Basic Concepts
Radiolysis - Corrosion

WHY CHEMISTRY CONTROL

- **MINIMIZE CORROSION** - To maintain system integrity, to preserve worker and public safety, and to minimize costs.

- **MINIMIZE ACTIVITY TRANSPORT** - To provide a healthy work environment and to minimize costs.

- **CONTROL REACTIVITY** - To obtain maximum reactor efficiency and to preserve worker and public safety.

- **MINIMIZE RADIOLYSIS** - To maintain system integrity and preserve worker and public safety.

- **MINIMIZE SURFACE FOULING** - To minimize heat transfer inefficiencies and costs to preserve system integrity.

Overhead 1.

ACTION LEVELS

- **ACTION LEVEL 1** - If a parameter is not within specification within one week, proceed to Action 2.
- **ACTION LEVEL 2** - If a parameter is not within specification within one day, proceed to Action 3.
- **ACTION LEVEL 3** - Shut down the unit within four hours.

HEAT TRANSPORT SYSTEM: Main System Control Parameters					
PARAMETER	SPECIFICATION	DESIRED VALUE	ACTION LEVELS		
			1	2	3
pH	10.3 - 10.7	10.3 - 10.5	< 10.3 > 10.7	< 8 > 12	- > 12.5
Dissolved O_2	3-10 cc/kg	7	< 3 > 10	< 1	- -
Chloride	≤ 0.2 mg/kg	ALARA	> 0.2	> 1	> 3
I-131	BNGS-A < 1.5 mCi/kg	ALARA	-	-	≥ 1.5 mCi/kg for ≥ 8 hrs*
	BNGS-B < 1.5 mCi/kg	ALARA	-	-	≥ 1.5 mCi/kg for ≥ 8 hrs*
	DNGS < 2.2 mCi/kg	ALARA	-	-	≥ 2.16 mCi/kg*
	PNGS < 2.7 mCi/kg	ALARA	-	≥ 2.7	≥ 6.4 mCi/kg*

*The action time for I-131 is an exception. The unit should be shut down immediately in a controlled fashion.

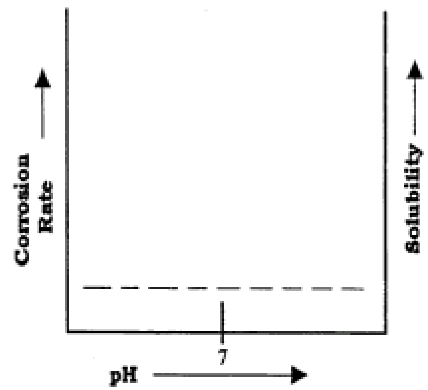
DIAGNOSTIC PARAMETERS

- A diagnostic parameter is used to troubleshoot a given situation.

HEAT TRANSPORT SYSTEM: Main System Diagnostic Parameters		
Lithium and conductivity are measured if the pH goes out of specification. The lithium/pH/conductivity relationships should be monitored for adherence to the theoretical correlation. A low pH can be the result of carbonate in the system, or lithium hideout in the pressurizer. The pH can go above specification if the Li is released from the pressurizer during a shutdown, and then circulated throughout the system upon startup.		
PARAMETER	TYPICAL OPERATING VALUES	TYPICAL CORRECTIVE ACTIONS
Lithium	0.44 - 1.10 mg/kg	Check IX performance. Valve in fresh columns or increase flow as appropriate. Use nonlithiated IX columns to reduce high pH conditions. If low pH exists, check lithium/pH correlation. If Li concentration is within specification, a fresh column should be valved in to remove carbonate. If lithium concentration is also low, LiOH addition may be required.
Conductivity	1.15 - 2.90 mS/m	

pH Versus Metal Corrosion

NOBLE METALS

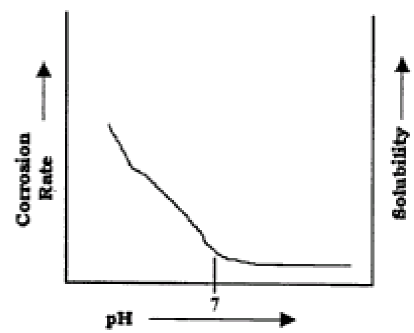


Inert to all pH Conditions

Examples: Gold
Silver
Platinum

pH Versus Metal Corrosion

ACID SOLUBLE METALS



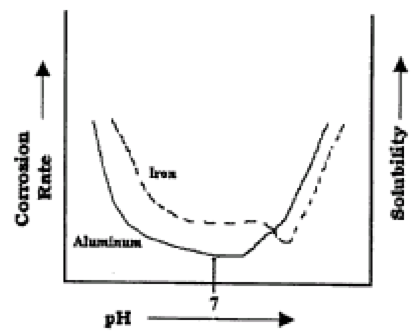
High Solubility in Acid

Examples:

- Copper
- Nickel
- Chromium
- Cobalt

pH Versus Metal Corrosion

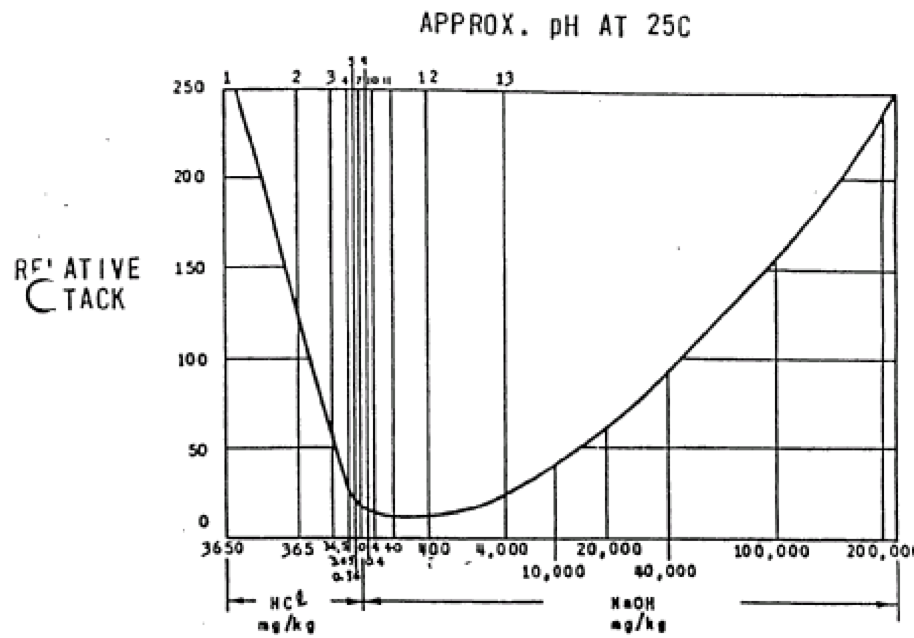
AMPHOTERIC METALS



- High Solubility in Acid and Base.
- Characteristic pH where solubility is minium.

Examples: Aluminum
Iron
Titanium
Zirconium

Corrosion Rate of Carbon Steel in Acids and Bases @ 310°C



Water Radiolysis

- Water is decomposed by radiation (neutrons, gamma, alpha,beta) to a mixture of molecules and free radicals.

$$D_2O \longrightarrow e^-, D_2, O_2, D_2O_2, D^*, OD^*, DO_2^*$$

- The two main reaction products of interest are OXYGEN and HYDROGEN. These products are produced by reactions involving the molecules and free radicals.

Water Radiolysis

OXYGEN PRODUCTION

- **The production of oxygen involves the OD radical and Deuterium Peroxide. The following series of reactions occur:**

$$OD + OD \longrightarrow D_2O_2$$

$$OD + D_2O_2 \longrightarrow DO_2 + D_2O$$

$$DO_2 \longrightarrow D^+ + O_2^-$$

$$DO_2 + O_2^- + D^+ \longrightarrow D_2O_2 + O_2$$

- **Deuterium Peroxide will also decompose thermally to form Oxygen:**

$$D_2O_2 \xrightarrow{\text{Heat}} D_2O + 1/2\ O_2$$

- **The presence of impurities in the water will increase the decomposition of Deterium Peroxide:**

$$D_2O_2 + \text{Impurities} \longrightarrow D_2O + 1/2\ O_2$$

Water Radiolysis

DEUTERIUM
~~HYDROGEN~~ PRODUCTION

- Hydrogen production by radiolysis is caused by reaction of D^{*} radicals and by the reaction of free electrons with the D_2O:

Radical Combination

$$D^{*} + D^{*} \longrightarrow D_2$$

Reducing Action of Electrons

$$D_2O + 2e^{-} \longrightarrow D_2 + 2OD^{-}$$

Water Radiolysis

OPERATIONAL CONCERNS

- The production of ~~Hydrogen~~ DEUTERIUM and Oxygen by Radiolysis is undesirable for the following reasons:

  – *Radiolysis of water will result in the presence of dissolved oxygen. Dissolved oxygen will increase the corrosion rate of metals -- carbon steel, alloy steel, zirconium.*

  – *Dissolved oxygen and hydrogen (Deuterium) produced by radiolysis can migrate from solution and enter the cover gas systems. This can result in explosive concentrations of hydrogen and oxygen.*

Water Radiolysis

Radiolysis Suppression

- **Hydrogen Addition -** Addition of hydrogen gas to the water will result in radiolysis suppression. When sufficient hydrogen is present, oxygen can no longer be produced from the OD radicals because they are scavenged by hydrogen:

$$OD + H_2 \longrightarrow D_2O + D$$

- Also a chain reaction ensures that the Deuterium Peroxide is removed by D atoms which are converted to OD radicals:

$$D + D_2O_2 \longrightarrow OD + D_2O$$

- If hydrogen is added to water already containing dissolved oxygen, radiation-induced recombination of the hydrogen and oxygen occurs.

$$2D_2 + O_2 \longrightarrow 2D_2O$$

Water Radiolysis

Radiolysis Suppression

- **Maintenance of Water Purity -**
  System purity is maintained by recirculating the water through Ion Exchange Columns. The ion exchange resin in these vessels will remove the ionic impurities (chloride, carbonate, nitrate, etc.) from the water.

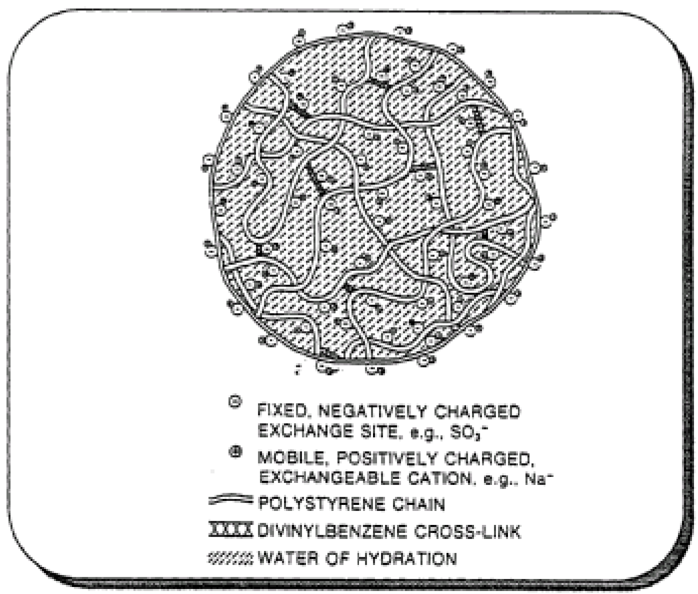
Water Radiolysis

Factors affecting Radiolysis

- **Radiation Flux** - The higher the flux, the greater will be the rate of radiolysis.
- **Impurities** - The presence of impurities can increase the rate of radiolysis. Ions such as chloride, nitrate, sulfate,carbonates, etc. can increase the radiolysis rate. Also organics, resin fines, introduction of air into the water can have the same effect.
- **Boiling** - Boiling can increase radiolysis due to the molecular hydrogen produced directly by radiolysis being stripped to the steam phase. This leaves the other precursors of oxygen formation, OD and D_2O_2 in the water, where they can produce more oxygen.
- **Added Hydrogen** - Suppresses Radiolysis.

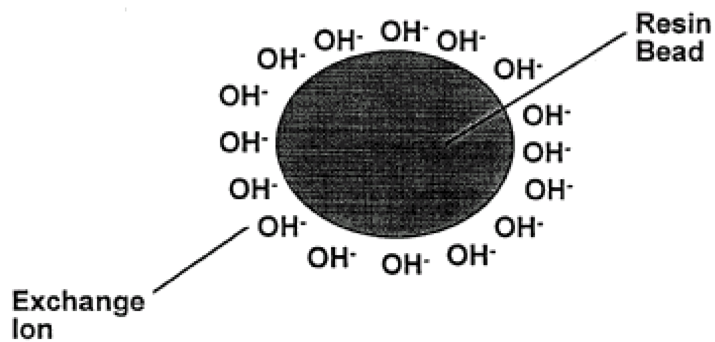
ION EXCHANGE RESIN

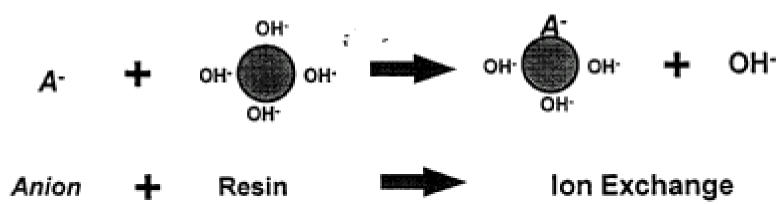
- Ion Exchange Resins are beads composed of strands of Styrene which are held together with Divinylbenzene. Attached to these Styrene/Divinylbenzene beads are ions (called fixed ions) which will exchange with the ions present in the water.
- The amount of Divinylbenzene present in the resin bead is expressed as the % Cross-Linkage.



ANION EXCHANGE RESIN

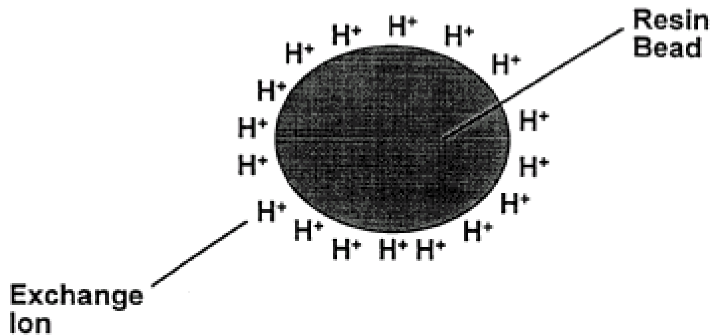
- **Ion Exchange Resin which removes negatively charged ions from solution**

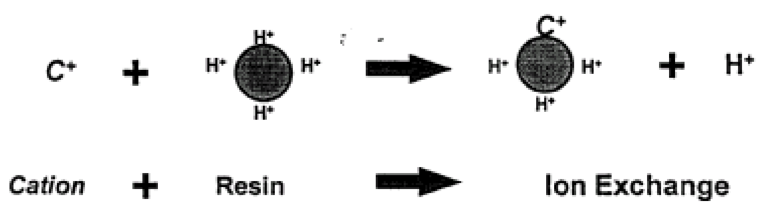


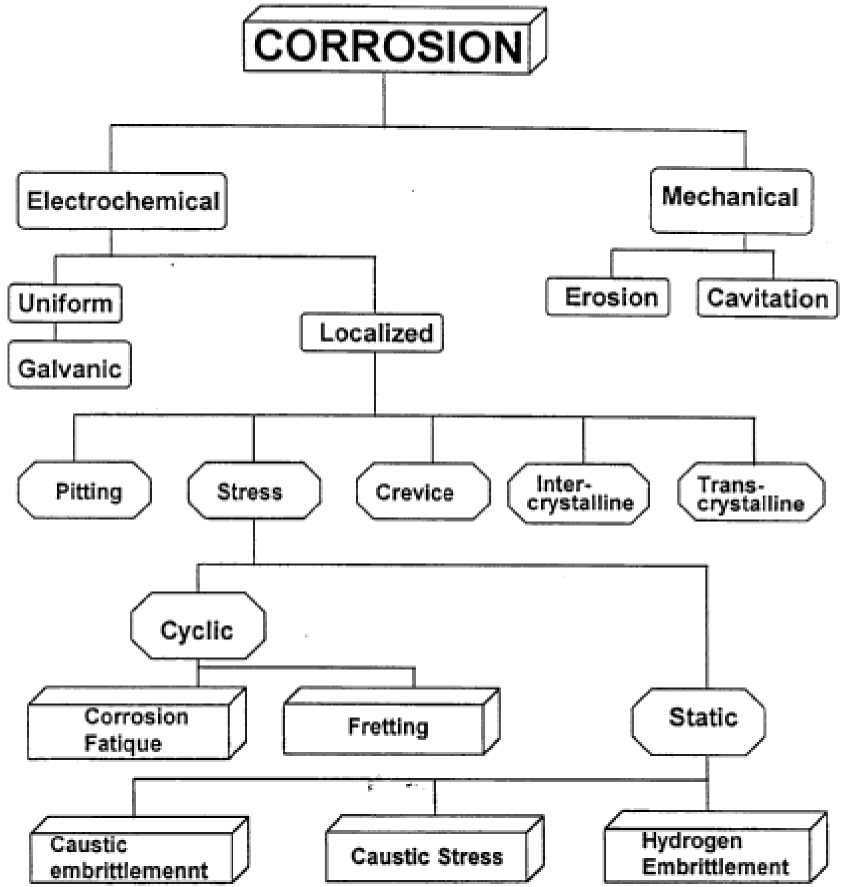


CATION EXCHANGE RESIN

- Ion Exchange Resin which removes positively charged ions from solution.



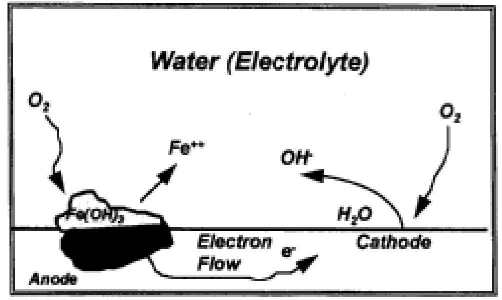




Overhead 18

AECB Conventional/Nuclear General

Iron Corrosion



- ***Corrosion is an electrochemical process in which the anode, where the dissolution is occuring, is separated by a physical distance from the cathode where a reduction reaction is occuring. A potential difference exists between these two sites; electrons flow through the metal (from anode to cathode) and ions move through the solution.***
- ***Oxidation occurs at the Anode:***

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

$$Fe^{++} + 2OH^- \longrightarrow Fe(OH)_2$$

The Ferrous Hydroxide will then combine with any oxygen and water to produce Ferric Hydroxide ($Fe(OH)_3$), which will then over time produce Fe_2O_3 (Rust).

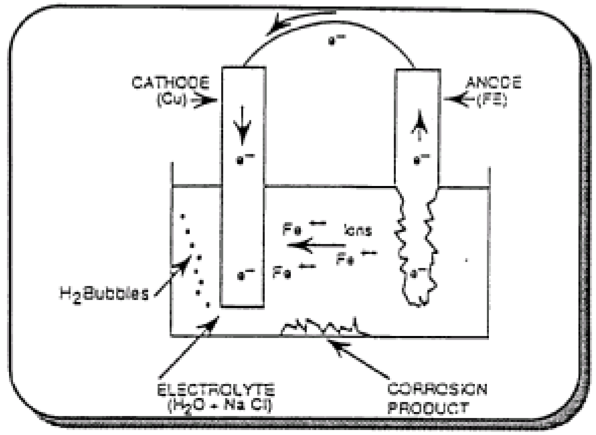
- ***Reduction occurs at the Cathode:***

$$1/2\ O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

Principle Factors Governing Carbon Steel Corrosion

- ***Solution pH*** - Solutions of pH less than 5 are highly corrosive to carbon steel. Alkaline solutions (pH between 9 - 12) insure minimum corrosion.
- ***Dissolved Oxygen*** - Corrosion rates of carbon steel will increase with dissolved oxygen concentration.
- ***Temperature*** - Higher temperature increases the corrosion rate by accelerating the diffusion of oxygen through the iron oxide layer.
- ***Dissolved Salts*** - The presence of acid or neutral salts may increase corrosion rates, whereas the presence of alkaline salts may lower corrosion.
- ***Fluid Velocity*** - In general, increasing the solution velocity will increase the corrosion rate of carbon steel. High solution flow rates can accelerate corrosion by eroding away the metals protective film. This corrosion mechanism occurs frequently at heat exchanger tubing inlets, U-bends and piping elbows.

Galvanic Corrosion



Anode Reaction

$$Fe \longrightarrow Fe^{++} + e^{-} \text{ (current)}$$

Cathode Reaction

$$2e^{-} + 2H^{+} \longrightarrow H_2 \text{ (bubbles)}$$

Electrolyte Reaction

$$H_2 0 \rightleftharpoons OH^{-} + H^{+}$$

$$Fe^{++} + 2OH^{-} \rightleftharpoons Fe(OH)_2 \text{ (corrosion product)}$$

Galvanic Series of Metals and Alloys

Corroded End

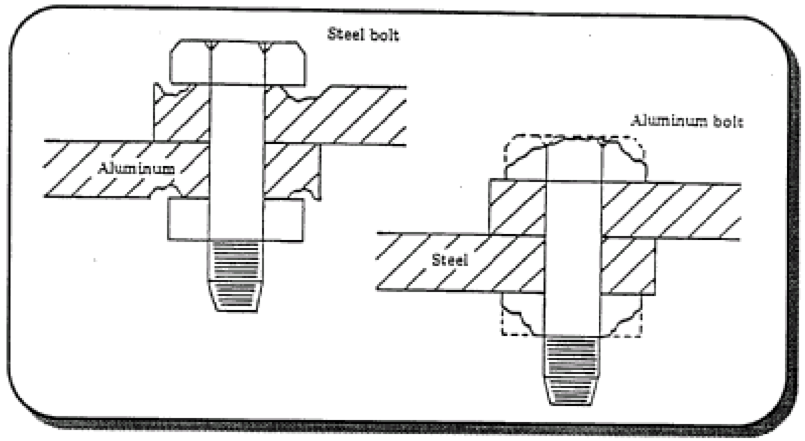
(anodic, or least noble)

Magnesium
Magnesium Alloys
Zinc
Aluminum 1100
Aluminum 6053
Cadminum
Mild Steel
Wrought Iron
Cast Iron
Type 410 Stainless Steel - 13% Cr (Active)
Type 304 Stainless Steel - 18% Cr, 8% Ni (Active)
Type 316 Stainless Steel - 18% Cr, 12% Ni, 8% Mo (Active)
Lead-Tin Solders
Lead
Tin
Nickel
Inconel
Brasses
Copper
Monel
Titanium
Silver Solder
Type 410 Stainless Steel - 13% Cr (Passive)
Type 304 Stainless Steel - 18% Cr, 8% Ni (Passive)
Type 316 Stainless Steel - 18% Cr, 12% Ni, 8% Mo (Passive)
Silver
Graphite
Gold
Platinium

Protected End

(cathodic, or most noble)

Galvanic Corrosion

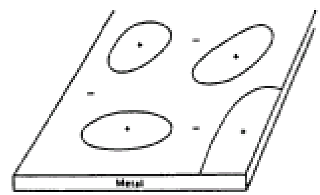


- ***Galvanic corrosion occurs when dissimilar materials are in contact in a conducting fluid (water). Accelerated corrosion attacks the least resistant alloy, while the more resistant alloy is protected.***

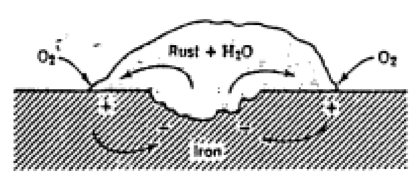
- ***The intensity of the attack is related to the relative surface areas of the metals in electrical contact. Large cathodic areas coupled to small anodic areas will aggravate galvanic corrosion and cause dissolution of the more active metal. The reverse situation - large anodic areas coupled to small cathodic areas - result in decreased corrosion intensity of the anode.***

LOCAL CORROSION CELLS

- *Local corrosion is the selective removal of metal by corrosion at small areas or zones on the metal surface in contact with a corrosive enviroment. Concentration Cell Corrosion is an electrochemical attack that is due to the differences in the corrosive enviroment between a shielded area and its surroundings.*

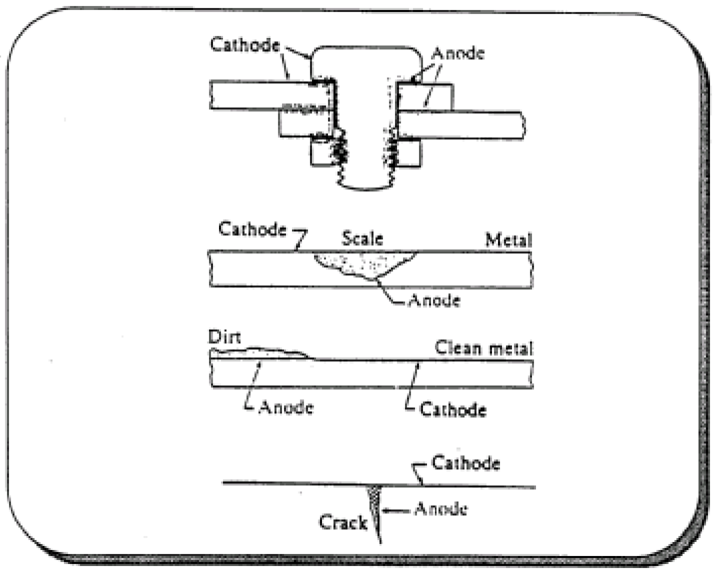


Metal surface enlarged, showing arrangement of Local-Action cells



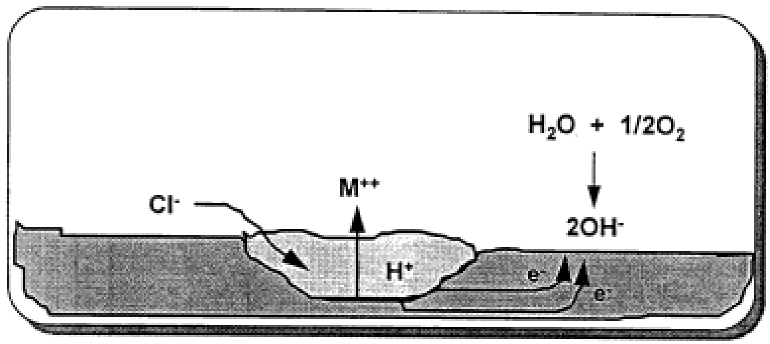
Differential areation cell formed by rust on iron

LOCAL CORROSION CELLS



Types of Local Corrosion Cells

PITTING CORROSION



- ***A Local Corrosion Cell is initially established on the surface of the metal***

Anode:

$$2M \longrightarrow 2M^{++} + 4e^-$$

Cathode:

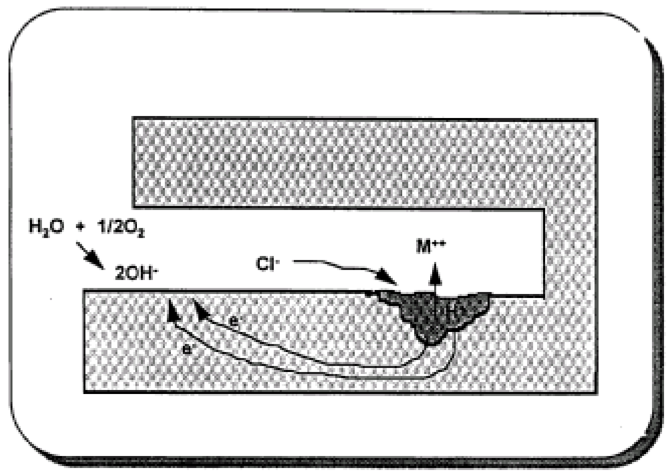
$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

- ***The solution within the pit is stagnant. The oxygen is consumed and the cathode reaction stops. The Anode reaction continues which results in an accumulation of positively charged metal ions. To balance this charge, the negatively charged chloride ions migrate into the pit. The resulting metal chloride is hydrolized by water to the hydroxide of the metal and free acid. The acid produced by the hydrolysis reaction drops the pH to values below 2, while the pH of the solution outside the pit remains neutral. These conditions within the pit will result in increased corrosion.***

$$M^{++} + 2Cl^- \longrightarrow MCl_2$$

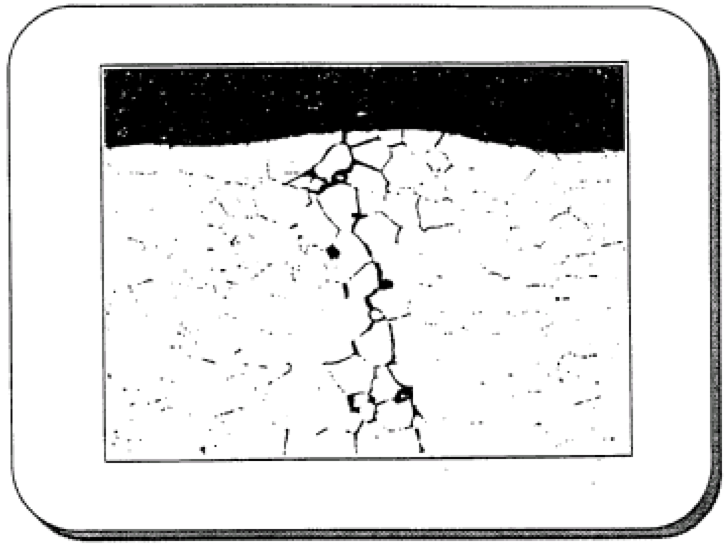
$$MCl_2 + 2H_2O \longrightarrow M(OH)_2 + 2HCl$$

CREVICE CORROSION



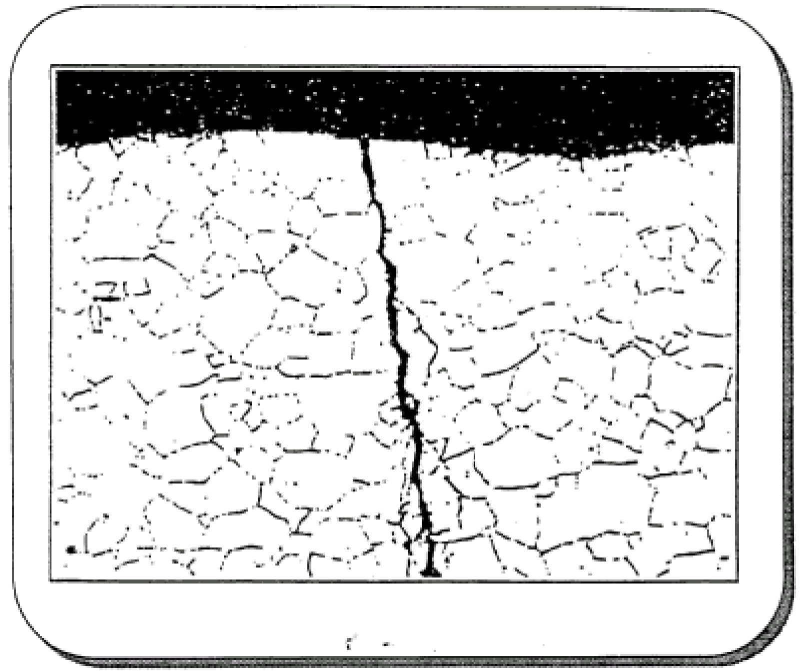
- ***Crevice Corrosion is similar to pitting corrosion. Crevice Corrosion describes the location: bolts, gaskets, valve seats, etc.***

INTERCRYSTALLINE CORROSION



Intercrystalline Corrosion

TRANSCRYSTALLINE CORROSION



Transcrystalline cracking of steel due to thermal cyclic stress

STRESS CORROSION CRACKING

- <u>Stress Corrosion Cracking</u> *is the brittle failure of a metal by cracking in the presence of a tensile stress and a corrosive environment. Elevated Temperatures are also usually required to promote Stress Corrosion Cracking.*

- **Tensile Stress:** The Tensile Stress can be an applied stress, a residual stress , or the combination of the two. Tensile Stresses can be the result of :

Rolling of tubes into tube sheets
Riveting
Welding
Bending
Thermal Stresses

- **Corrosive Environment:** The Corrosive Enviroment can include the following:

Halogens (chloride,fluoride,bromide)
High concentrations of Hydroxide
Sulfates
Amines (ammonia) for copper alloys
Dissolved Oxygen

CAUSTIC CORROSION

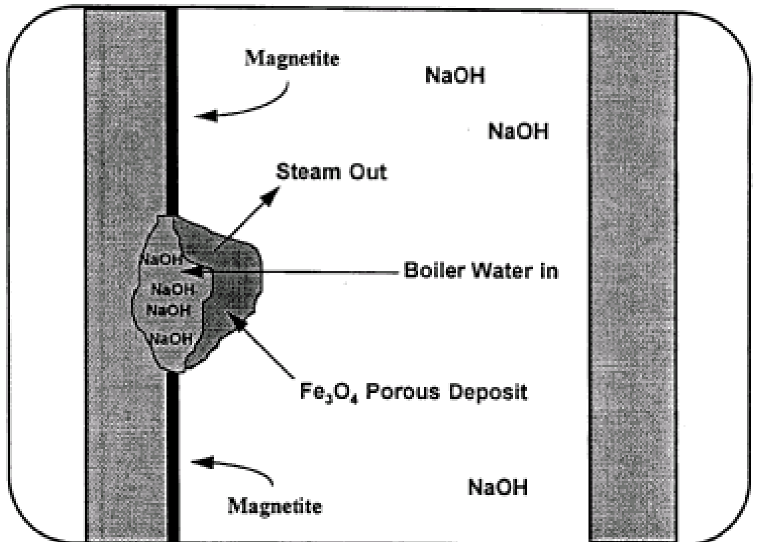
- **Caustic Corrosion includes both "Caustic Embrittlement" and Caustic Stress or Attack".**

- Caustic Embrittlement *is the failure that results in the presence of highly concentrated caustic solutions. The metal fails in a sudden or brittle manner with no apparent deformation of the metal prior to actual failure. The failure path is intercrystalline in nature. This type of corrosion is common in Boiler metal and generally occurs in the following areas:*

  Crevices
  Tube Sheets
  Welds
  Rivets (on old style boilers)

- Caustic Stress or Attack *can occur on boiler tubes. It commonly results in tube pitting or general thinning of the tube. It is commonly encountered in phosphate-treated boilers where tube deposits can form. Deposits of a pourous nature will allow boiler water to permeate the the deposits, developing a continuous buildup of boiler water solids between the metal and the deposit itself.*

CAUSTIC ATTACK



Pourous deposits provide conditions that cause high concentration of boiler water solids, such as sodium hydroxide

This concentration of sodium hydroxide in the trapped liquid can reach very high concentrations, forming complex caustic-ferritic compounds as a result of the caustic dissolving the protective film of magnetite. Iron in contact with the water attempts to restore the protective layer of magnetite. As long as the high concentrations remain and continue to develope, the destructive process causes a continuous loss of metal in the area. The resultant thinning caused by caustic attack assumes irregular patterns and is often refered to as Caustic Gouging, Caustic Pitting, or simply Caustic Attack.

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Hydrogen Embrittlement

- Hydrogen embrittlement is the corrosion of metals as a result of absorption of hydrogen.

- A concern in thermal plants operating at pressures of 1800 psig. or greater. Superheater tubes very susceptible.

- Occurs under hard scale/sludge deposits where acid conditions exist. In low pH conditions, hydrogen will be generated. The atomic hydrogen will be absorbed by the metal. Here it reacts with the carbon in the steel forming methane. This methane formation causes excessive pressure within the metal resulting in rupture and cracking of the metal.

- Hydrogen damage mainly a concern when dealing with Zirconium Alloys. Hydrogen is absorbed by these alloys, forming Hydrides which can lead to corrosion of these materials - Pressure tubes - Fuel cladding

Corrosion Fatique

- Fatique is the condition leading to fracture under a repeated of flucuating stress - this failure occurs at a stress level lower than the tested tensile strength of the metal. Fatique fractures start out as small cracks and then grow under the action of a fluctuating stress.

- Metals have what is called a normal Fatique limit or Endurance limit, below which no failure will occur. However when the metal is subjected to a cyclic stress in a corrosive environment, the number of cycles required to cause failure at a given level of stress will be reduced below the number of cycles in a non - corrosive enviroment.

- Localized corrosion, such as pitting or intercrystalline corrosion, has a greater accelerating action than does uniform corrosion.

- Failures that occur on vibrating structures (taunt wires, stranded cables) exposed to weather under stresses below the fatique limit are usually caused by corrosion fatique. Corrosion Fatique observed in boilers is due to alternating stresses caused by thermal cycling.

Fretting

- Rapid localized corrosion that occurs on closely fitting surfaces in contact under a load and subject to chafing or vibrations.

- Close fitting surfaces subjected to increased pressure can cause these metals to touch and eventually weld together. Vibrating motions can then cause the metals to tear apart from each other - this action can result in small pieces of metal being removed . This process will remove the protective oxide layer from this section of the metal - increased corrosion will result.

- Fretting corrosion can be prevented by eliminating the slipping movement between two surfaces. Increasing the applied load on the components may also reduce fretting corrosion by preventing the motion of these components.

Cavitation

- Cavitation corrosion is a form of localized corrosion that occurs in turbulant or rapidly moving liquids.

- Caused by sudden formation and collapse of bubbles in a liquid. Voids or cavities are formed in the liquid, due to turbulence or temperature that causes the pressure in a local zone of the liquid to fall below vapor pressure. This is common on the back side of ship propellers, water turbine blades, in pumps, and in high velocity flow lines.

- Changes in liquid pressure in the liquid turbulant zone causes these voids to collapse. When this occurs, large amounts of energy is released (pressure gradients).

- This collapse of voids or cavities can break away the protective surface film (steels) and may lead to the initiation of corrosion. The collapse can also damage the material simply by errosion action.