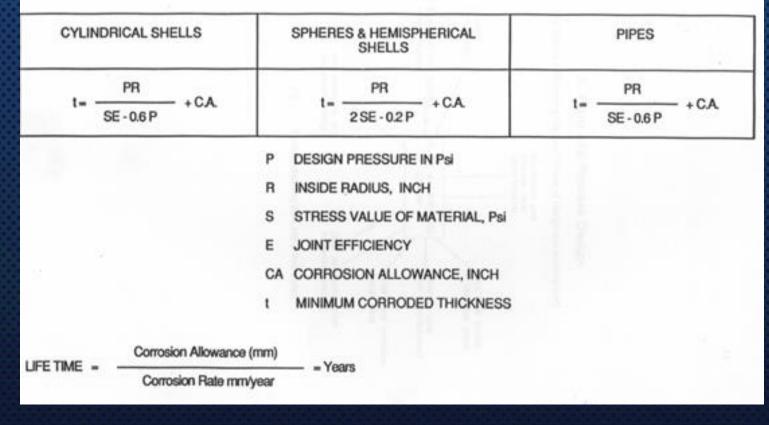
 $CA = CR \times LT$ 

Where CA is the Corrosion allowance in mils (1/1000 inch) or in mm CR is the estimated corrosion rate in such an environment in mil/year or mm/year LT is the required lifetime in years.

Calculating a corrosion rate is either uniform or considering the maximum localized corrosion rate (which is always harder to quantify)

# **Corrosion Allowance (Cont.)**

#### **CORROSION ALLOWANCE & DESIGN**



**CA involvement in codes** 

### **3. Materials Selection in Selected Environments**

The following shall present the methodology of materials selection in some selected corrosive environments in the oil/gas industry

# **3.1. HIGH TEMPERATURE SULFUR CORROSION**

(

Crude oils and their fractions contain sulfur compounds including polysulfides, hydrogen sulfide, mercaptans, aliphatic sulfides, disulfides and thiophenes. At temperatures in the range 260°C to 540°C steels are significantly corroded by these compounds.

Corrosion rates reduce above 540°C if a protective coking layer forms and is maintained.

As a first approximation, corrosion rates for the various steels used in such applications (carbon steel, 1¼Cr to 9CrMo steels, 18/8 stainless steels) may be estimated using Modified McConomy Curves factored for sulfur content

# 3.1. HIGH TEMPERATURE SULFUR CORROSION (CONT.)

Crude oils and their fractions contain sulfur compounds including polysulfides, hydrogen sulfide, mercaptans, aliphatic sulfides, disulfides and thiophenes. At temperatures in the range 260°C to 540°C steels are significantly corroded by these compounds.

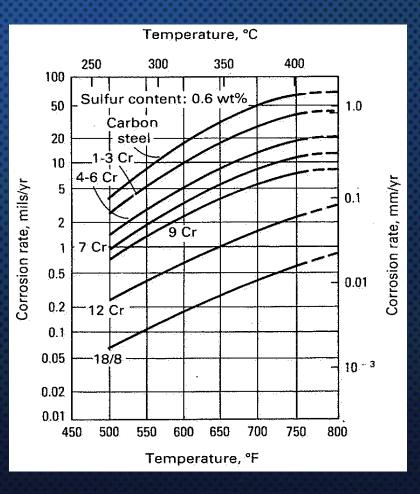


Sulfur corrosion depends on temperature and total sulfur content

# 3.1. HIGH TEMPERATURE SULFUR CORROSION (CONT.)

Couper and Gorman curve for determination of corrosion rate for crudes containing sulfur

Rate of sulfur attack on steels depends on Cr content

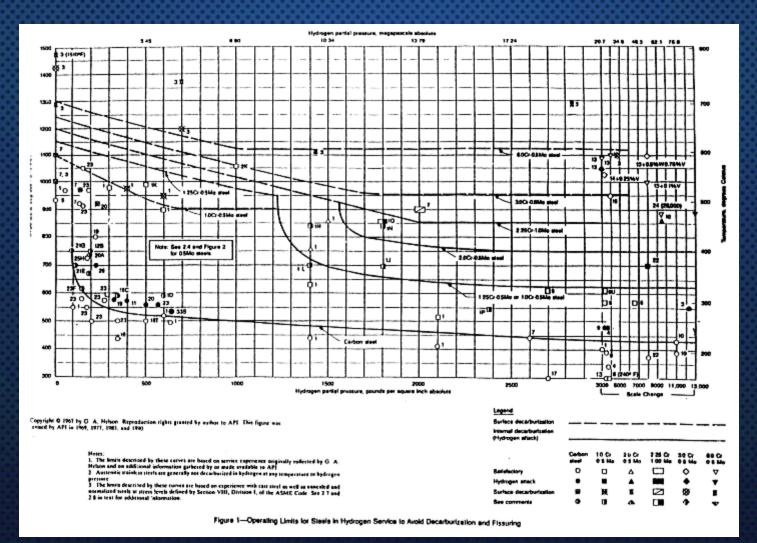


### **3.2. HYDROGEN ATTACK**

Hydrogen service is defined as one in which the partial pressure of hydrogen exceeds 100 psig

Hydrogen service damage of steels consists of internal fissuring and is avoided by selection of steels in accordance with API 941

### **3.2. HYDROGEN ATTACK(CONT.)**



**API 941 for Hydrogen Service** 

#### **3.3. NAPHTHENIC ACID CORROSION**

Crude oils are considered to be "Naphthenic" in character and to give rise to corrosion at temperatures above about 230°C by organic acids when the Neutralization Number exceeds 0.5 mg KOH/g of crude oil.

Carbon steel becomes not suitable in Naphthenic acid service.

Wet H<sub>2</sub>S service is one in which liquid water with sufficient dissolved hydrogen sulfide is present to cause sulfide stress corrosion cracking (SSCC) and/ or hydrogen induced cracking (HIC) of vulnerable materials.

The tendency for SSCC to occur in materials is a function of material type, condition, applied tensile stress and the amount of  $H_2S$  present in the water phase.

The threshold conditions above which precautions have to be taken to avoid SSCC are defined in NACE MR0175



H<sub>2</sub>S is soluble in water



Its aqueous solution behaves as a week acid

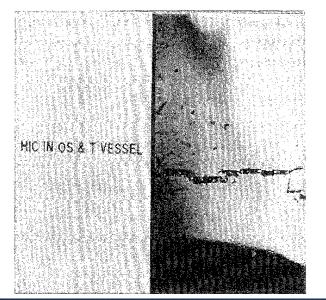


CS shall:

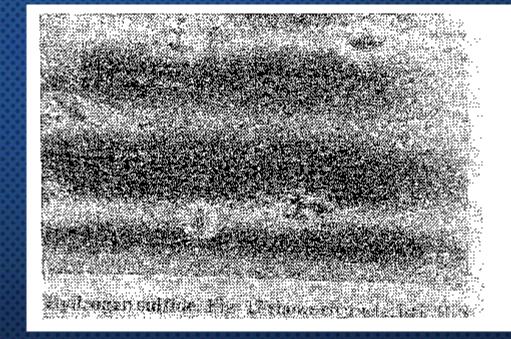
- contain Ni < 1% and S < 0.02
- be normalized and thermally stress relieved
- Have hardness < 22 HRC
- have reasonable corrosion allowance



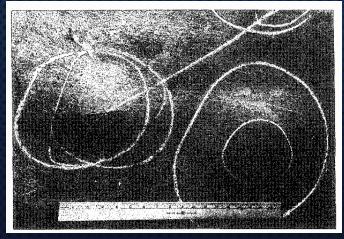
Use of austenitic stainless steel and CRA



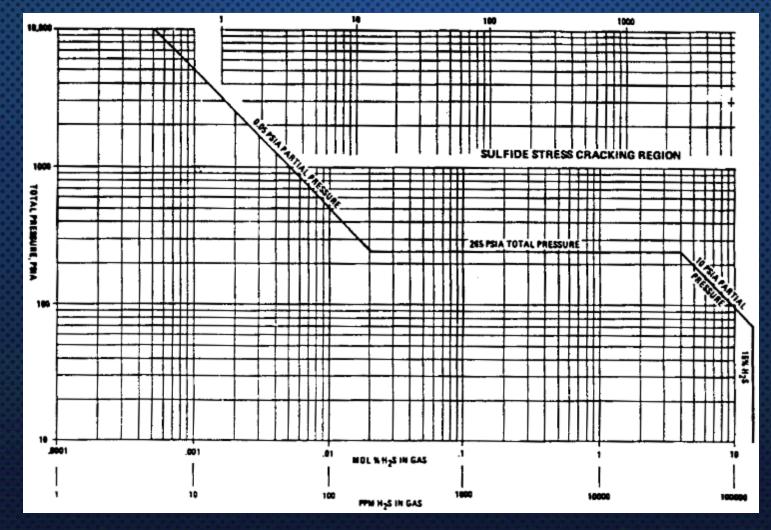
SCC



#### Pitting



#### Hydrogen embrittlement



NACE MR-01-75 in multiphase systems

# **3.5. POLYTHIONIC ACID CORROSION**

Is a mixture of sulfurous acids formed by the interaction of sulfides, moisture, and oxygen, and occurring when equipment is shutdown

Austenitic stainless steels operating in sulphurous service in excess of 400° C can suffer a very severe and rapid form of intergranular stress corrosion on shutdown caused by polythionic acids (PTA) which form when moisture condenses and combines with high temperature sulfide scales in the presence of oxygen.

Two strategies to avoid PTA are available. The most resistant grades of stainless steel, type 347 and 321, can be selected or the equipment can be provided with an alkaline wash on shutdown, as outlined in NACE RP0170

# **3.6. AMINE SERVICE**

Amine service is one containing aqueous solutions of monoethalomine (MEA), or diethanolamine (DEA), or methyldiethanolamine (MDEA), or di-isopropanolamine (DIPA), usually in about 30 % concentrations. DEA is to be used mainly in hydrogen sulfide removal units.

Some precautions shall be made for the use of materials in amine units where amine solutions are capable of causing stress corrosion cracking of welded or coldformed steel parts

# **3.6. AMINE SERVICE (CONT.)**

item	requirements
Carbon and carbon manganese steel equipment (vessels, exchangers, filters etc.), paperwork and instrumentation (wetted parts).	Fully killed steel (i.e. contains > 0.1% Is) "Requirements for Wet H₂S Service" apply in the case of Rich Amine Service. Cold formed items, including exchanger tubing bends shall be stress relieved. Post weld heat treat irrespective of thickness and operating temperature, including attachment and repair welds.
Screwed connections	Not permitted
Copper or copper based alloys	oNot permitted
Aluminum or aluminum based alloys	NNot permitted in Rich Amine Service

**Requirements For Materials In Amine Service** 

### **3.7. CAUSTIC SERVICE**

Depending on concentration and temperature, sodium hydroxide solutions can cause stress corrosion cracking of weldments and cold-formed items in carbon steels.

 $\checkmark$ 

Care should be made on using carbon steel for caustic service

# 3.8. WET CO<sub>2</sub> CORROSION

 $\checkmark$ 

This corrosion mechanism, less commonly encountered in refineries than upstream oilfield and gas plant operations, is caused by carbonic acid.

Carbonic acid is corrosive to carbon and low alloy steels, corrosivity being dependent on a range of factors including CO<sub>2</sub> partial pressure, temperature, and liquid phase composition and flow velocity. Corrosion rates have been calculated using de Waard et al formulae

# **CARBON DIOXIDE CORROSION**

CO<sub>2</sub> Gas is soluble in water
 CO<sub>2</sub> Solubility increases with temperature and pressure
 CO<sub>2</sub> Dissolves in water forming carbonic acid which attacks carbon steel



With CS, use of filming and neutralizing inhibitors + suitable corrosion allowance

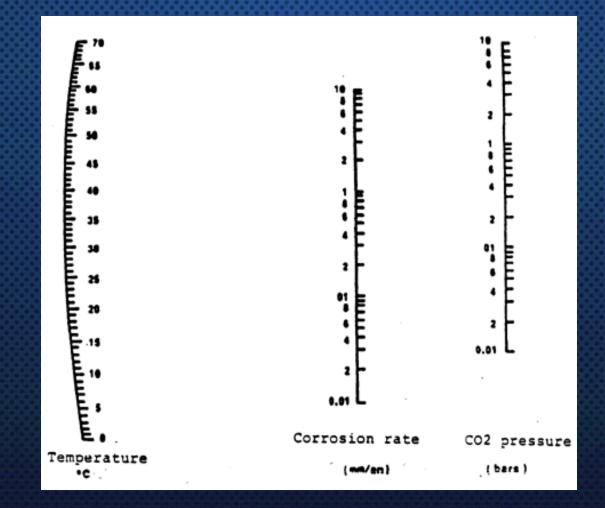


Use of austenitic stainless steel if water contains less than 400ppm Cland temperature less than 50 Deg C



The best alternative is the use of duplex stainless steels or higher corrosion resistant alloys (CRA)

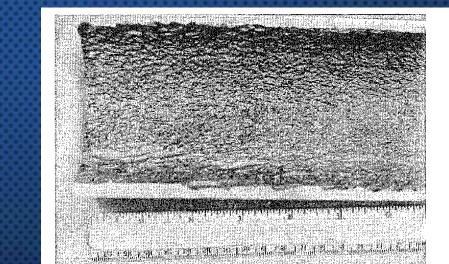
## 3.8. WET CO<sub>2</sub> CORROSION (CONT.)



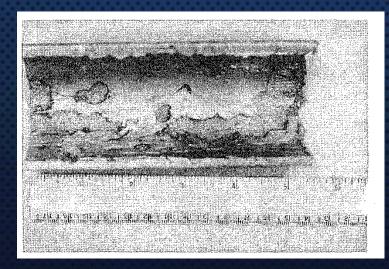
Nomogram for CA of CS in CO<sub>2</sub> Service, De-Waard and Milliams

# FORMS OF CO<sub>2</sub> CORROSION (CONT')





#### CO2 Pitting Corrosion



#### Uniform

#### Pitting with scales in turbulent

## **3.9. CHLORIDES CORROSION**

Austenitic stainless steels and high alloys may be prone to pitting, crevice or stress corrosion cracking in chlorides environment

The standard 300 series austenitic stainless steels are potentially at risk of stress corrosion cracking in chloride containing environments at temperatures above about 60°C. It is common to apply external coatings, or foil wrapping under insulation, to such pipework in marine environments to prevent access of chlorides from rainwater and concentration at the metal surface.

# **3.9. Chlorides Corrosion**



Formation water is the main source of salts

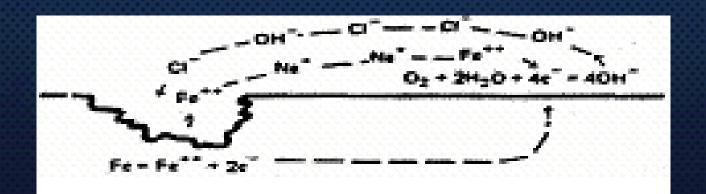




Austenitic stainless steel shall not be used at high levels of salinity

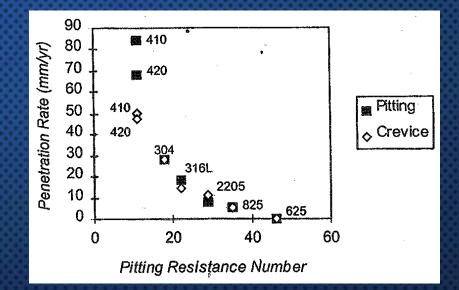


CRA with a PREN>40 or a non-metallic material shall be used for handling high salinity water.

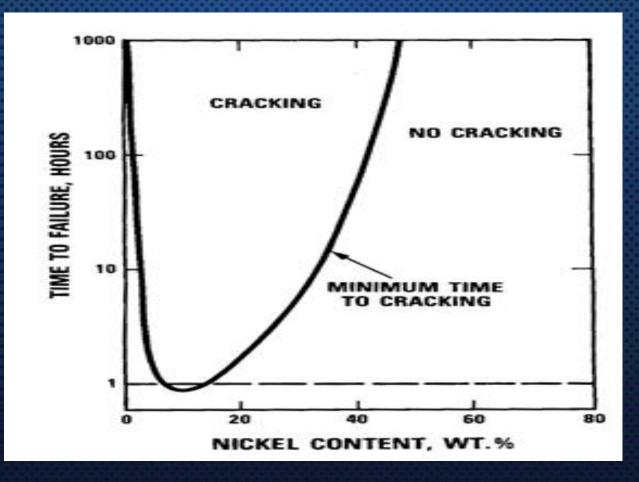


## **CHLORIDES PITTING**

Reduction in pitting and crevice attack with increasing Pitting resistance Number



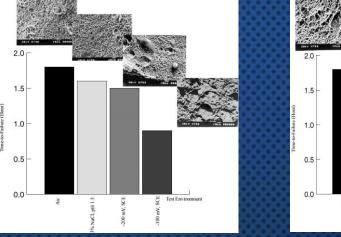
3.9. CHLORIDE PITTING, CREVICE AND STRESS CORROSION OF STAINLESS AND HIGH ALLOY MATERIALS(CONT.)

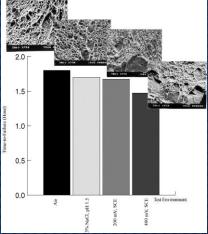


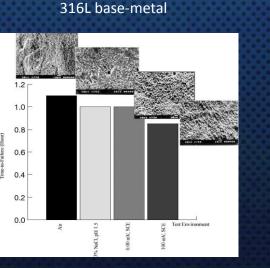
Effect of Ni content on SCC of high alloys- Copson

#### **CHLORIDES SCC**

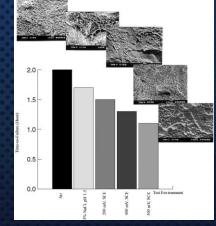
- TIME-TO-FAILURE HAS BEEN SELECTED AS A SCC CRITERION
- ALL TESTED SPECIMENS SHOWED A DECREASE IN TIME-TO-FAILURE ON TENSILE TESTING IN SOLUTION AT OPEN CIRCUIT POTENTIAL AND AT APPLIED POTENTIALS AND EVEN WITH INCREASING POTENTIALS IN THE NOBLE DIRECTION.
- OPPOSITE GRAPHS SHOW THE REDUCTION IN TIME-TO-FAILURE WITH A CORRELATION TO THE FRACTOGRAPHS OF OUTER ZONES OF FRACTURED SURFACES.







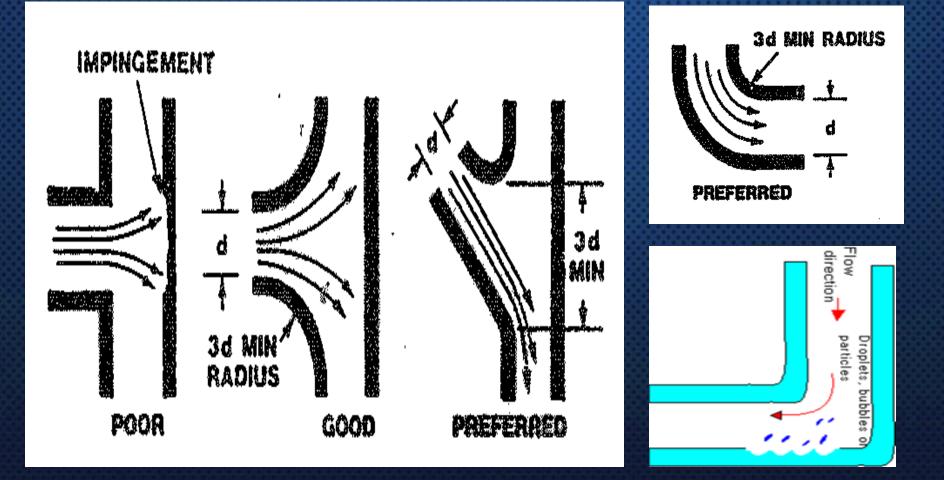
6% Mo base-metal



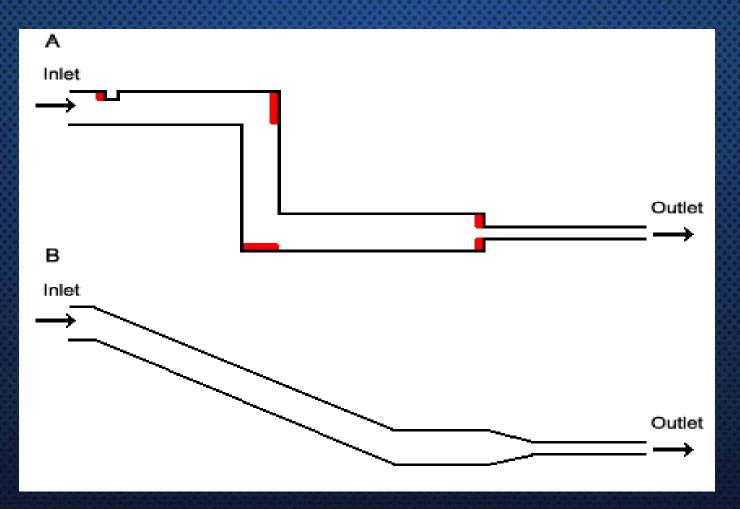
316L weldment

6% Mo weldment

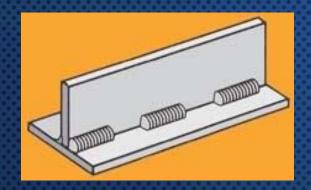
# **II. Improved Design**



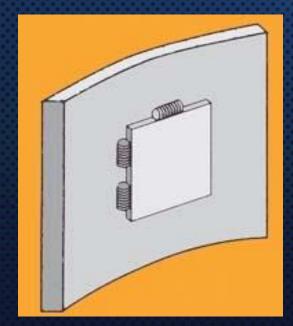
#### **Examples of Impingement Corrosion**



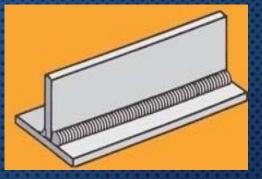
Examples of avoiding impingement corrosion by design



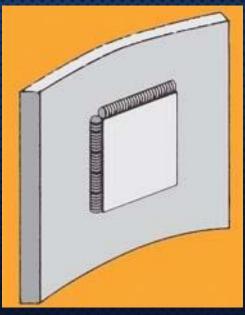
Bad



Examples of avoiding crevice corrosion by design



Good



Improved Design, e.g.:

**Incorporation of corrosion allowance** 

 $t_{(required)} = t_{min} + CA$ 



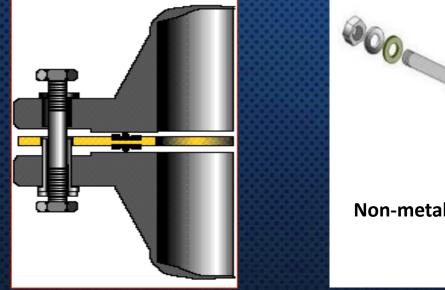
Life time = corrosion allowance (mm) / corrosion rate (mm/year)

Incorporation of corrosion allowance

CYLINDRICAL SHELLS	SPHERE SHELLS	PIPES
$T = \frac{PR}{$	$T = \frac{PR}{2SE-0.2P} + C.A$	PR T =

P: design pressure in N/mm<sup>2</sup>
R: inside radius, mm
S: stress value of material, N/mm<sup>2</sup>
E: joint efficiency
CA: corrosion allowance, mm
t : min. corroded thickness, mm

### Avoiding contact between dissimilar metals using Isolating Flange Kit







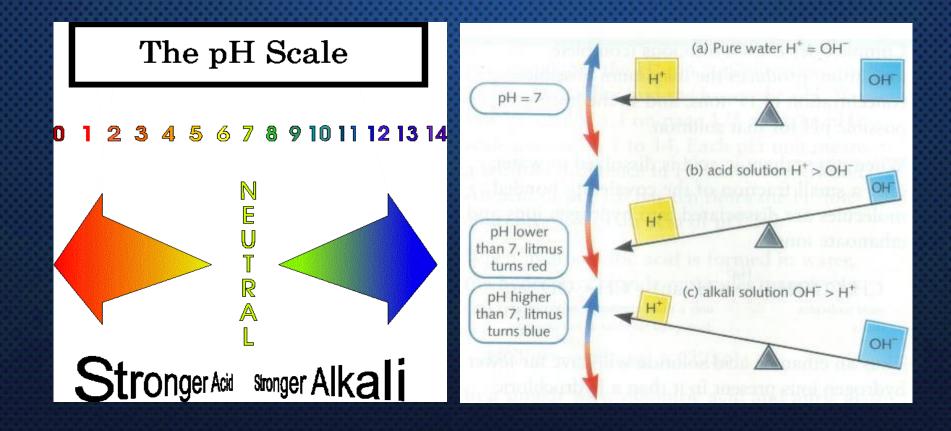
Chemical treatment involves injecting chemicals that Retard the corrosion of a metal.

**Types of Treatment :** 

	<b>_</b>
	/
_	

Neutralization ( pH control ) Removal of dissolved gases ( scavengers ) Corrosion inhibitors Biocides

### A. pH Control

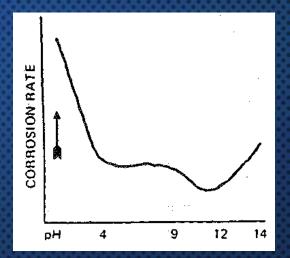


### A. pH Control

Steel corrosion rate related to hydrogen ion concentration in electrolyte To avoid acid corrosion, the pH of the medium shall be raised up to about 7 by injection of

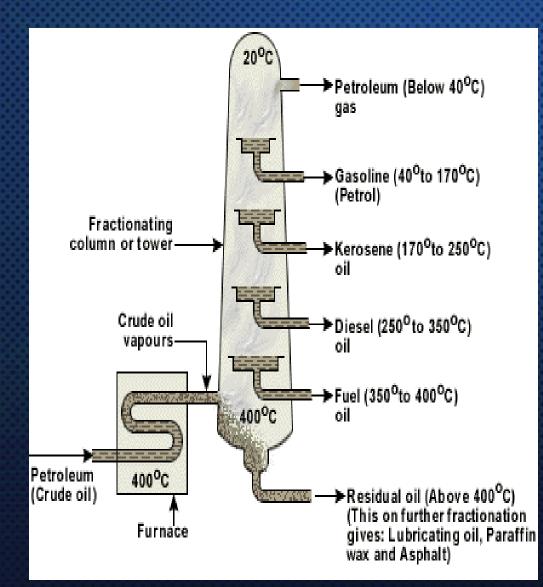
- Caustic Soda NaOH
- Ammonia NH<sub>3</sub>

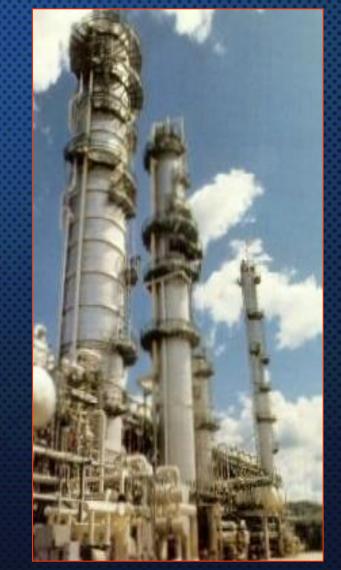




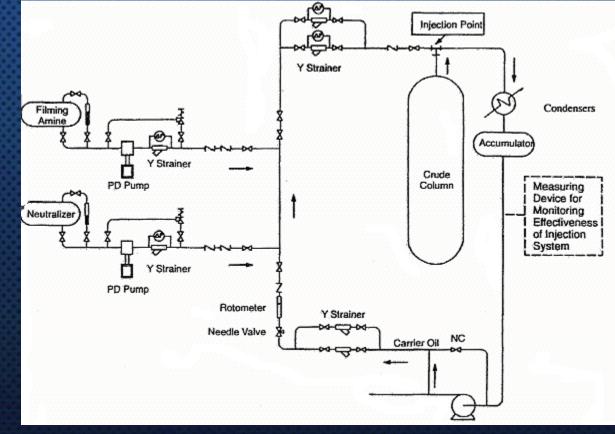


### **Crude Oil Fractional Distillation**





Chemical injection system for a crude distillation column overhead



### **B. Removal of Dissolved Gases**

- Dissolved oxygen can be removed by injection of oxygen scavengers
- Mechanical deaerator can also be used to remove all dissolved gases: O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S
- Amine units can be used to remove CO<sub>2</sub> & H<sub>2</sub>S
- Periodical checks on dissolved O<sub>2</sub> concentration by means of O<sub>2</sub> probes

### **C.** Corrosion Inhibitors

**NACE definition :** 

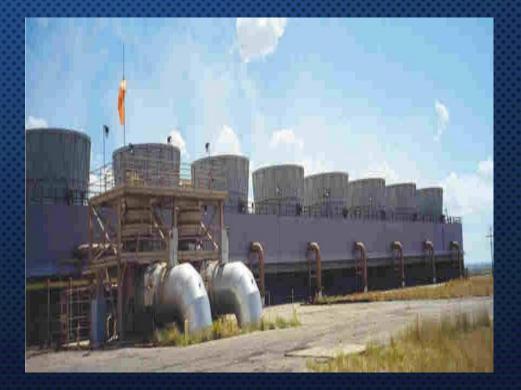
" Chemicals which reduce the corrosion rate when added to a normally corrosive medium in small concentrations."

Inhibitors selection is based on:

- Metal
- Environmental chemical composition
- Service condition (e.g. temperature, flow rate)

## **Application of Corrosion Inhibitors**

- Oil refineries
- Petrochemical plants
- Oil and gas production
- Desalination plants
- Cooling water installations
- storage facilities
- Hydro tests



**A Cooling Tower Unit** 

### **Classification of Inhibitors**

Inhibitors for Acid media

pH < 5

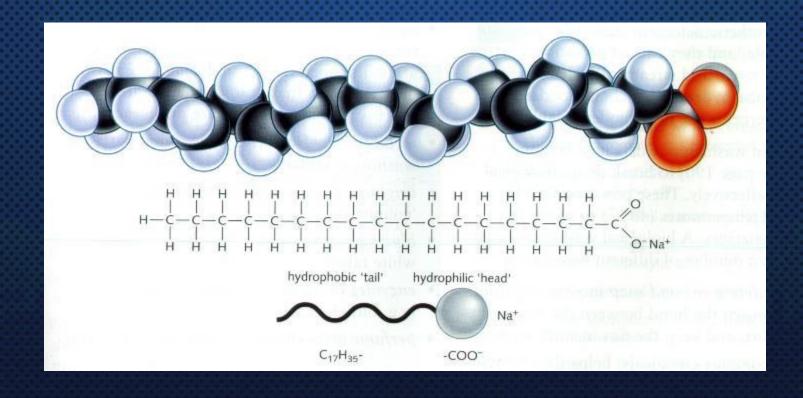
Inhibitors for Near-Neutral media

pH 5 – 10

 Above pH 10, the alkalinity (OH<sup>-</sup> ions) of the medium is selfinhibiting

### A. Inhibitors for Acid Media

Usually organic compounds with long hydrocarbon chains with polar (charged) head



### **B. Inhibitors for Near Neutral Media**

Usually are inorganic compounds

- Anodic
- Cathodic, or

Mixed (Mixtures of both anodic and cathodic inhibitors )

### **C. Inhibitors for Near Neutral Media**

In case of Absence of the inhibitor: usually are categorized as:

Safe or Dangerous

- Safe

General Corrosion 

### **Mixed Inhibitors**

Mixtures of both anodic and cathodic inhibitors

Block both anodes and cathode

Compatible mixture

### **Efficiency of Inhibitors**

**Expressed** as :

**Protective Power (Z)** 

Where,

 $Z = [(R_0 - R) / R_0] X 100$ 

**R**<sub>o</sub>: Corrosion rate in absence of inhibitor.

**R** : Corrosion rare in presence of inhibitor.

### **Efficiency of Inhibitors**

Curve showing drop in corrosion rate as a function of inhibitor concentration

**Corrosion** rate

## Corrosion inhibitor concentration

### **D.** Biocides

#### Definition

A substance that is capable of killing a certain micro-organism or spectrum of Micro-organisms

• Biocidal activity

The concentration needed to kill the micro-organisms MKC VALUE = minimum killing concentration

### **Biocides role in corrosion control**

- KILL MICRO-ORGANISMS THAT FEED ON THE CORROSION INHIBITORS
- KILL MICRO-ORGANISMS THAT PRODUCE CORROSIVE METABOLITES

#### Sulfate-reducing bacteria (SRB)



### **Control of Microbial Corrosion**

**USE OF BIOCIDES IN CLOSED SYSTEMS** 

- CAPABLE OF KILLING WIDE RANGE OF MICROBES
- BIODEGRADABLE, ENVIRONMENTALLY FRIENDLY
- NON-HARMFUL FOR HUMANS AND OTHER LIVING ORGANISMS
- COMPATIBLE WITH THE METAL, I.E. NON-CORROSIVE
- TWO DIFFERENT BIOCIDES TO BE USED ALTERNATIVELY



### **Chemical Injection**

#### **Chemical Injection Skid :**

Chemical Tanks

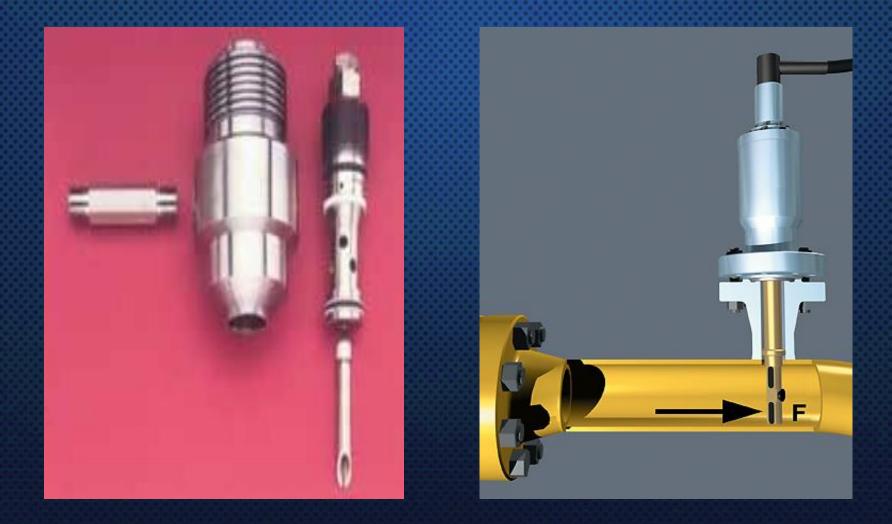
Chemical Injection (Dosing) Pumps



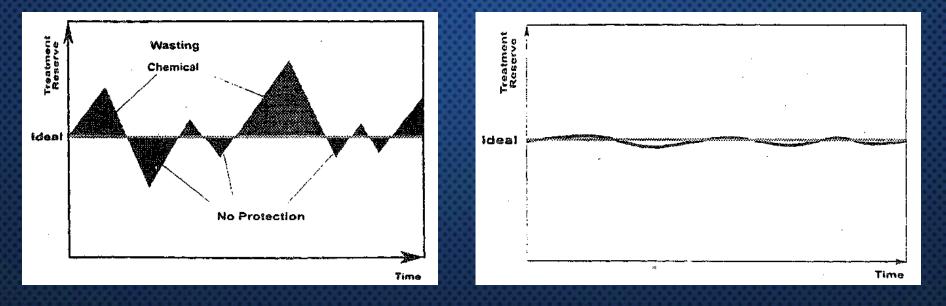
**Non-metallic Tanks** 



### **Chemical Injection Point**



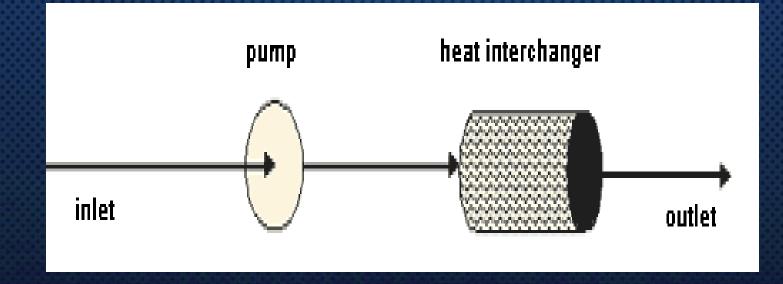
**High Alloy Quell** 



#### **BAD CONTROL**

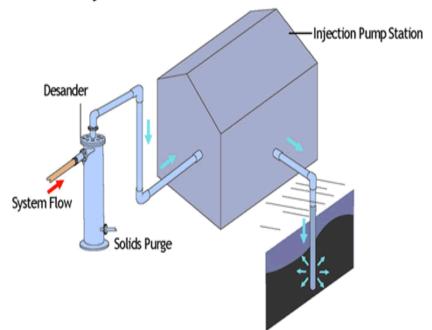
#### **GOOD CONTROL**

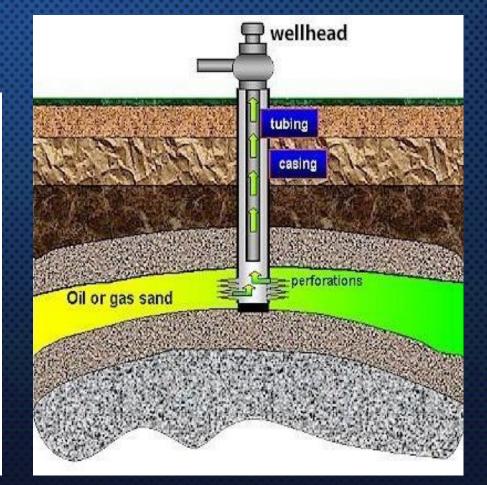
Once – through Systems



#### Water Flooding & Wells

Waterflood Injection Protection







#### **Definition :**

*"the systematic measurement or evaluation of the corrosion rate and type of corrosion occurring on an equipment "*.

#### **Advantages of Corrosion Monitoring**

- Avoids unplanned shutdowns
- Avoids loss of production resulting from unforeseen corrosion failure
- Effective scheduling of maintenance works
- Reduction of inspection activities

The efficiency of corrosion inhibitors is checked by means of monitoring system.

Coupons

Electrical Probes

#### **Corrosion Coupons**

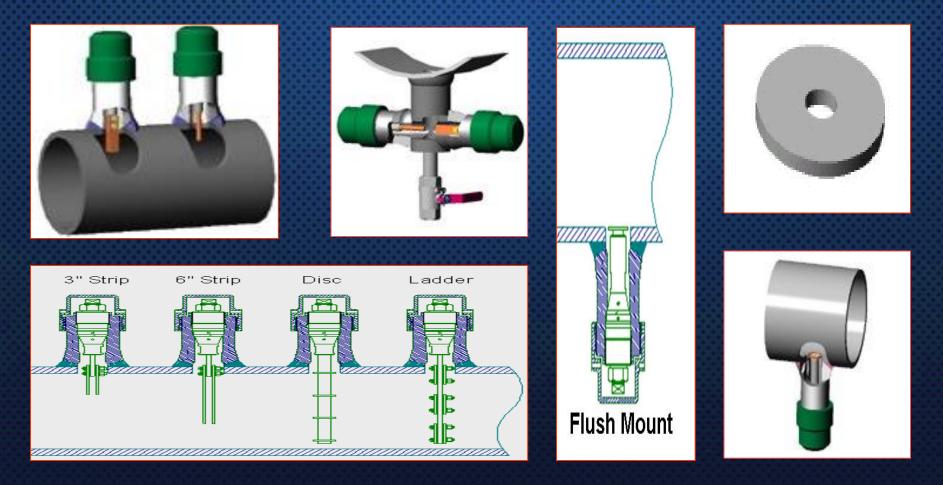


#### **Cylindrical Coupons**



#### **Strip Coupons**

#### **Typical corrosion monitoring point**



#### **Coupon Handling**



**Retrieving the coupon** 



Removal of corrosion product by soft wire mesh Removal of corrosion product by soaking in inhibited acid The coupon is accurately weighed

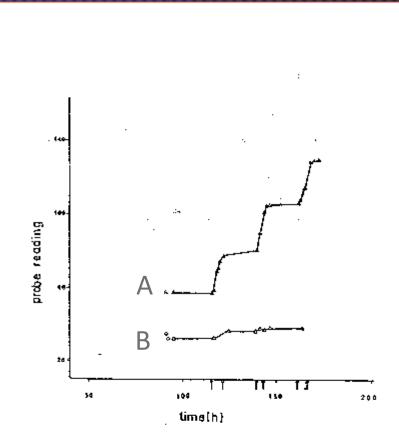
**Electrical Resistance (ER) Probe- Corrosometer** 



Electrical resistance probe measurements for mild steel coupons

A. In corrosive mediaB. In non-corrosive media





Electrical resistance probe measurements for mild steel foils exposed to SRB cultures purged with nitrogen (A) and air ( $\Delta$ ); t = sparge on/off

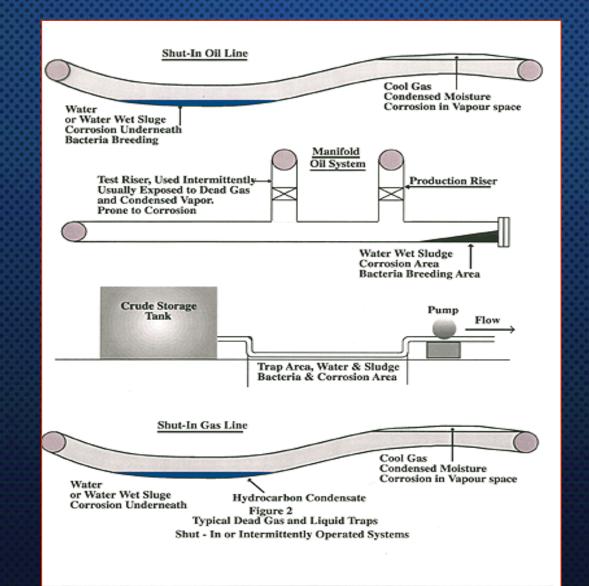
#### **Corrosion Monitoring Point**

#### **Usually includes:**

Corrosion Coupon ; mainly for visual evaluation of corrosion type

Electrochemical Probe ; for more accurate instantaneous corrosion rate determination, e.g. ER probe





On-Line Wall Thickness (UT) Measurements



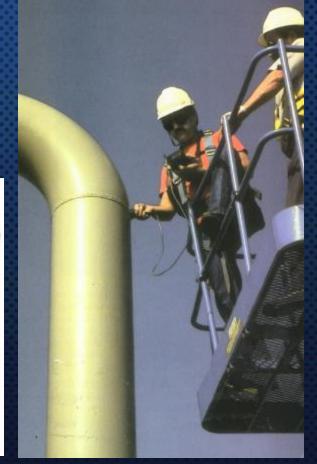
Base-line readings are taken at selected locations before and placing the

equipment in service



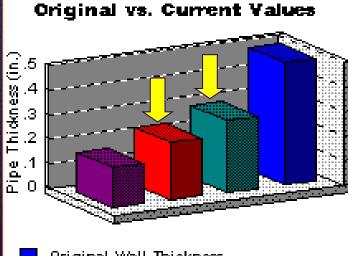
A-scan (Spot),
B-scan (Linear),
C-scan (3D)





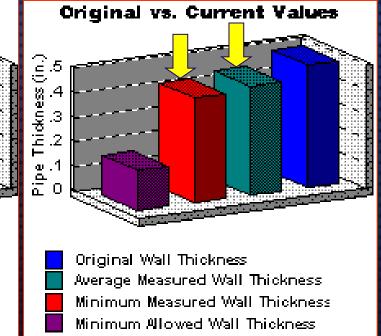
On-Line Wall Thickness (UT) Measurements

#### Without Inhibition

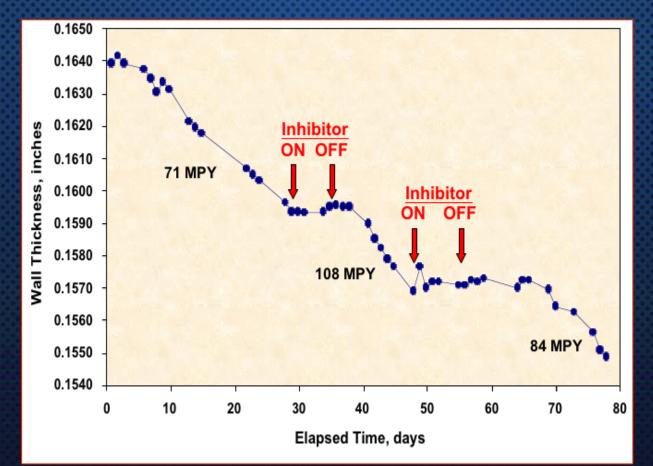


Original Wall Thickness Average Measured Wall Thickness Minimum Measured Wall Thickness Minimum Allowed Wall Thickness

#### With Inhibition



#### On-Line Wall Thickness (UT) Measurements



# IV. PROTECTIVE COATINGS

# **3. Protective Coatings**



A material that adheres to and covers the metal surface

 The coating can be applied :
 onto external surfaces; external coating and / or
 onto internal surfaces; internal coating (Lining)

# **Types of Coatings**







#### Paints

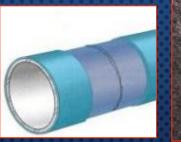
Applied externally & internally

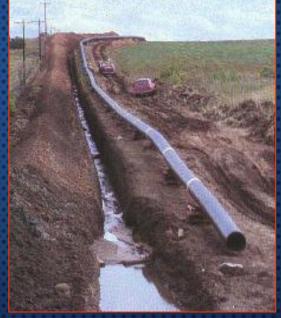
#### Wrapping

Applied externally only Heat-Shrinkable Sleeves Applied externally only

# Wrapping & Sleeves

### Used mainly for field joints





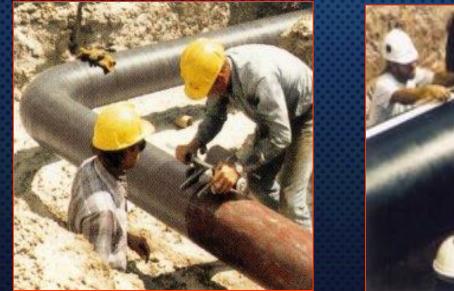






# Wrapping & Sleeves

Wrapping can be used for under- ground in-plant piping, e.g. open & closed drain piping network





# Corrosion Control Techniques 3. Protective Coatings



Definition : " a liquid material, which can be applied on a surface, and which – after drying – forms a thin, cohesive, non-porous film with good adhesion to the surface".



### **Surface Preparation**

Performed prior to coating application:



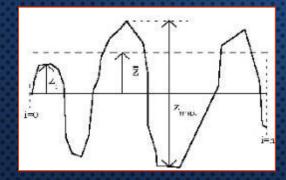




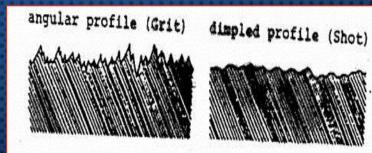


### **Surface Profile**

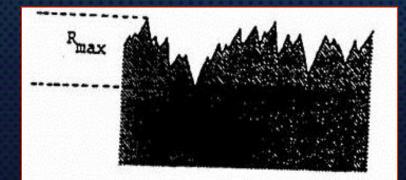
### THREE PARAMETERS ARE IMPORTANT TO OBTAIN ACCEPTABLE SURFACE PROFILE :

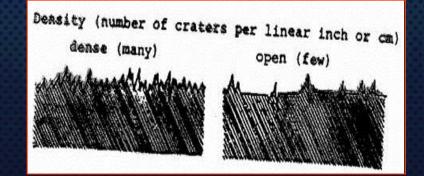


#### 1-Peak to valley depth



#### 2-Shape of craters





#### **3-Density**

# **Surface Cleanliness International Standards**

Surface Finish	USA Spec. SSPC	NACE	British Std. BS 4232	Swedish SIS 05 5900	Japanese Std. SPSS
White Metal	SSPC-SP 5	NACE 1	1st quality	SA 3	
Near White Metal	SSPC-SP 10	NACE 2	2 nd quality	SA2 1/2	JA Sh2 or JA Sd2
Commercial Blast	SSPC-SP 6	NACE 3	3 rd quality	SA 2	JA Sh1 or JA Sd1
Brush Off Blast	SSPC-SP 7	NACE 4	-	SA 1	-

# **Surface Cleanliness**

Removal of scales, rust, dirt, grease, etc... Done by : Water jetting Abrasive blasting (<u>provides surface roughness</u>)

Sand blastingGrit blasting



# Water Jetting





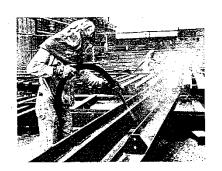
### **Abrasive Blasting**

Sand blasting

not recommended as it causes air pollution by increasing the amount of suspended solids



Provides reasonable surface roughness



Sand-blast, Open Yard Cleaning

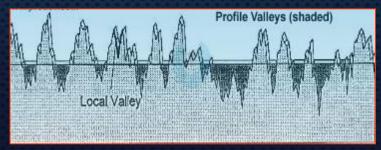
#### SAND BLASTING

# **Grit Blasting**

- By using metal shots with sharp edges
- Recommended as it does not cause air pollution
- Provides excellent surface roughness ( profile )
- Recyclable







### **Chemical Composition of Paints**

Primary Components : Resin ( binder / vehicle / base ) Hardener ( curing agent ) Solvent ( thinner )

Secondary Components : Color Pigments Cementing Particles Corrosion Inhibitors

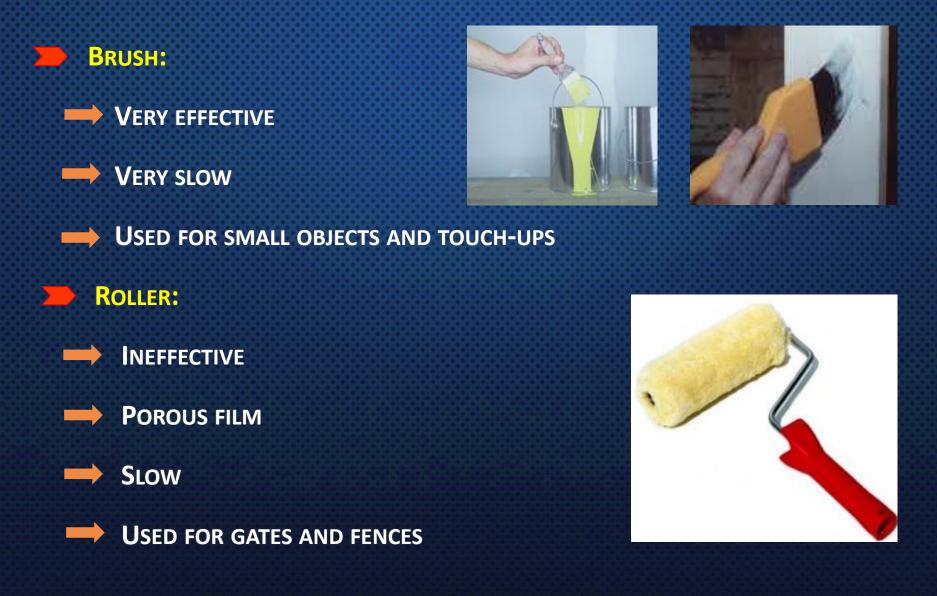
# **Painting Application**



PAINT APPLICATION METHODS PAINT APPLICATION CONDITIONS PAINT APPLICATION DEFECTS PAINT INSPECTION



# **Paint Application Techniques**



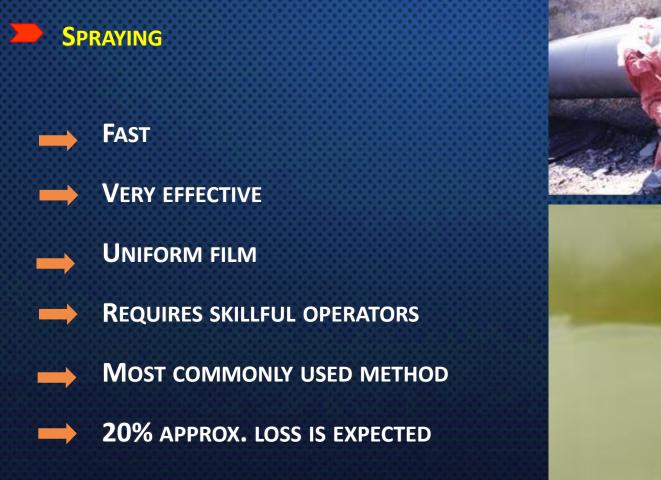
# **Spray Application**

Fan

Atomization : converting a liquid into tiny minute droplets

SPRAYING = ATOMIZATION

# Spraying (cont.)







# **Air Spray**



ATOMIZATION OF PAINT IS ASSISTED BY AIR

**REQUIRES AIR COMPRESSOR + AIR FILTERS** 



AIR QUALITY IS A MUST

NOT SUITABLE FOR PAINTS CONTAINING OXIDIZABLE METAL PARTICLES , E.G. ZINC-RICH PAINTS





# **Airless Spray**

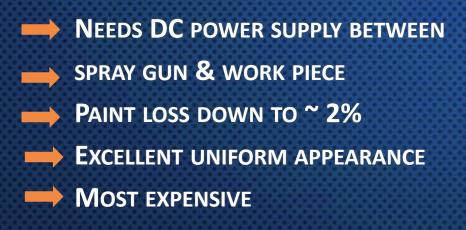


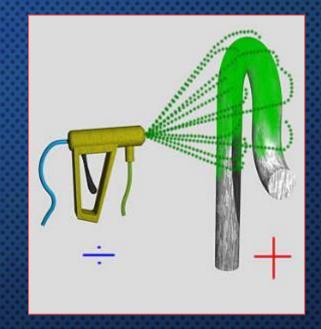
**SUITABLE FOR METAL-CONTAINING** PAINTS **REQUIRES HIGH PRESSURE PUMPS**  $\rightarrow$  Atomization is due to  $\Delta P$ 





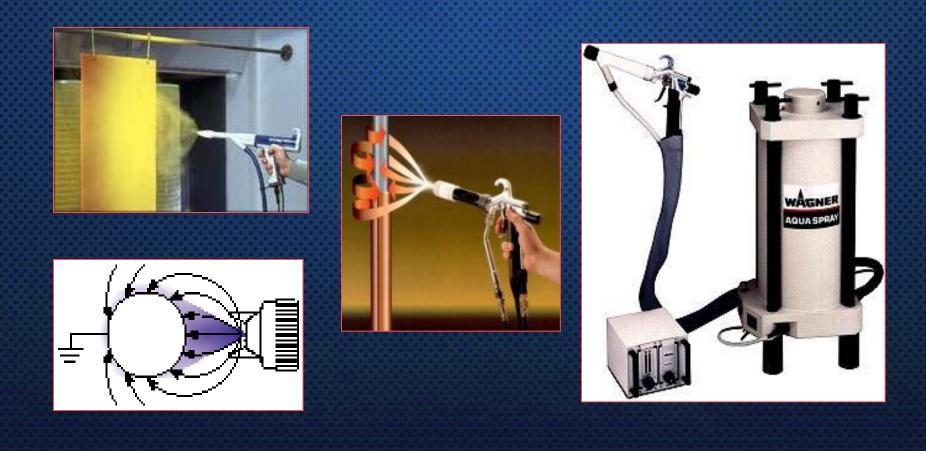
### **Electrostatic Painting**







# **Electrostatic Spray**



# Painting System (Cycle)

#### The 3-layer paint system :

Primer :1<sup>st</sup> layer
Provides corrosion protection
Provides adhesion to metal surface

Inter-coat : 2<sup>nd</sup> layer
Provides mechanical strength to the system

Top (Finish) : 3<sup>rd</sup> outmost layer
 Provides UV resistance
 Provides abrasion resistance
 Provides the specified color code

Steel

### **3-Layer Paint System**

Primer : Zinc-rich compounds Inter-coat : High build / solids epoxy Top (Finish) : Polyurethanes

Recommended paint system For external steel surfaces at ambient temp. up to 94°C

For higher temperatures, special painting systems to be specified

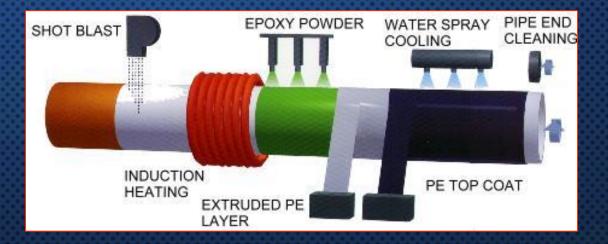
For internal surfaces, No need for neither top coat Nor color code. Use extra thicker inter-coat instead

**Pipeline Coating System** 

3-Layer System
 Polyethylene
 Or



2-3 mm Thick



# **Keys of Coating Success**



SURFACE PREPARATION MATERIALS COATING APPLICATION INSPECTION



### Corrosion Control Techniques 3. Protective Coatings

**CONDITIONS OF SUCCESSFUL PAINTING APPLICATION :** 

**1.** Adequate lighting 500-1000 lumen /  $M^2$ 

**2.** PROPER VENTILATION FOR CONFINED OR CLOSED AREAS TO ENSURE PAINT DRYING

**3.** Skin temperature between 3-45°C

# **Dew Point Measurement**

# DATASET

#### MEASURES

- Ta air temperature
- Ts surface temperature
- RH relative humidity

#### CALCULATES

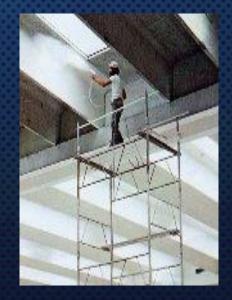
- Td dew point temperature
  - the difference between surface and dew point temperatures



#### **Key to Successful Painting**

- 1. NO RAIN
- 2. No dust
- **3.** Relative humidity does not exceed 85%
- 4. No wind
- 5. Atmosphere temperature should be between 10-50 °C
- **6.** GOOD ACCESSIBILITY FOR THE WORK PIECE





# **Key to Successful Painting**

#### **6.** PAINT INSPECTION

- INTEGRITY OF CANS
- SHELF-LIFE
- POT LIFE
- INDUCTION TIME
- COLOR CODE (TOP COAT)

#### 7. PAINT SYSTEM / CYCLE

- PRIMER
- INTER-COAT
- TOP COAT OR FINISH





# **Key to Successful Painting**

- 8. PAINT TECHNICAL DATA SHEET
  - GENERIC TYPE
  - CURING TIME
  - **DFT (**DRY FILM THICKNESS) LIMITS

9. PAINT APPLICATION DATA SHEET

- MIXING RATIO
- SAFETY REGULATIONS DURING APPLICATION

**10. PAINT SAFETY DATA SHEET** 

11. OPERATOR SKILLS (WORKMANSHIP)





# **Painting Data Sheet**

Company		Pf	AINTING	SPEC	TFICAT	ΠON				000	D-00	0.10	10-2
. ,	-						Re	0	1	2			
							v						
				YE/	<b>VR</b>		200	ß					
			PAI	INTIN	G SYSI	EMS	•						
			PAIN	<b>IING</b> :	SYSTEP	MNO.	. 2						
SERVICE													
Material	Cat	oone	steels & lo	ow all o	ys(�%	Cr)	C:T	emp	l				
Environment	Ons	hore	, above gr	round			From		]	To			
Items		External surfaces of piping vessels,			Aml	nien	t	9	13				
	heat	heat ex changers, towers, columns, etc.		s, etc.									
AINTING CY													
Preparation/pai	inting	I			Require	ments	1				DF	Т	
										A)	Aicr(	ons)	
Surfaceprepar	ation		SA2.5										
Primer			Inorgani								75		
Inter-coat			Polyamic	de MC	) epoxy:	sealari	t				125	5	
Top-coat			Polyareti	hane							50		

Steel

#### **Coating Properties**



IN ORDER TO PERFORM EFFECTIVELY, A CORROSION RESISTANT PAINTING MUST BE CHARACTERIZED BY SOME ESSENTIAL PROPERTIES.

- WATER RESISTANCE
- CHEMICAL RESISTANCE
- **PROPER ADHESION**
- COHERENT
- ABRASION RESISTANCE
- ABILITY TO EXPAND AND CONTRACT
- WEATHER RESISTANCE
- Non-porous
- PLEASING APPEARANCE



**Environmentally Friendly** 



**Rigid non-flexible paint** 

### **Paint Inspection**

Surface cleanliness
Surface roughness
Conditions of paint application & equipment
Coating defects & holidays
Coating adhesion
Coating dry film thickness

#### **Surface Cleanliness Inspection**

Visual inspection for surface solid particles, e.g. dust



#### **Magnifying Lenses**

Torch

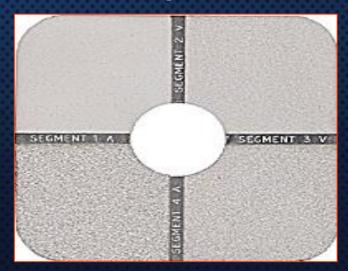
**Masking Tape** 

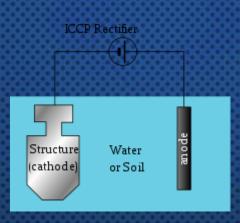
#### **Surface Cleanliness Inspection**

SA 2.5 : Near-white, for external surfaces
 SA 3 : White, for internal surfaces



Comparator

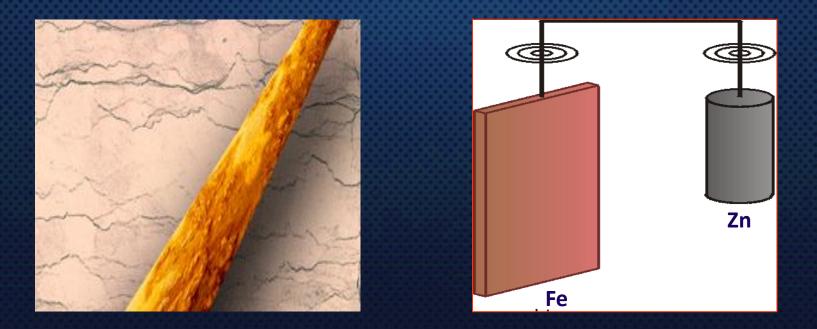




# V. CATHODIC PROTECTION

#### **Corrosion Control by Cathodic Protection**

- Cathodic protection is defined as the means of using galvanic series as well as polarization principles to protect the structure against corrosion.
- Cathodic protection has been discovered as galvanic corrosion occurred on using copper rivets in ship hulls.

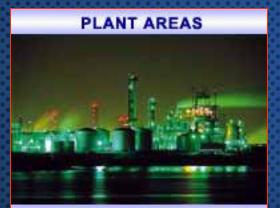


#### **Application of Cathodic Protection**

In industry cathodic protection is applied to:

- Ship hulls
- Offshore jackets
- Offshore jetty piles
- Offshore sheet piles
- Offshore pipelines
- Buried piping and pipelines
- On-grade storage tank bottoms
- Buried tanks
- Water tank interiors (as well as water portion of crude storage tanks)
- Any other electrolyte immersed structure

#### **On-Shore Applications of CP Systems**



Underground pipelines Tank bottoms Earthing conductors Power cables



Oil well casings Gas well casings Water well casings



Oil pipelines Gas pipelines Water pipelines Service lines

#### INTERNAL PROTECTION



Storage tanks Heat exchangers Coolers, Turbines Condensers, Pipelines

### **Off-Shore Applications of Cathodic Protection**



Platforms, Oil rigs Jetties, Harbours Water intakes, Sluices Vessels, Pipelines



#### **CP Codes and References**

There are numerous codes and references that shall be referred to when dealing with cathodic protection among these are:

- NACE RP 0169
- NACE RP 0176
- NACE RP 177
- NACE RP 575
- BS 7361 PART I
- DNV RP B 401
- API 651
- J. Morgan, "Cathodic Protection"
- A.W. Peabody, "Control of Pipeline Corrosion"

#### **CP** Techniques

There are two cathodic protection techniques these are:

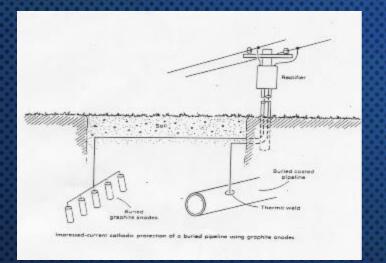
-Sacrificial (Galvanic): Involves the use of a more active metal as a source of protection current (anode)

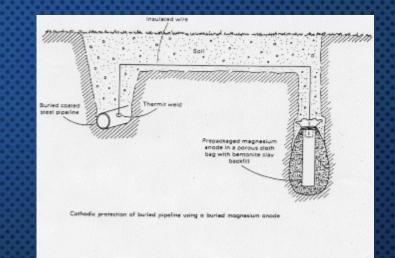
-Impressed current: Involves the enforcement of protection current by the use of a DC power source connected to anodes (positive terminal) and to cathode (negative terminal)



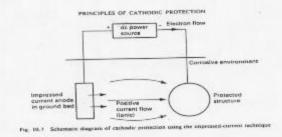


#### **CP** Techniques









ICCP

Sacrificial

#### 196

## Sacrificial and Impressed Current CP

Sacrificial	Impressed current
No need for external power source	Requires an external power source
Easy to design and install	Requires skillful design and installation
uncontrollable	Can be controlled
Used only for limited surface areas and well coated structures	Can be used for uncoated surfaces and used for any surfaces
Has no detrimental effects	Can cause serious problems if not handled carefully
Is limited to low resistivity	can be used at any resistivity
Low maintenance	High maintenance

#### **Cathodic Protection Criteria**

There are several criteria for determining whether a structure has adequate cathodic protection. Once a testing method is adopted, it should continue to be used. The following methods are discussed:

Potential- instant off

• Potential- shift criteria

### **Instant off Potential**

Material Potential in mV (VS. Cu/CuSO<sub>4</sub>)

Steels, cast irons, alloy steels and stainless steels • Anaerobic Conditions • Aerobic Conditions Copper Lead Aluminum

-950 -850 -500 -600 -950

## **100mV Potential Shift**

- When the potential shift is 100mV or more then the structure is said to be cathodically protected.
- Method involves the registry of structure's natural potential and then recording potential shift.
- Method difficulty remains in isolating all sources of current.

#### **Sacrificial Anodes**

For soil applications, anodes used are either magnesium or zinc.

- Zinc use in soil is restricted above soil resistivity of 1000 Ω.cm
- Magnesium come in two types, standard and high potential.

#### **High Potential Mg Anodes**



High potential magnesium anodes are used for higher resistivity applications

Element	ASTM B843 Industry Standard for M1C High Potential Anodes
Aluminum	0.01% max
Manganese	0.50 - 1.3%
Silicon	0.05% max
Copper	0.02% max
Nickel	0.001% max
Iron	0.03% max
Others, each	0.05

# **Standard Mg Anodes**

#### Standard Mg anodes use is restricted above a resistivity of 3000 Ω.cm

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Aluminum	5.3 - 6.7%
Zinc	2.5 - 3.5%
Manganese	0.15 - 0.7%
Silicon	0.10% max
Copper	0.20% max
Nickel	0.002% max
Iron	0.003% max
Others	0.30% max
Magnesium	Remainder

**Typical Chemical Analysis** 

# **Electrochemical Properties of Mg**

Properties	High Potential Mg	Standard Mg
Specific gravity	1.77	1.80
<b>Open Circuit Potential (V, Cu/CuSO4)</b>	-1.75	-1.55
Efficiency (%)	50	50
Effective Current Capacity (A.hr/kg)	1,100	1,100

### **Zinc Anodes**

#### **Chemical Composition**

Zinc anodes are used either for soil cathodic protection at low resistivities or in sea water applications. Zinc has a limited output capacity.

Component	Composition (%, weight)
Fe	0.005 max.
Cd	0.025 ~ 0.07
Pb	0.006 max.
Cu	0.005 max.
Al	0.1 ~ 0.5
Zn	Remainder

#### **ASTM B 418 Type I Properties**

Properties	Zincano
Specific gravity	7.14
Open Circuit Potential (V, Ag/Agcl)	-1.05
Efficiency (%)	95
Effective Current Capacity (A.hr/kg)	780

#### **Sacrificial Anode Backfill**

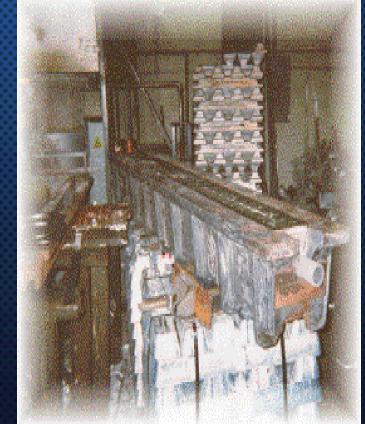
This specially formulated anode backfill is used with either magnesium or zinc anodes. The standard anode mixture consists of: •75% gypsum, •20% bentonite •5% sodium sulfate



#### **ALUMINUM ANODES**

# • Typical chemical composition of aluminum anodes is shown

Element	Percentage	
Indium (In)	0.016 to 0.02%	
Zinc (Zn)	4.75 to 5.75%	
Silicon (Si)	0.08 to 0.12%	
Copper (Cu)	0.003% Maximum	
Iron (Fe)	0.12% Maximum	
Cadmium (Cd)	0.002% Maximum	
Others, each	0.02% Maximum	
Others, total	0.05% Maximum	
Aluminum	Remainder	



#### **ALUMINUM ANODES**

#### Electrochemical properties of aluminum anodes can be seen in the table.

Anode Capacity Potential (Calomel) Consumption Rate 1150 amp hours per pound (Minimum)1.080 volts (Minimum)7.6 pounds per amp year

 Aluminum anodes are used for ship hulls, offshore pipelines, jackets, etc.



#### **ALUMINUM ANODES**

 Aluminum anodes come in numerous shapes. Bracelet, slender or flush type are the aluminum anodes shapes used.



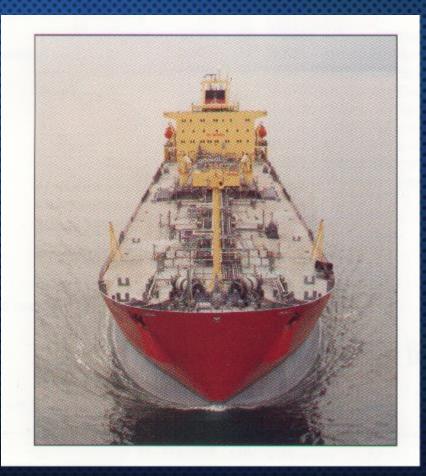




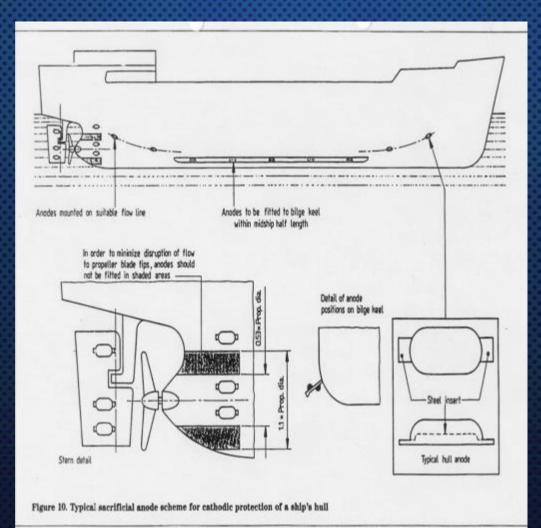
# **ZINC ANODES FOR MARINE APPLICATIONS**

 Zinc anodes are used for marine applications and for fresh water applications, it is readily used for tank interiors as well as other marine applications.

 Zinc anodes are used primarily for the protection of ship hulls



#### **Zinc Anodes**



#### **Impressed Current Anodes**

Impressed current anodes involves any material.

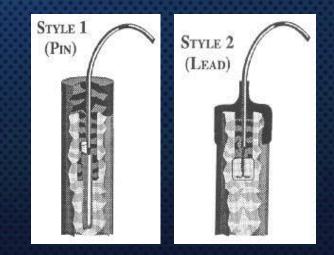
The most common impressed current anode materials are:

- FeSiCr
- Graphite
- Mixed metal oxide
- Platinized
- Elastomeric anodes

# Fe Si Anodes

- Are the most common impressed current anodes
- Are used in soil, water or sea water
- Come in two grades; FeSi and FeSiCr for sea water applications
- Anode typical chemical composition as well as electrochemical properties are shown.
- Anodes could be a single head type or double head, solid or tubular.
- Cable connection to anode shall be handled with great care.
- There are numerous methods of cable connections to anode.



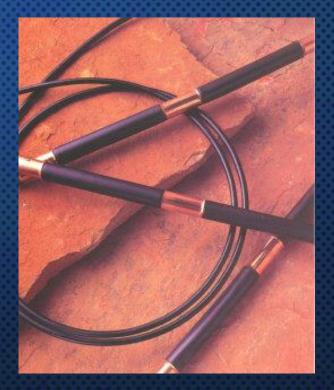


# Fe Si Anodes

	Silicon	14.20 - 14.75%
	Chromium	3.25 - 5.00%
	Manganese	1.50% max
Composition, ASTM A518 Gra	de 3 Carbon	0.70 -1 .10%
	Copper	0.50% max
	Molybdenum	0.20% max
	Electrochemical properti	<mark>es and an and a second s</mark>
Average soil resistitivity along groundbed, Ohm-cm	Maximum Amps per anode in coke breeze column, 12'' OD b 60''	- · · · ·
• •	coke breeze column, 12" OD b	y surface of coke breeze column,
groundbed, Ohm-cm	coke breeze column, 12" OD b 60"	oy surface of coke breeze column, Milliamps/sq ft
groundbed, Ohm-cm Less than 1000	coke breeze column, 12" OD b 60" 2.00	by surface of coke breeze column, Milliamps/sq ft 127 (see note)
groundbed, Ohm-cm Less than 1000 1000 - 1500	coke breeze column, 12" OD b 60" 2.00 1.75	by surface of coke breeze column, Milliamps/sq ft 127 (see note) 111 (see note)

## **MMO** Anodes

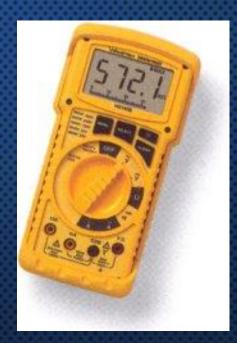
- Are termed non-consumable anodes
- They are used in extremely low resistivity soils and sea water applications.
- MMO anodes are platinum or titanium coated
- MMO anodes have the advantage of having a very light weight in comparison to its current output.



# **Potential Monitoring**

 As previously mentioned, cathodic protection criteria is achieved when a metal reaches a certain potential against a reference electrode.

 Potential is measured using a high impedance multimeter utilizing a reference electrodes.



# **Potential Monitoring**

- Reference electrodes could be portable or permanent.
- Reference electrodes shall be placed the closest to the structure being monitored.
- For soil applications Cu/CuSO4 reference electrodes are being used.
- For sea water applications either zinc or Ag/AgCl electrodes are used.

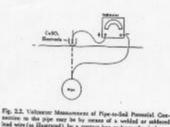




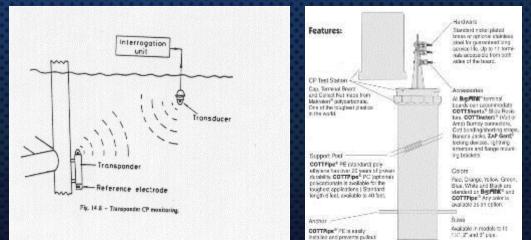
## **Test Stations**

Test stations are used as a mean for potential monitoring. It involves cable connection to the structure being monitored as well as other terminal for reference electrode.

 Test stations take many shapes and forms all of which serve the same purpose.



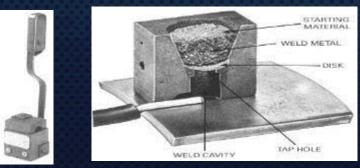
<sup>1</sup> and <sup>1</sup> variable resultance of Pipe-to-Sal Possonial Contraction to this pipe marks but by means of a welded or subkered lead wire (in illustrated), by a contact bar, or by sochastical consections to a value or fitting above the sublex. The latter should be used with mavies, an flanged fittings accretions introduce setimeness permittil. If the soil of m, a little water may be added to lower the downer maintance; it is unsally adresance to fig a little know the unsalts.



atio

## **Cable Connections**

- In general cables are connected to structures either mechanically or by metallurgically (welding)
- Mechanical joining is made to ensure easy replacement of anodes, it involves bolting and joining through a mechanical coupling.
- Metallurgical joining involves coupling through welding. Arc welding of anode inserts is made. Cable connections is made through either CAD welding or through pin brazing.
- CAD welding is made using a crucible, flint gun and thermite weld powder.
- Pin brazing involves the use of pin brazing machine and requires more skilled labor.







### **Cable to Cable Connection**

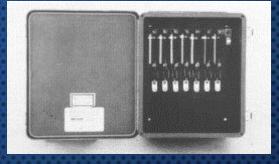
- In the case of impressed current anodes, cable to cable connection in the positive circuit is an extremely sensitive process, it requires a full isolation from the electrolyte.
- Impressed current cable to cable connections is made through splicing kits which involves full sealing with epoxy resin.
- Cable to cable connection in case of impressed current is not recommended for marine installations.



## **Cable to Cable Connection**

The second method for connection of cable to cable is through a junction box
Sometimes junction boxes are used to control current through variable resistors

- In the case of deep wells resistor cabinet is used to adjust anode outputs
  - Negative output of T/Rs is sometimes connected to negative junction boxes to balance output current to protected structures

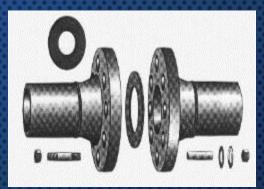






# **Electrical Isolation**

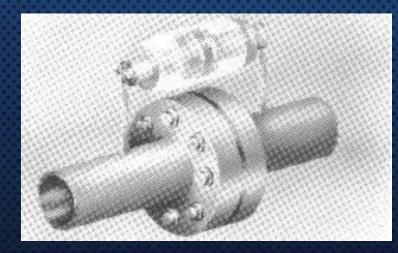
- Structures to be protected shall be isolated from portions that doesn't require protection. Hence electrical isolation shall be made.
- In case of underground piping, electrical isolation is made through the use of either isolating flange kits or through the use of monolithic joints.
- Isolating flange kits have the disadvantages of maintainability, can leak at high pressures.
- Isolating flange kits shall not be used in offshore environments
- Isolating flange kits have the advantage of having a relatively low cost and is easy to install.
- Monolithic isolating joints can be used at under any operating pressure.





## **Electrical Isolation**

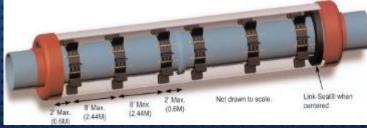
 Isolating flange kits can be a source of hazard and thus a spark gap shall be used with the IFK in hazardous areas.

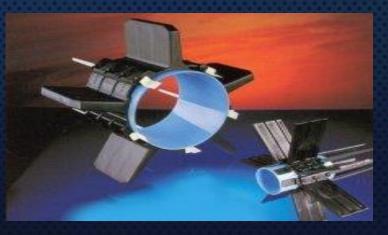


## **Pipeline Metallic Casing**

- Pipeline inside casing is not cathodically protected
- It shall be electrically isolated from casing
- Pipeline inside casing shall be protected and full sealing of casing shall be made
- Casing insulation from pipe is made using casing spacers and end seals.







### **Impressed Current Power Source**

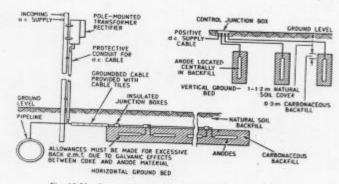
- Any DC power source can be used for energizing the impressed current for protection.
- The most common DC power sources used are the transformer rectifiers, which are either air cooled or oil cooled. Control of rectifiers is selected according to purpose.
- Solar power stations are used where there is no power supply
- DC generators could be used where there is an ample diesel supply

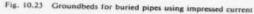


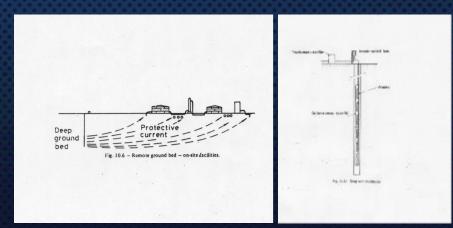


#### **Impressed Current Groundbed**

- Impressed current anodes are placed together in a 'groundbed'
- Groundbeds are either shallow (horizontal or vertical) or are deep (depth >30m)
- Shallow horizontal or vertical groundbeds are used where there is a single structure to be protected with no obstacles in between
- Deep anode wells are used in the case of protecting a congested plant and in the case of high resistivity.







## **Carbonaceous Backfill**

- Inorder to minimize the electrical resistance between groundbed anodes and earth, carbonaceous backfill is used.
- Coke breeze comes in many grades but the most important factor is the elctrical resistivity that shall be a minimum of 1 Ω.cm
- Impressed current anodes are some times cannistered with the backfill.
- Backfill shall be well tamped to eliminate air gaps and voids





# **Carbonaceous Backfill**

Property	218-L	218-R	251	251-P	4518
<ul> <li>Resistivity, ohm-inch</li> </ul>	0.02	0.02	0.01	0.01	0.01
<ul> <li>Resistivity, ohm-cm</li> </ul>	0.05	0.05	0.03	0.02	0.03
• Carbon (L.O.I. method)	99.0	99.0	99.8%	99.8%	99.9%
Moisture	0.10%	0.10%	0.07%	0.07%	0.02%
• Ash	0.35%	0.35%	0.12%	0.13%	0.10%
• VCM	0.30%	0.30%	0.02%	0.02%	0/22%
• Sulfur	3.75%	3.75%	5.8%	5.8%	4.3%
<ul> <li>Bulk Density (lbs/ft3)</li> </ul>	46-50	48-53	64-72	64-72	62-66
<ul> <li>General Sizing</li> <li>+ 4 Mesh</li> <li>+ 8 Mesh</li> <li>- 8 Mesh</li> </ul>	+4M < 10% +8M > 90% -8M < 10%	+4M 25% +8M > 70% -8M < 5%	+100N	Л <5% Л >70% Balance	4M 10% +20M > 80% -20M 10%
• Applications	Use for Ground Beds & Deep Wells				

#### **Cathodic Protection Surveys**

- Cathodic protection surveys are made for:
  - Gathering information regarding the electrolyte through resistivity and pH measurement
  - Gathering information with regards to any existing cathodic protection system
  - Information with regards to sources of corrosion hazard (sources of stray current)
  - Information with regards to power sources
  - Cathodic protection surveys could be made to existing underground facilities as means of evaluating the status quo of the structure survey includes:
    - DCVG survey
    - Line current survey
    - Potential Survey
    - Close interval survey
    - Interference survey

## **Soil Resistivity Surveys**

Table 2.3.3 Average resistivity of different environments <sup>64</sup>

Environment	ohm cm		
Sea water	25		
Brackish river water	1		
Town water supply	1000- 1200		
Alluvial soils	1000- 2000		
Clays	1000- 5000		
Mixed clays	4000-10000		
Gravel	10000-25000		
Sand	25000-50000		
Porous rock	> 50000		
Non-porous granite	>500000		

### Soil Resistivity

Up to 10 ohm.m

: Severely Corrosive

10 ohm.m to 50 ohm.m : Corrosive

50 ohm.m to 100 ohm.m : Moderately Corrosive 100 ohm.m to 200 ohm.m : Slightly Corrosive

200 ohm.m and above : Non-Corrosive

### **Interference Surveys**

 Interference survey is made to determine the detrimental effects caused by the interference of two cathodic protection systems

 Interference is eliminated in the case of pipelines through solid bonding or resistor bonding

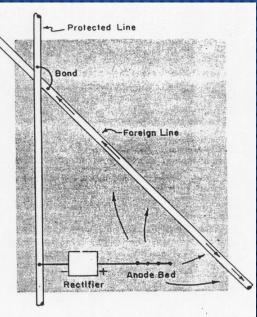


Fig. 10.6. An Obscure Case. Much of the current collected on the foreign line flows toward the crossing, where it can be safely handled with a simple bond. Some of it, however, flows in the opposite direction, and is discharged over a relatively large and remote area. Such a situation does not arise often, and probably does little damage in any case, because of the large discharge area. It can be avoided by proper anode bed placement, and can be remedied by the use of auxiliary drainage anodes.

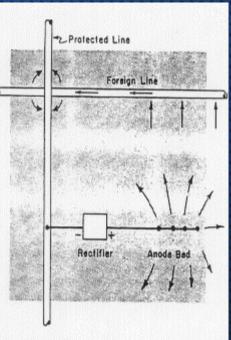


Fig. 10.1. Interference. Some of the current flowing from the anode bed to the protected line collects on the foreign line, flows along it toward the crossing (from both sides), and then discharges through the soil to the protected line. Damage is inflicted on the foreign line in the neighborhood of the crossing.

# **Stray Current**

- Stray current is an unintentional or accidental source of current that is picked up by the underground pipes
- Sources of stray current are:
  - Electric tramways
  - High tension power cables
- Drainage of stray current to earth is essential or inclusion of the stray current source could be done.
- For protection against stray current from high tension lines, dual zinc electrodes or polarization cells are used





# **DCVG Surveys**

- Used to determine the status of a buried pipeline
- Is made using reference electrodes, data logger and processor
- Can detect the location and severity of corrosion
- Can detect locations of coating deterioration

