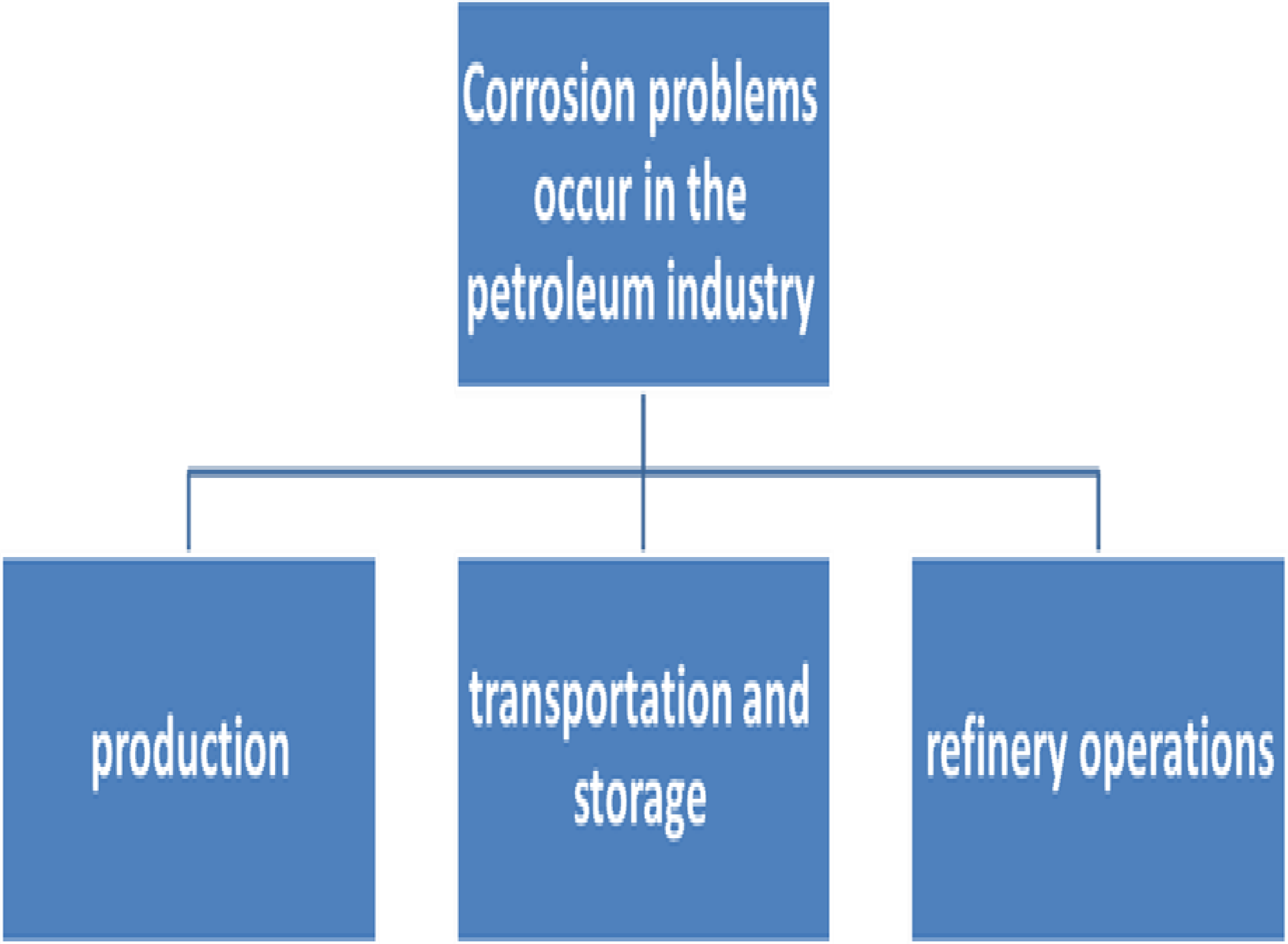
Corrosion in Petroleum industry 2016(Part I)

Prof. Dr. M.M. B. El Sabbah
AL-AZHAR UNIVERSITY
FACULTY OF SCIENCE
CHEMISTRY DEPARTMENT


Corrosion problems occur in the petroleum industry
production
transportation and storage
refinery operations

1-Types and prevention of corrosion in production of petroleum industry.

Corrosion of metal in the presence of **water** is a common problem across many industries. The fact that most oil and gas production includes co-produced water makes corrosion a pervasive issue across the industry. **Age and presence of corrosive materials such as carbon dioxide (CO_2)and hydrogen sulfide (H_2S) exacerbate the problem.**

Corrosion chemistry of steels

Most of the petroleum and petrochemical industry depend on <u>carbon steel alloys</u> as primary backbone and skeletons.

Corrosion chemistry of steels

Corrosion of steel is an "electrochemical process," involving the transfer of electrons from iron atoms in the metal to hydrogen ions or oxygen in water. The corrosion reaction of

iron with acid is described by the equation

$$Fe + 2H^{+} \rightarrow Fe^{++} + H_2 \qquad (1)$$

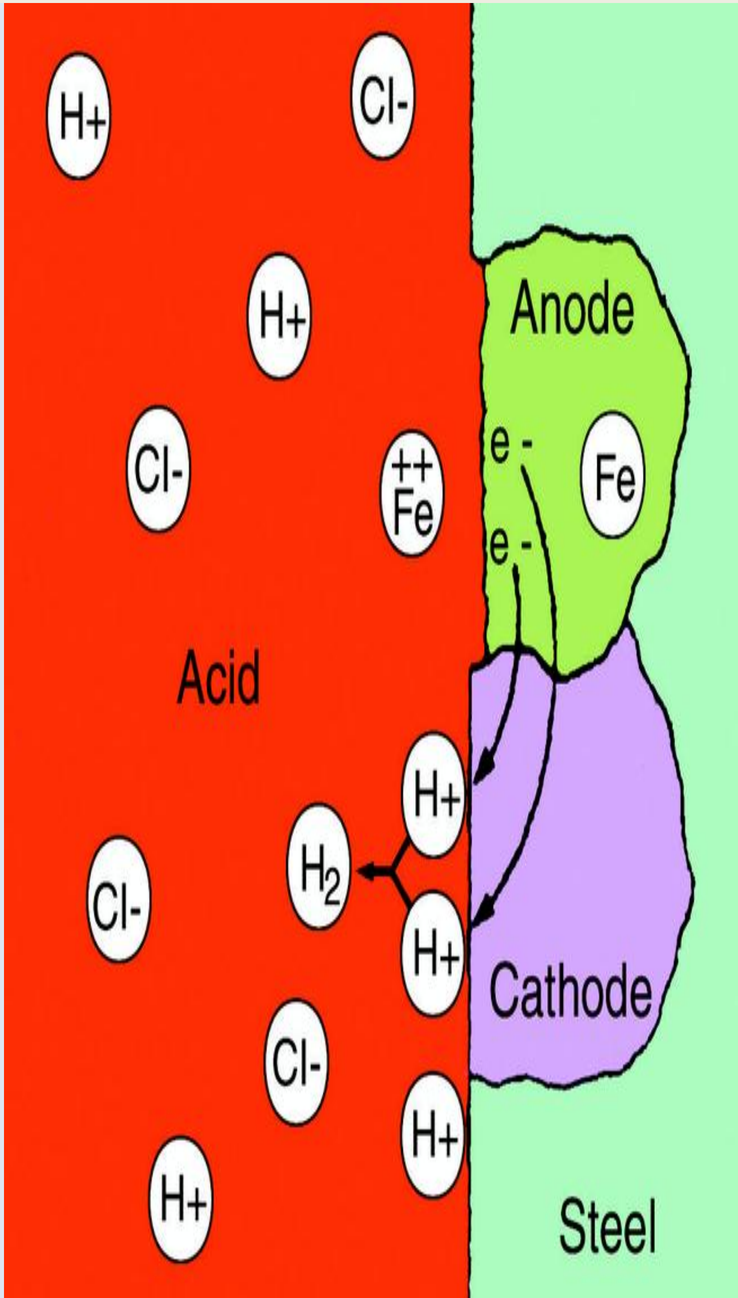
This reaction is made up of two individual processes, which are

$$Fe \rightarrow Fe^{++} + 2e^{+} \qquad (2)$$

[the generation of soluble iron and electrons (this is the "anodic" process—the oxidation of the metal)] and

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad (3)$$

[the consumption of the electrons by acid to generate hydrogen gas (this is a "cathodic" process—the reduction of protons)].

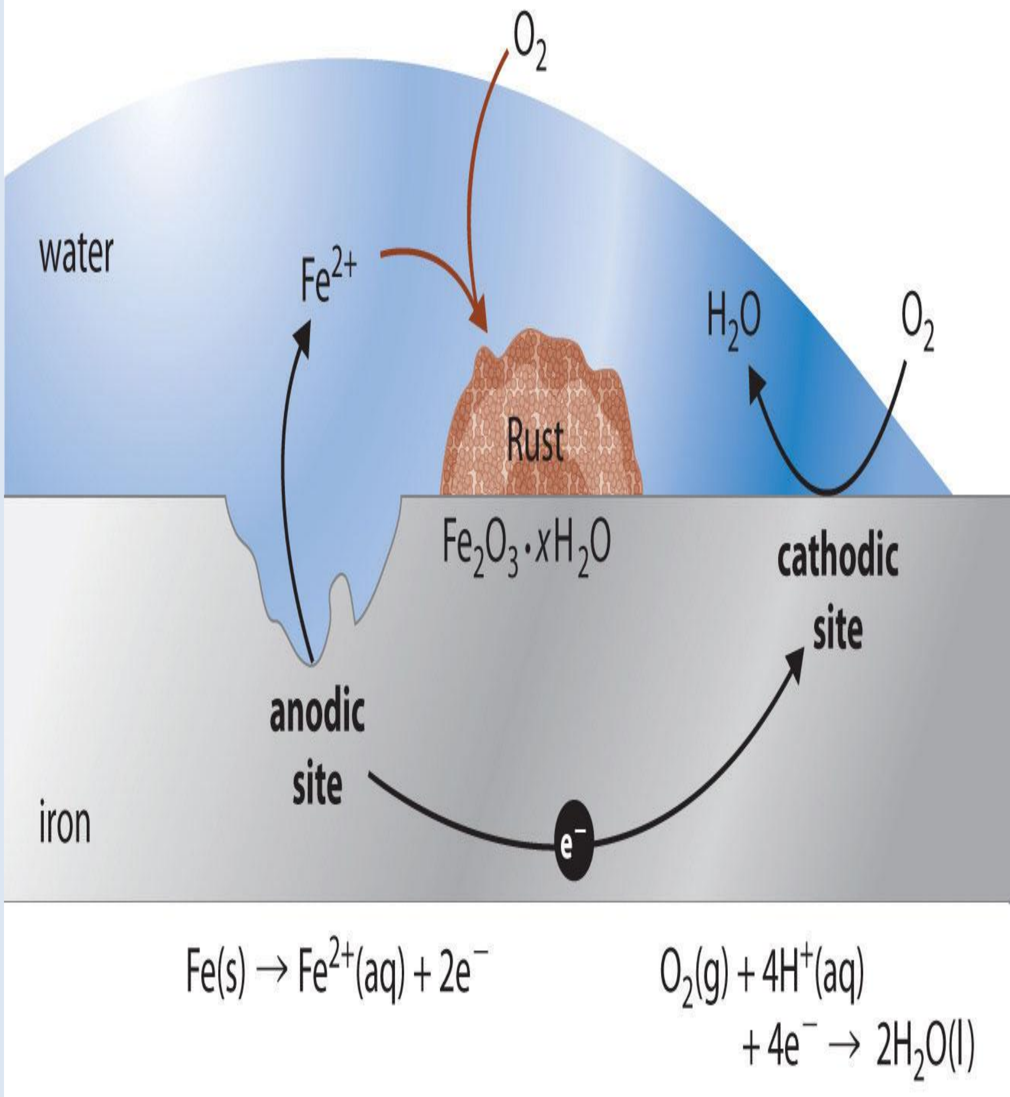


Corrosion chemistry of steels

Acid is not the only corrodant possible. Another common cathodic process is the reduction of oxygen, which is written as

$$O_2 + 4H^+ + 4e^- = 2H_2O. \qquad (4)$$

This reaction can also take place at a location different from that of iron dissolution.



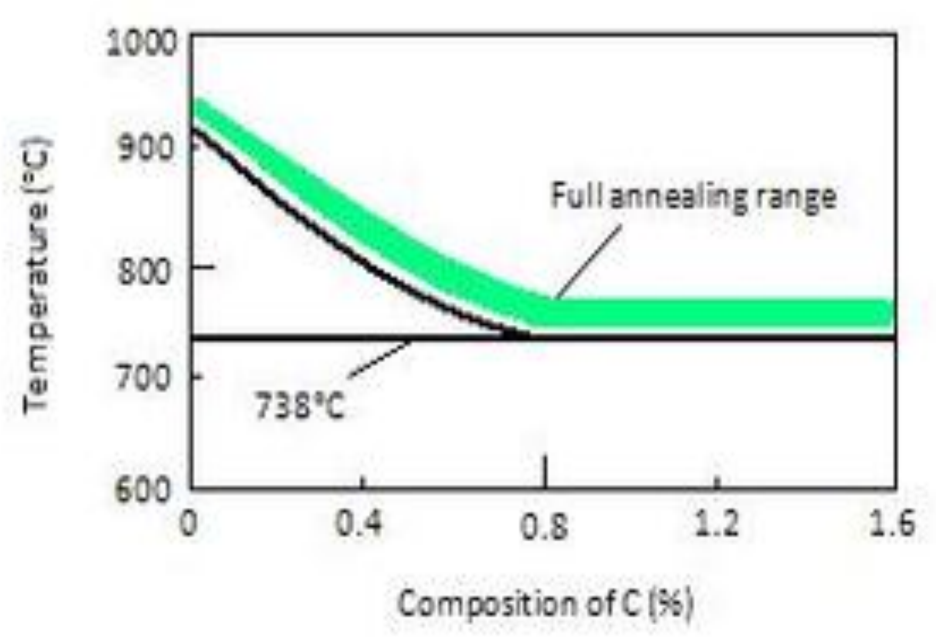
Nature of steels :-

Alloying iron with carbon (usually 0.2 to 1%) forms steel (low-alloy steel) a far stronger metal than iron, hence, suitable for oilfield use. Other components can be added to iron to **enhance corrosion-resistance properties**.

Plain carbon steels are processed by one of four heat treatments:-

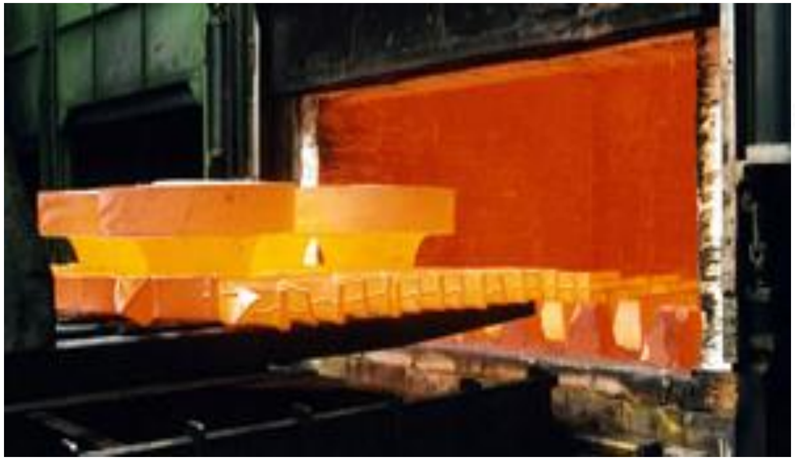
<u>I- Annealing :</u>

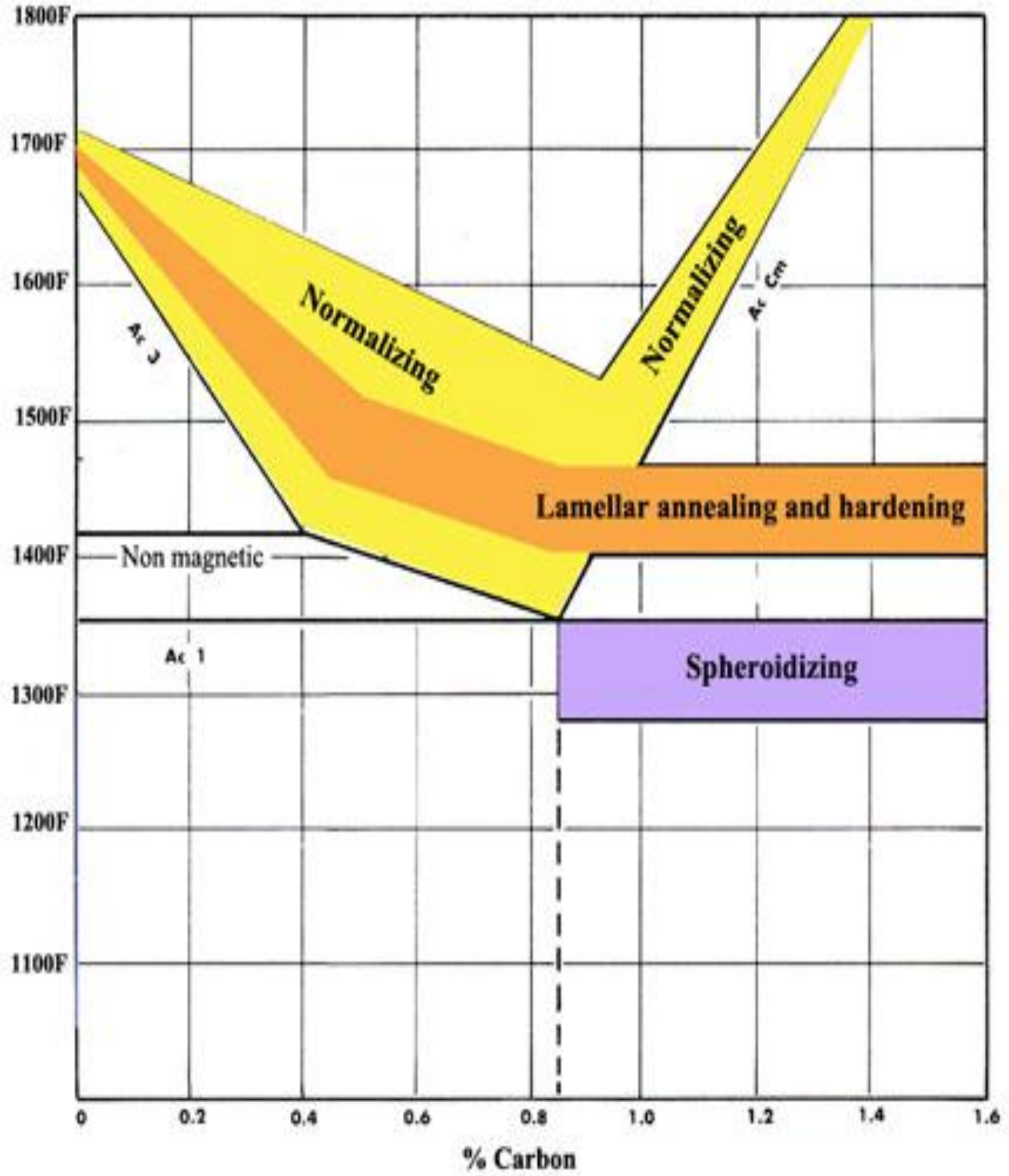
Heat (metal or glass) and allow it to <u>cool slowly</u>, in order to remove <u>internal stresses and toughen it.</u>



II-Normalizing :

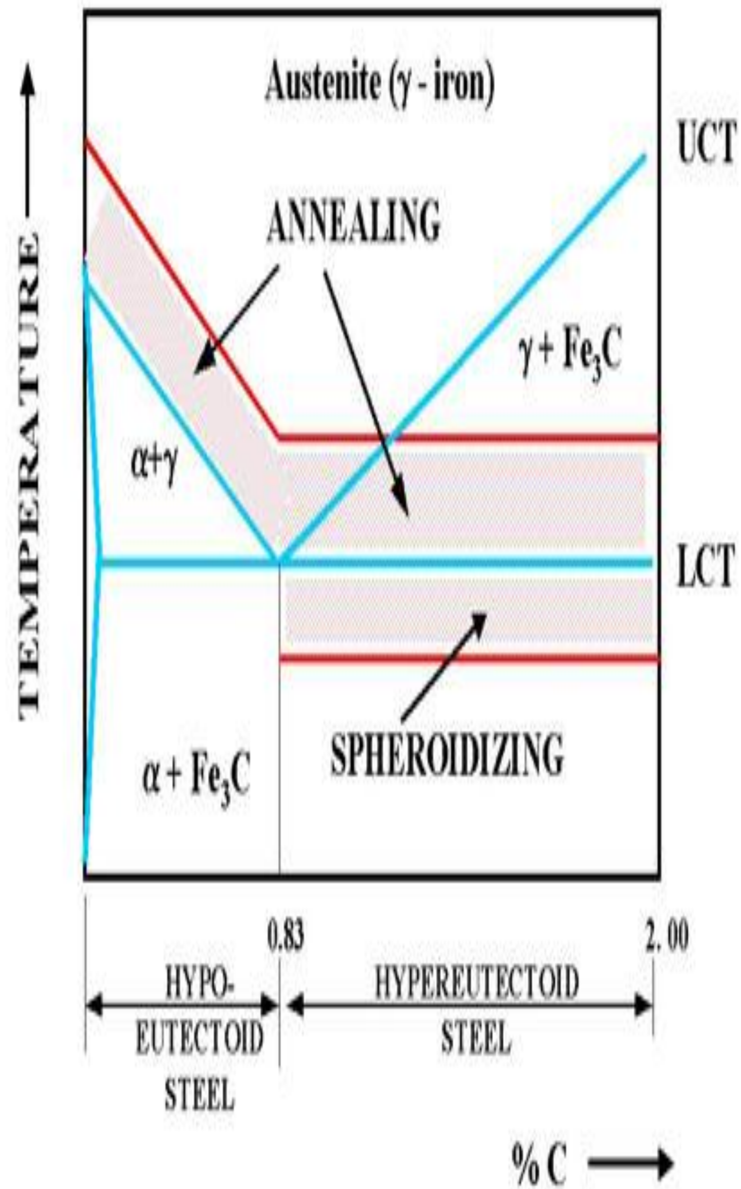
The steady heating of a metal above the recrystallization phase, followed by a cooling process at a moderate pace. Normalized metals are often cooled in open air at room temperature..





III-Spherodizing:

Spheroidize annealing is applicable to steels which have more than 0.8% carbon. Parts are heated to between 1150°F and 1200°F and holding it at this temperature for a period of time to convert the microstructure.



IV-Quenching :

Carbon steel with at least 0.4 wt.% C is heated to normalizing temperatures and then rapidly cooled (quenched) in water, brine, or oil to the critical temperature. The critical temperature is dependent on the carbon content, but as a general rule is lower as the carbon content increases .

Corrosion-resistant alloys:-

Stainless steels are iron-based alloys containing a minimum of about 10.5% chromium; this forms a protective self-healing oxide film, which is the reason why this group of steels has their characteristic "stainlessness" or corrosion resistance.

There are **four classes** of stainless steels that are based on chemical content, metallurgical structure, and mechanical properties.

four classes of stainless steels

1- Austenitic stainless steels .

2-Ferritic stainless steels.

3-Duplex stainless steels.

4- Martensitic stainless steels.

Table 1. Difference in the properties of ferritic and austenitic stainless steels.

Properties	Ferritic	Austenitic
Toughness	Moderate	Very high
Ductility	Moderate	Very high
Weldability	Limited	Good
Thermal expansion	Moderate	High
Stress corrosion cracking resistance	Very high	Low
Magnetic properties	Ferro magnetic	Non-magnetic

In the Oil and Gas Production Industries, the Major forms of Corrosion Include

Oilfield corrosion

1-Sweet corrosion

2-Sour corrosion

3-Oxygen corrosion

4-Galvanic corrosion

5-Crevice corrosion

6-Erosion corrosion

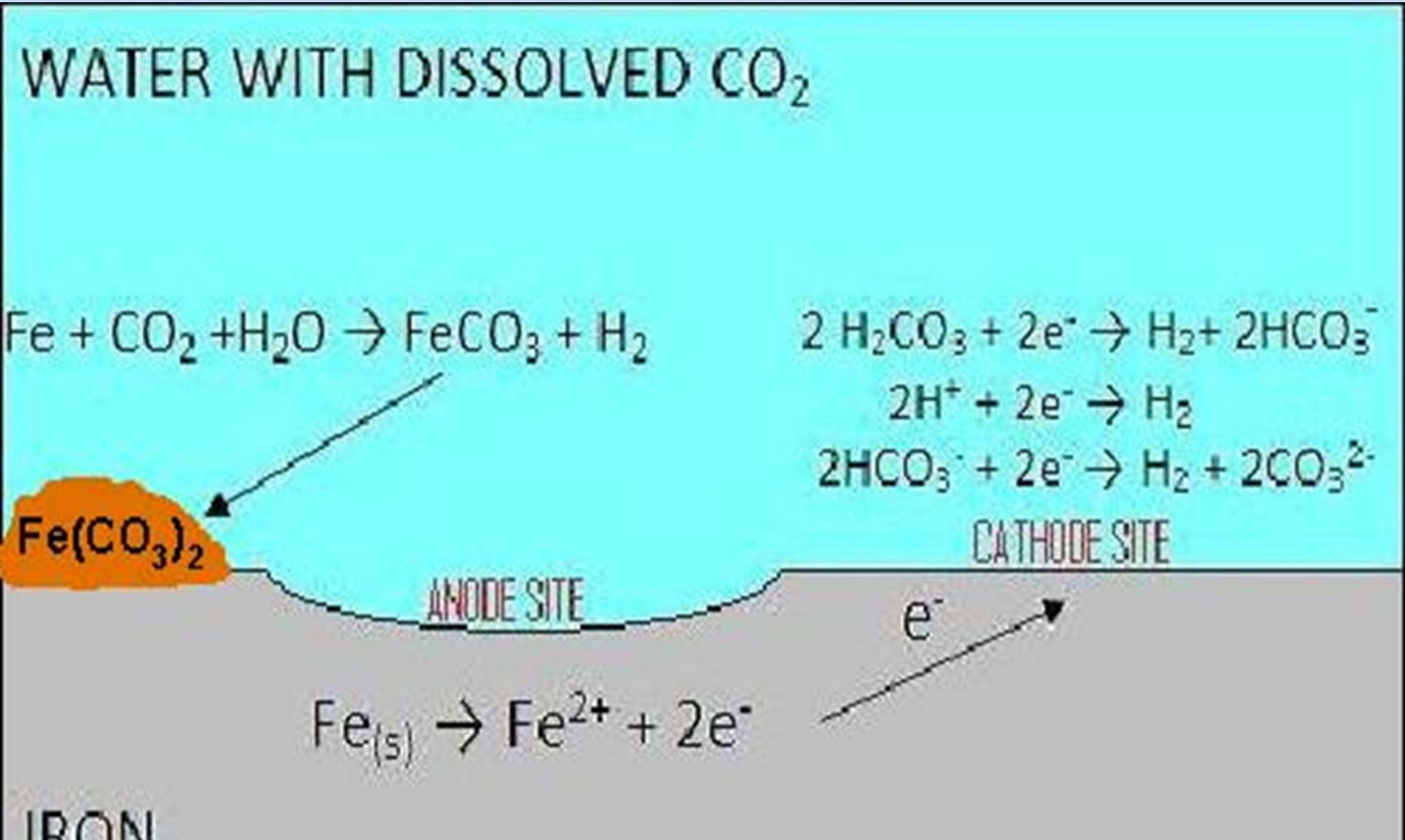
7-Microbiologically induced corrosion

8-Stress corrosion cracking.

1-Sweet corrosion (CO_2 corrosion)

CO_2 corrosion has been a recognized problem in oil and gas production and transportation facilities for many years .CO_2 is one of the main corroding agents in the oil and gas production systems .Dry CO_2 gas is not itself corrosive at the temperatures encountered within oil and gas production systems but is so when dissolved in an aqueous phase through which it can promote an electrochemical reaction between steel and the contacting aqueous phase.

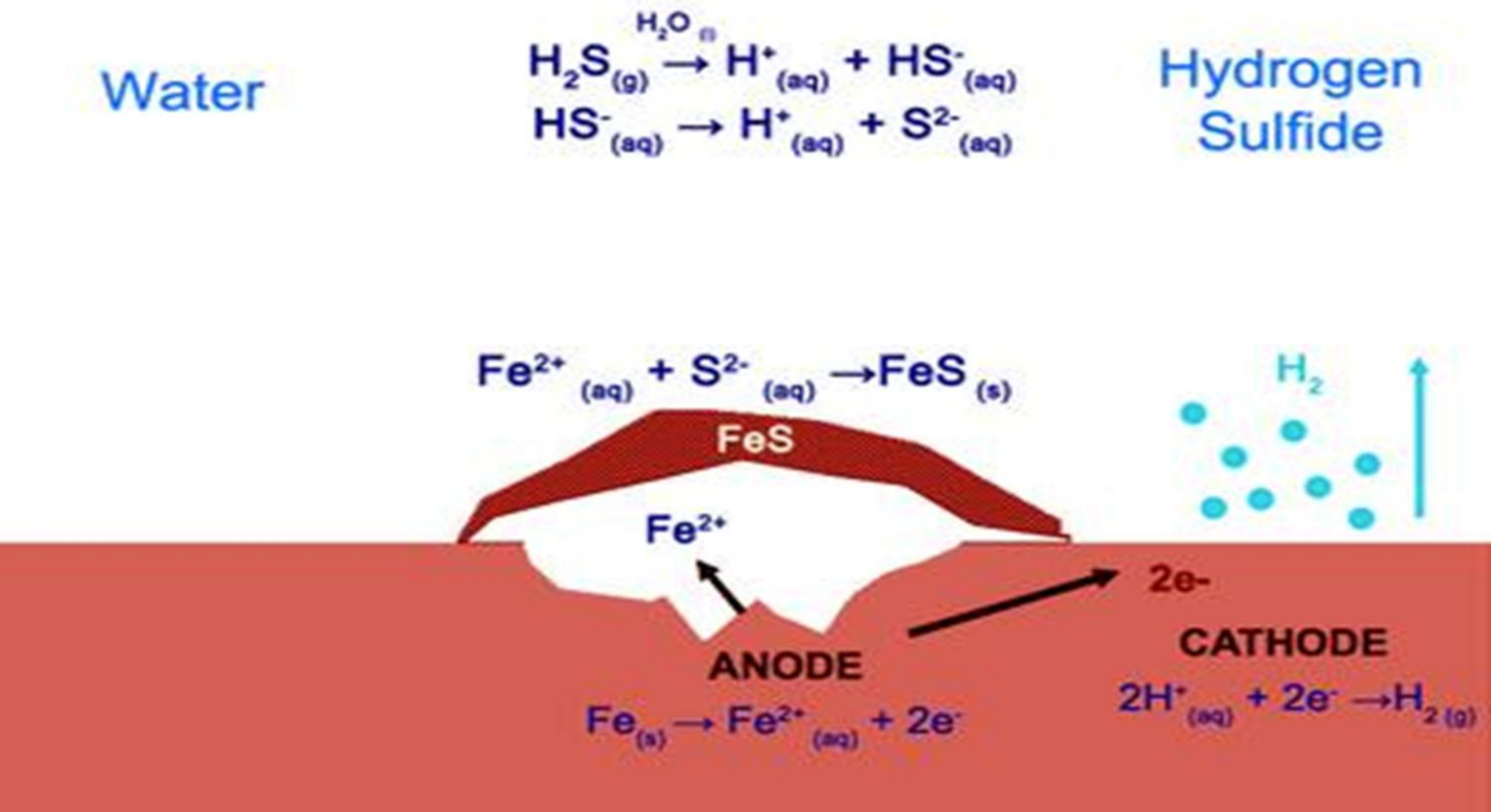
1-1-Sweet corrosion (CO2 corrosion)



2-Sour corrosion (H_2S corrosion)

The deterioration of metal due to contact with hydrogen sulfide (H_2S) and moisture is called sour corrosion which is the most damaging to drill pipe. Although H_2S is not corrosive by itself, it becomes a severely corrosive agent in the presence of water ,leading to pipeline embrittlement .Hydrogen sulfide when dissolved inwater is a weak acid, and therefore, it is a source of hydrogen ions and is corrosive. The corrosion products are iron sulfides (FeS_x) and hydrogen. Iron sulfide forms a scale that at low temperature can act as a barrier to slow corrosion .The forms of sour corrosion are uniform, pitting, and stepwise cracking.

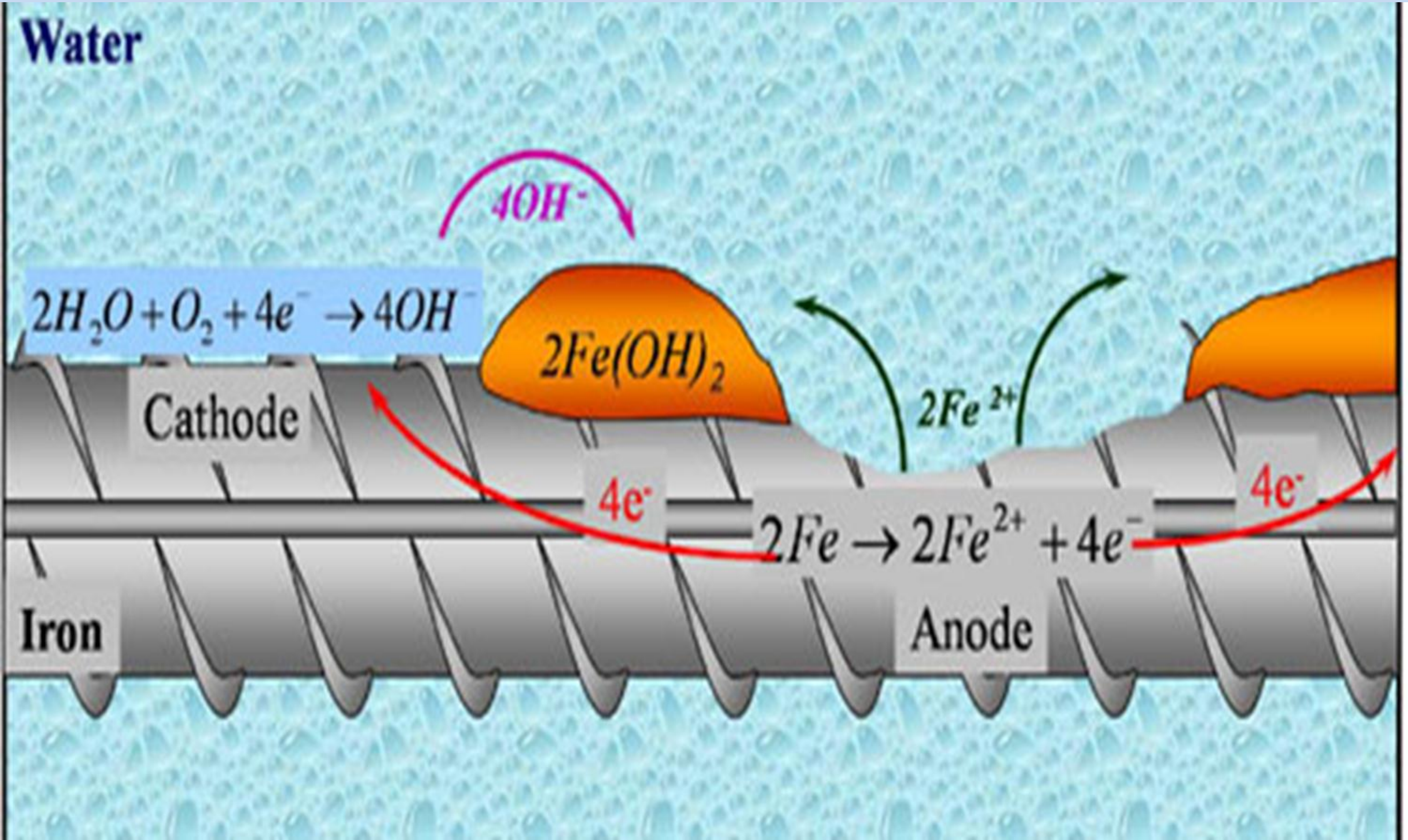
2-1-Sour corrosion (H2S corrosion)



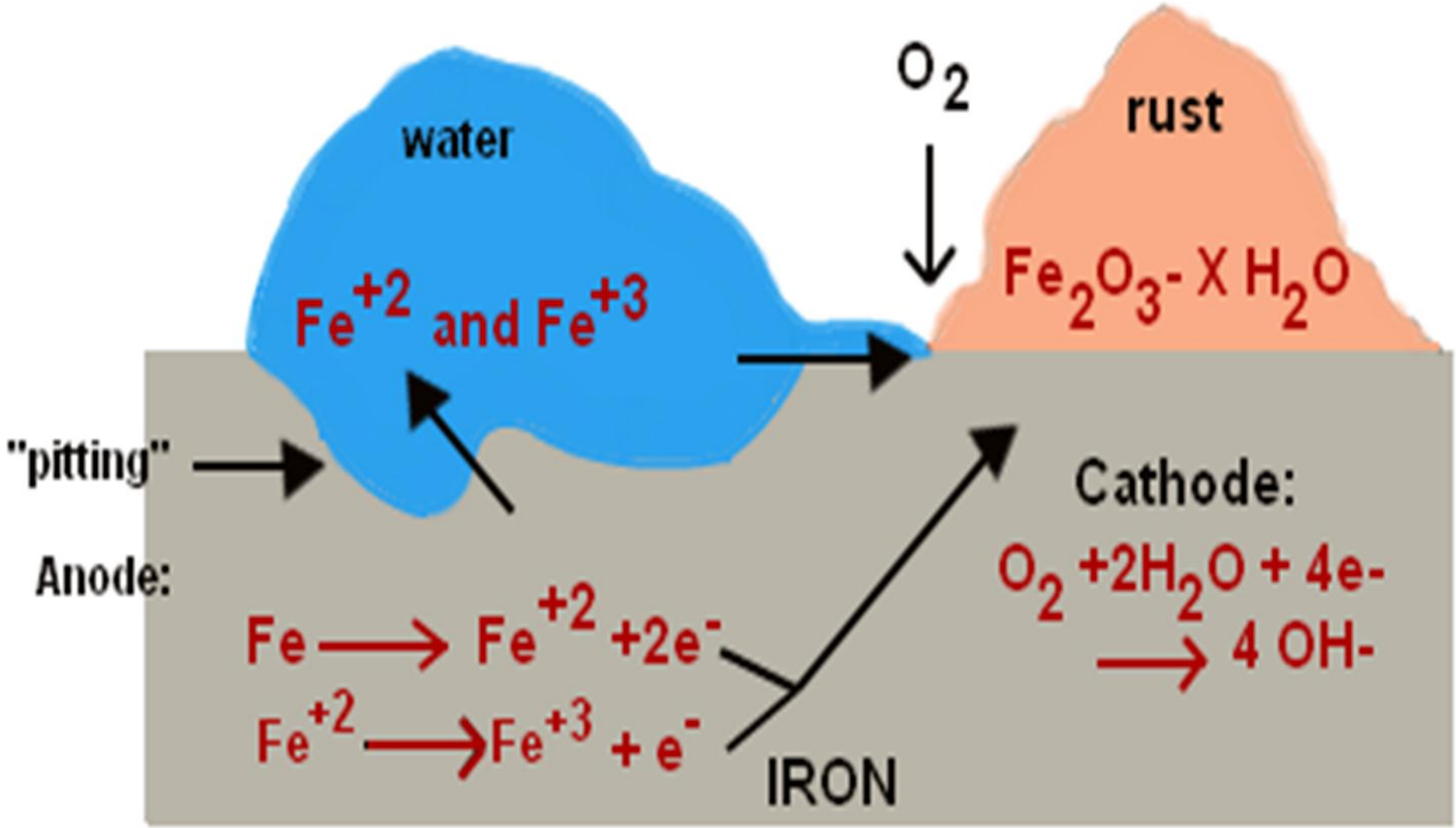
3-Oxygen corrosion

- Oxygen dissolved in **drilling fluids** is a major cause of drill pipe corrosion.
- Oxygen ingress takes place in **the well fluids through leaking pump seals, casing, and process vents and open hatches**.
- The high-velocity flow of drilling fluids over the surfaces of a drill pipe continues to supply oxygen to the metal and is destructive at concentrations as low as 5 ppb.
- The presence of **oxygen** magnifies the corrosive effects of the acid gases (**H_2S and CO_2**).
- The forms of corrosion associated with oxygen are mainly **uniform corrosion and pitting-type corrosion.**
- xygen is a **strong oxidant** and reacts with the metal very quickly.

3-1-Oxygen corrosion

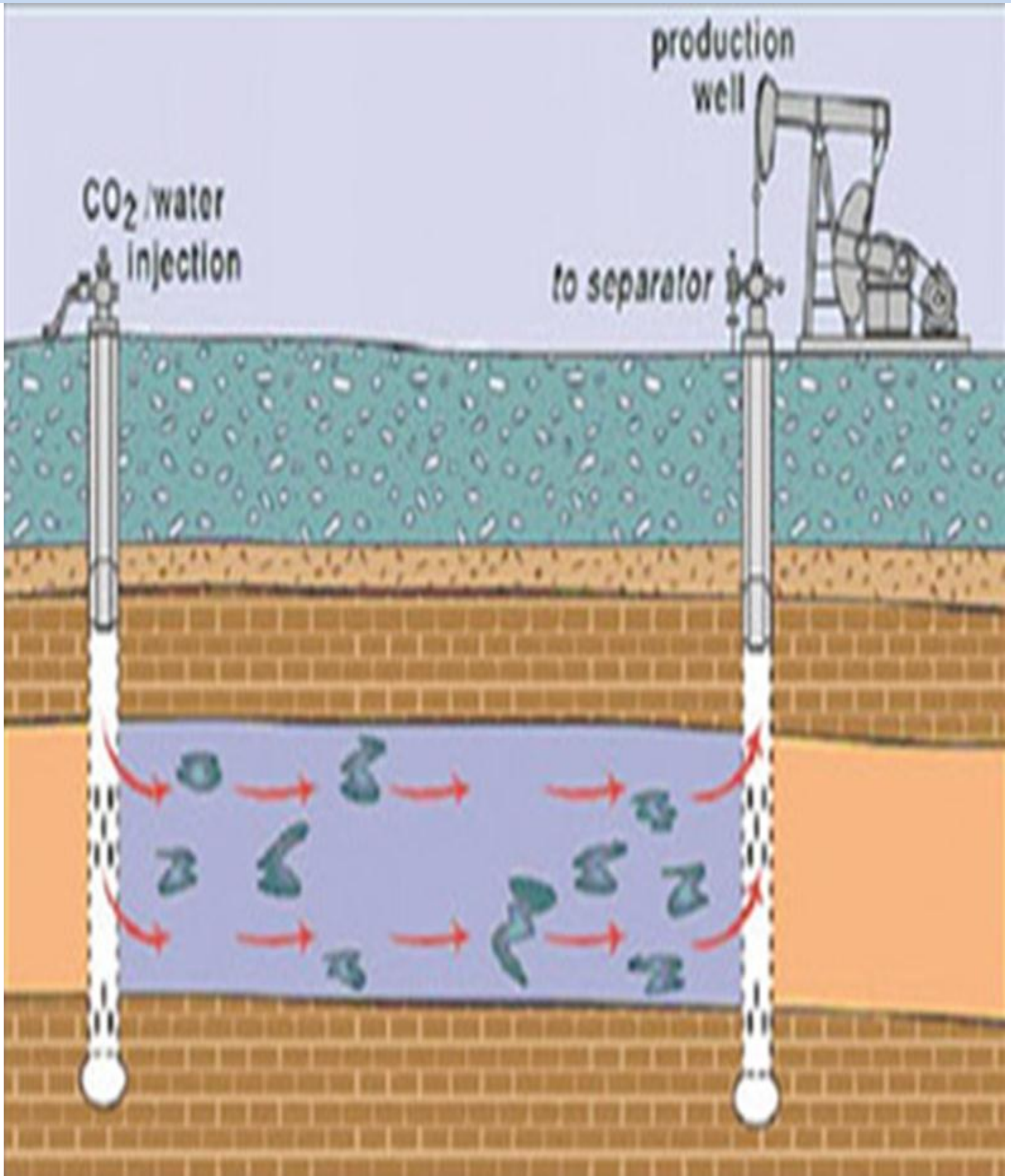


3-2-Oxygen corrosion



3-3-Oxygen corrosion

Oxygen is found with surface equipment and can be found down hole with the oxygen introduced by [water flooding](#) *{Waterflooding is the use of water injection to increase the production from oil reservoirs. Use of water to increase oil production is known as "secondary recovery" and typically follows "primary production," which uses the reservoir's natural energy }*



4-Galvanic corrosion

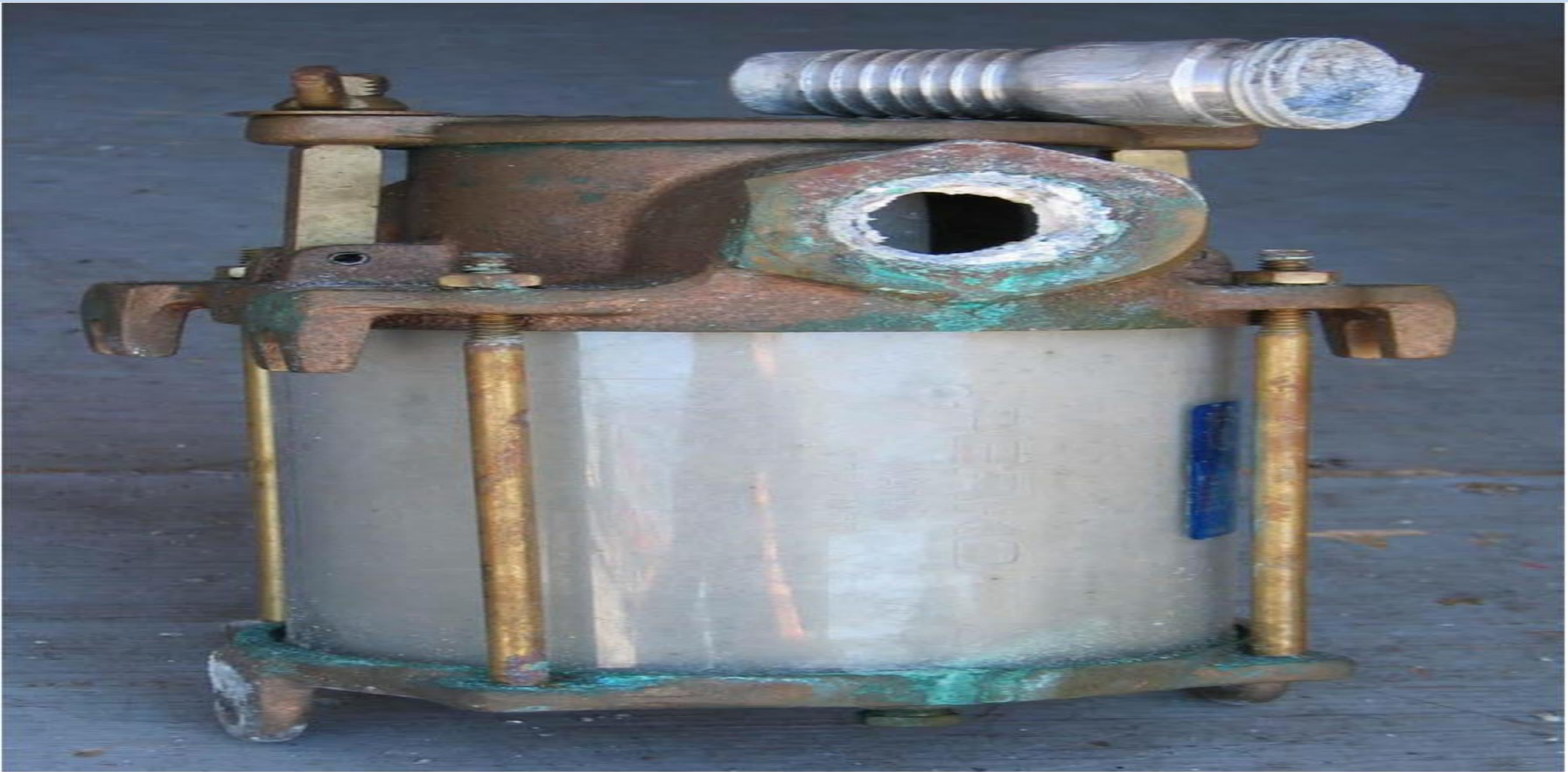
- **This type of corrosion occurs when two metallic materials with different nobilities (electrochemical potential) are in contact and are exposed to an electrolytic environment.**

- **In such situation, the metal with less or the most negative potential becomes the anode and starts corroding .**

- **Problems are most acute when the ratio of the cathode-to-anode area is large .**

4-1-Galvanic corrosion

Galvanic corrosion resulting from placing a bronze sea strainer on an aluminum hose barb.



4-2-Galvanic corrosion

5-Crevice corrosion

*Crevice corrosion is normally a localized corrosion takingnplace in the narrow clearances or crevices in the metal and the fluid getting stagnant in the gap.

*This is caused by concentration differences of corrodents over metal surface .

*Electrochemical potential differences
result in selective crevice or pitting corrosion attack.

*Oxygen dissolved in drilling fluid promotes crevice and pitting attack of metal in the shielded areas of drill string and is the common cause of washouts and destruction under rubber pipe protectors .

5-1-Crevice corrosion

Oil and gas pipeline under crevice

6-Erosion corrosion

1-The erosion corrosion mechanism increases corrosion reaction rate by continuously removing the passive layer of corrosion products from the wall of the pipe.

2-The passive layer is a thin film of corrosion product that actually serves to stabilize the corrosion reaction and slow it down.

6-1-Erosion corrosion

3-The erosion corrosion is always experienced where there is high turbulence flow regime with significantly higher rate of corrosion and is dependent on fluid flow rate and the density and morphology of solids present in the fluid.

4-High velocities and presence of abrasive suspended material and the corrodents in drilling and produced fluids contribute to this destructive process.

6-1-Erosion corrosion

5-THIS FORM OF CORROSION IS OFTEN OVERLOOKED OR RECOGNIZED AS BEING CAUSED BY WEAR CAUSING THE CORROSION RATE TO INCREASE.

6- THE EROSION CORROSION IS ALWAYS EXPERIENCED WHERE THERE IS HIGH TURBULENCE FLOW REGIME WITH SIGNIFICANTLY HIGHER RATE OF CORROSION AND IS DEPENDENT ON FLUID FLOW RATE AND THE DENSITY AND MORPHOLOGY OF SOLIDS PRESENT IN THE FLUID.

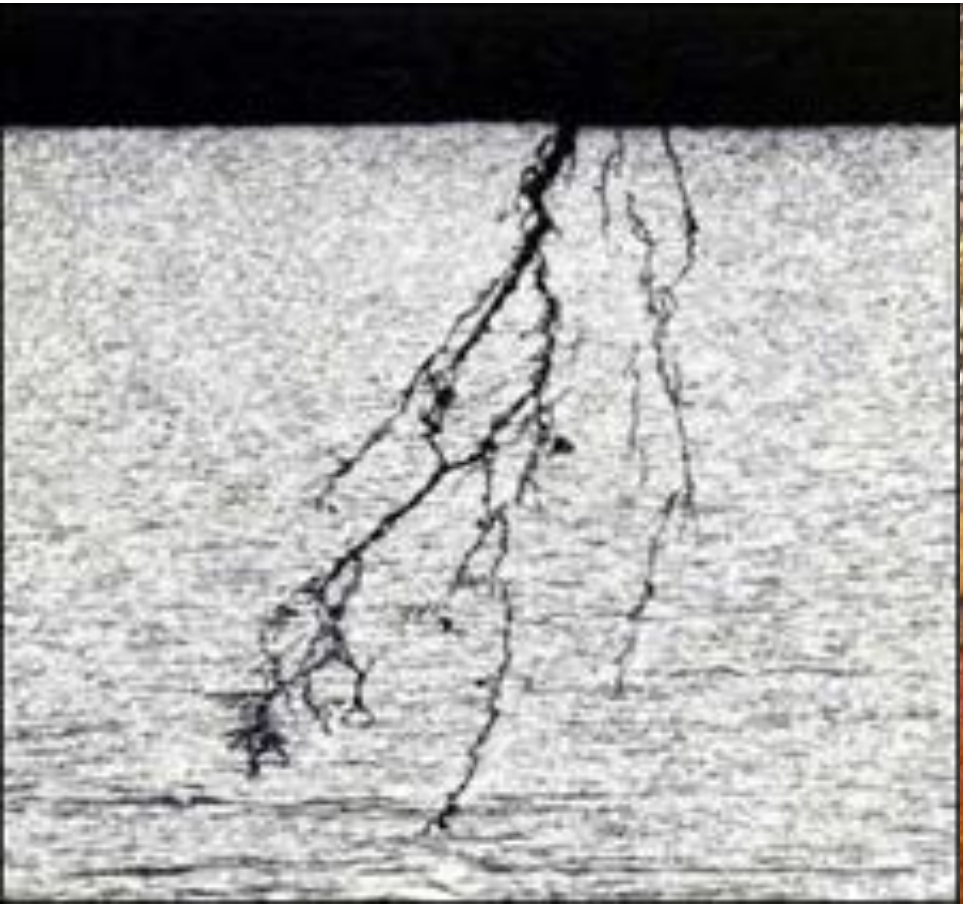
7-Microbiologically induced corrosion

This type of corrosion is caused by bacterial activities.

The bacteria produce waste products like CO_2, H_2S, and organic acids that corrode the pipes by increasing the toxicity of the flowing fluid in the pipeline

8-Stress corrosion cracking.

Stress corrosion cracking (SCC) is a form of localized corrosion which produces cracks in metals by simultaneous action of a corrodent and tensile stress.

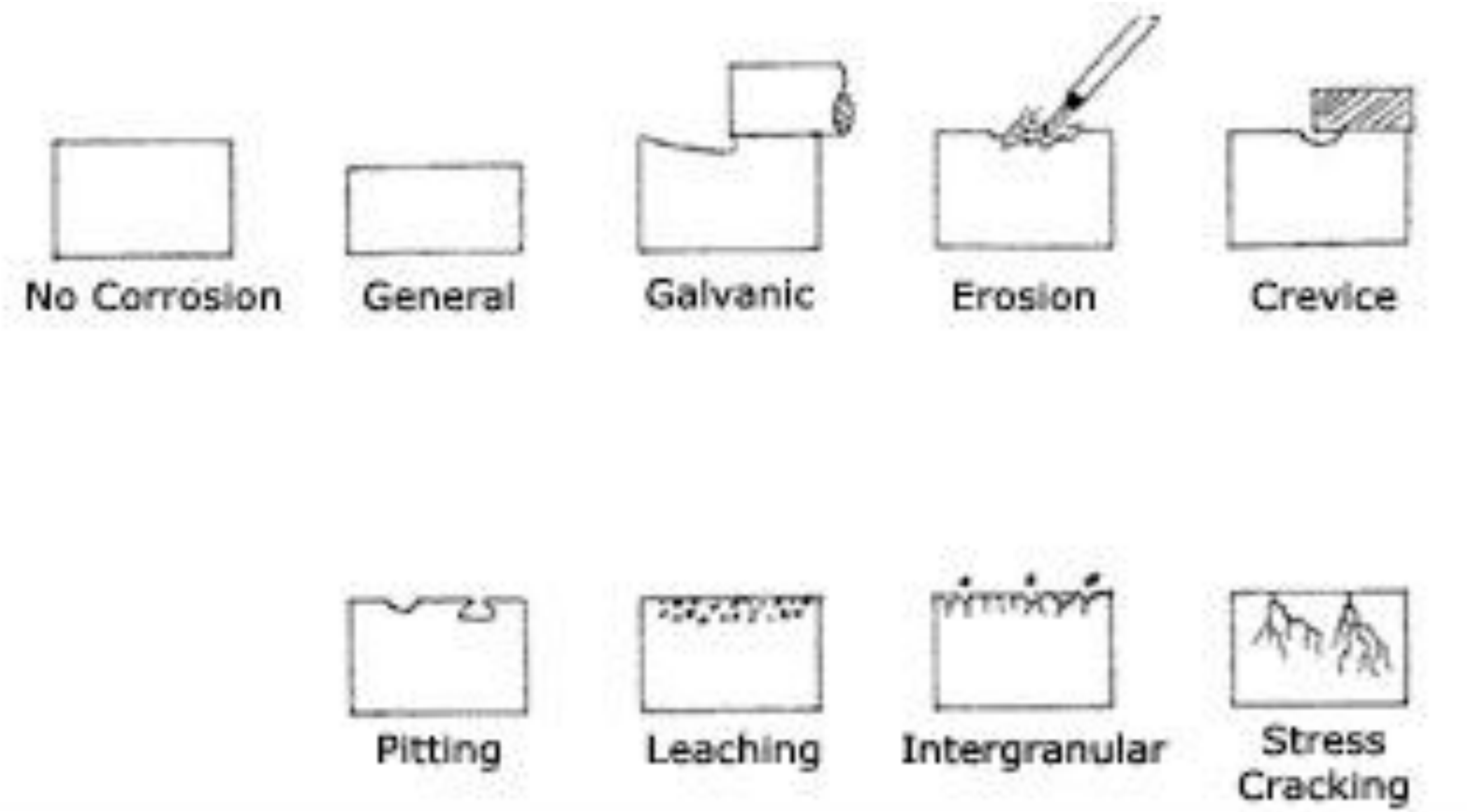


Corrosion mitigation in the oil and gas industry

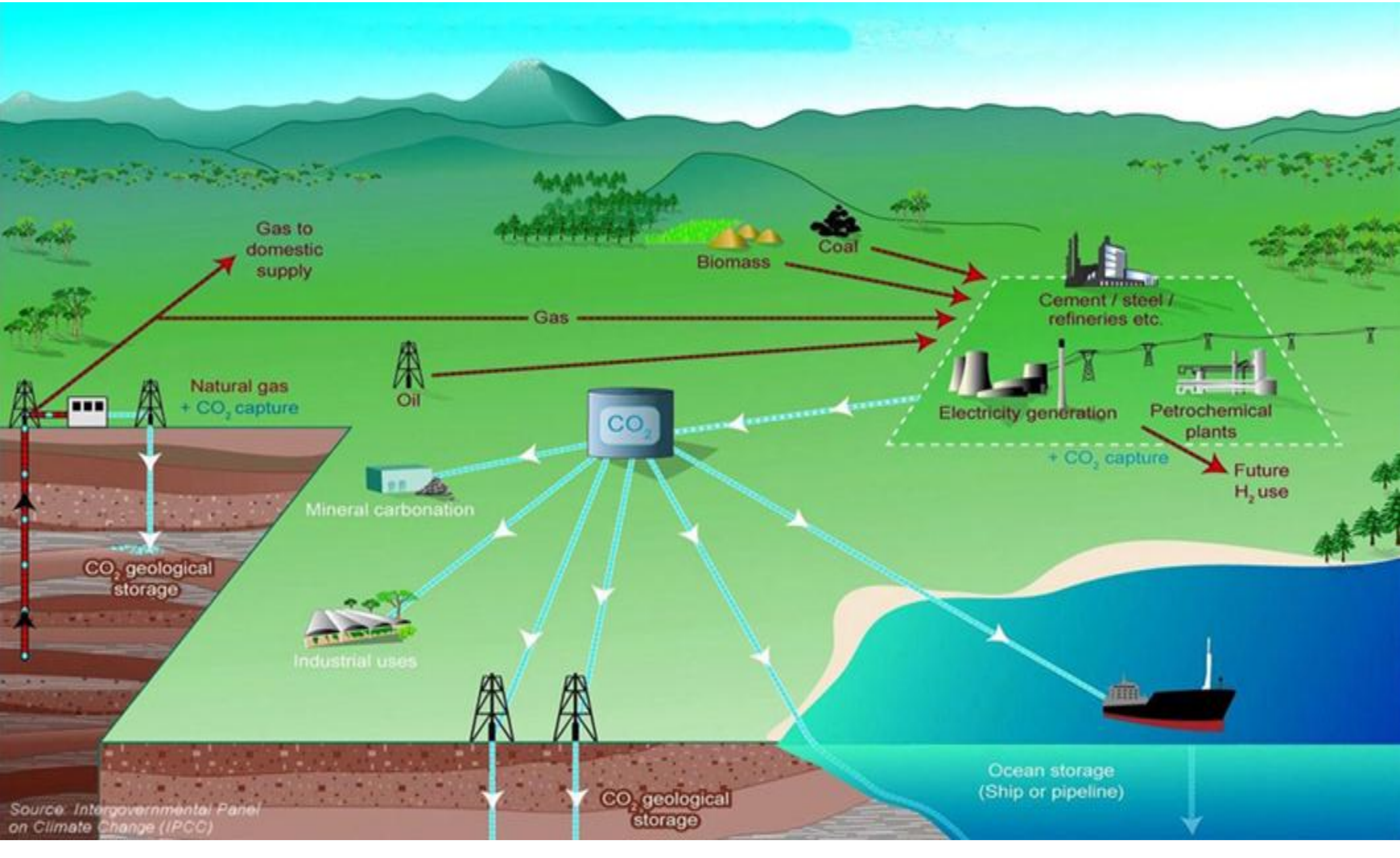
Oil field corrosion challenges are not static phenomena. Fluid characteristics change over time, resulting in systems becoming less responsive to established corrosion mitigation programs.

- **Selection of appropriate materials**
- **Use of inhibitors**
- **Use of protective coatings**
- **Adequate corrosion monitoring and inspection**
- **Cathodic protection technique**

Oilfield corrosion can take specific forms:



2-Types and prevention of corrosion in transportation and storage of petroleum industry



All aspects of oil and gas **<u>production, processing, transportation, and storage</u>** are subject to problems related to the presence and activities of **<u>microorganisms</u>**

Such microbiologically-related problems include :-

1-biofouling (slimes),

2-deposition

3-microbiologically influenced corrosion (MIC).

In petroleum storage and transportation (PS&T) facilities, these problems often compromise the function and integrity of system components by

1-reducing flow rates.

2-plugging equipment.

3- filters.

4- contaminating products with corrosive and odiferous materials.

5-initiating or accelerating corrosion.

Why PS&T Facilities Experience Microbiologically-Related Problems ?

PS&T facilities are susceptible to microbiologically-related problems where there is long-term exposure of metals to MIC-related microbes—including :-

aerobes, slime formers, iron-related bacteria, anaerobes, organic acid-producing bacteria, and sulfate-reducing bacteria (which produce corrosive sulfides and consume hydrogen)—which are found both in water and in hydrocarbons carrying even small amounts of entrained water, water, nutrients (principally the hydrocarbons themselves), and corrosive ions such as chloride

Accumulation of water under hydrocarbons at low points in pipelines, tanks (including home heating and service station tanks and tanks on trucks and boats), and process equipment provides an ideal habitat for the growth of problem-causing microbes. The water phase accumulates water-soluble materials required for microbial growth and concentrates corrosive materials while the overlying hydrocarbon provides a practically inexhaustible supply of food for the microbes. Since petroleum products are added frequently to PS&T facilities, food, oxygen, and water are replenished, allowing biofouling and corrosion to continue.

External corrosion of PS&T facilities

Including pipelines and storage tanks, occurs because coatings have developed holidays and disbondments.

When these areas of disbondment come into contact with soils that contain microbial, chemical, and conductivity conditions permissive of microbial colonization of the metal under the disbonded coating, MIC can rapidly develop.

Cathodic protection (CP) is ineffective in controlling this corrosion since the corrosion is occurring *under* the disbonded coating and, therefore, is *shielded* from CP. The occurrence of MIC and its severity is determined largely by local conditions, which can change within a space of inches

Microbiologically-Related Problems Experienced in PS&T Systems.

PS&T systems may experience a variety of microbiologically-related problems.

Many times these problems occur simultaneously in an affected system and may not affect all systems uniformly due to differences in local environmental, operational, chemical, and biological factors.

Microbial problems may include:

1. **Reduced porosity in production and storage zones and, thereby, production rates due to microbial biomass and biofilms.**
2. **Reduction of flow rates and plugging of process and filtration equipment—including those in service stations, vehicles, boats, and ships—due to biofilms and deposition.**

3. **Contamination of products with corrosive and odiferous materials due to microbial metabolic by-products.**

4. **Compromised system component integrity in production equipment, pipelines, processing equipment, and storage tanks in processing and distribution facilities due to under-deposit pitting type corrosion.**

5. **Component failures due to under-deposit leaks.**

6. **Damage to coatings and destruction of underlying metal due to microbial activities.**

Materials Affected

Most metals and alloys, except titanium, are affected by microbial problems, including MIC. The majority of PS&T components are made of carbon steel, and under many operating and storage conditions these components are susceptible to MIC.

Systems Affected

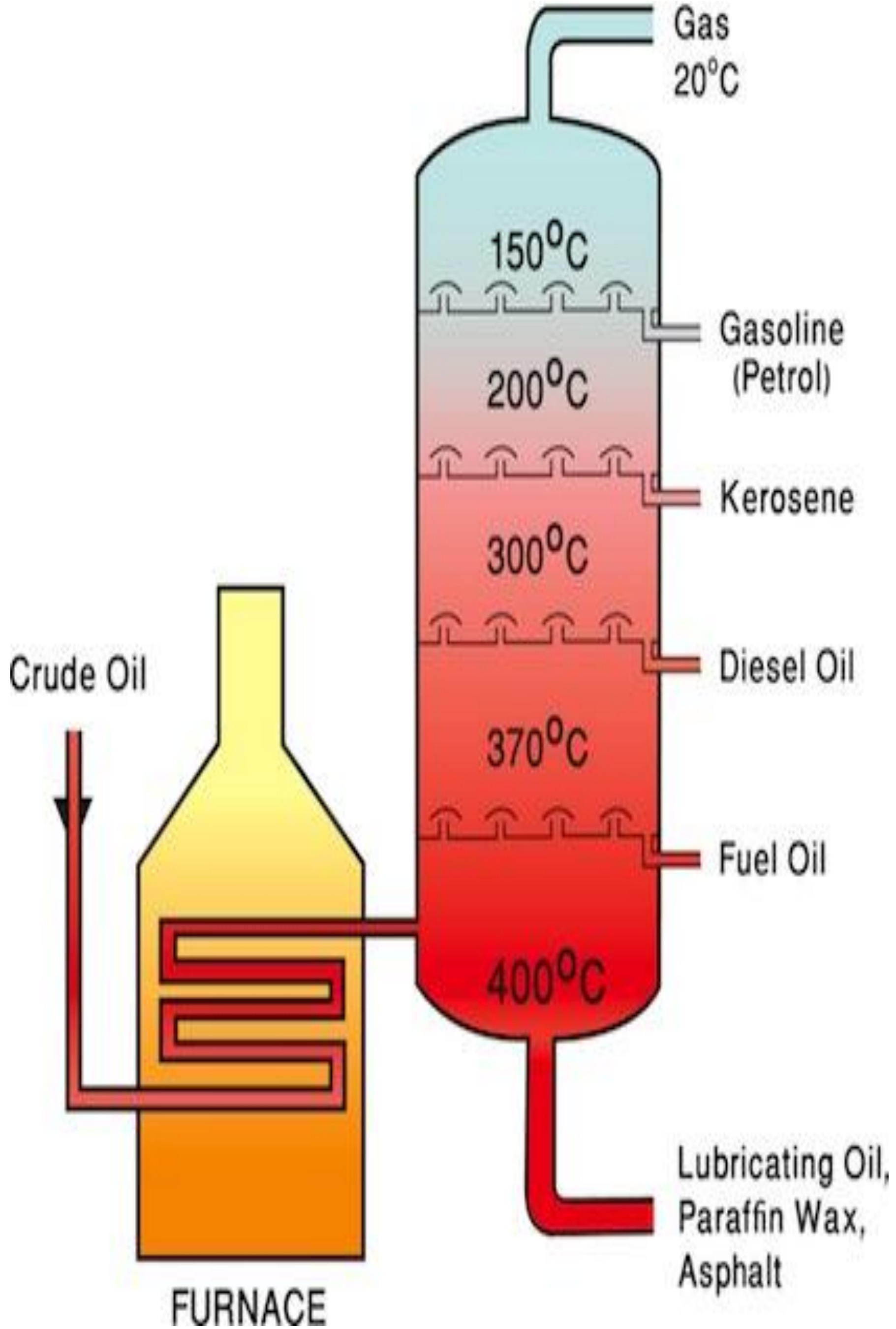
The following PS&T facility systems are all potentially susceptible to biofouling, deposition, and MIC:

- Transportation (pipelines, rail cars, trucks, tankers, and barges)
- Storage (tanks, underground storage fields, and salt dome storage)
- End-use (ships, boats, over-the-road carriers, and aircraft)

3-Types and prevention of corrosion in refinery

An **oil refinery** or **petroleum refinery** is an industrial process plant where crude oil is processed and refined into more useful products :- such as

petroleum naphtha, **gasoline**, **diesel fuel**, **asphalt base**, **heating oil**, **kerosene** and **liquefied petroleum gas**.

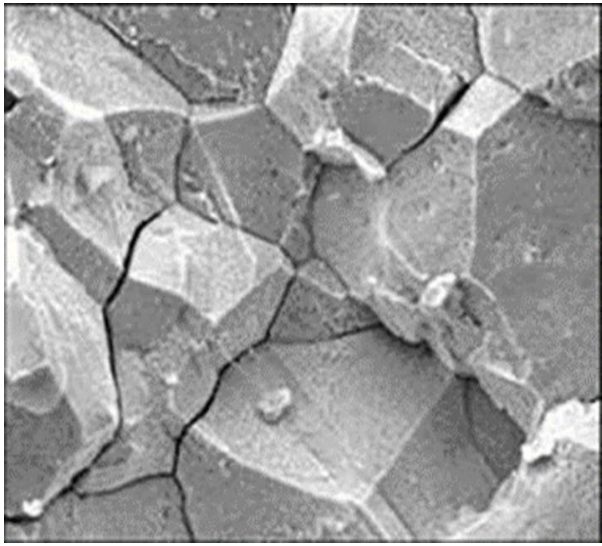


Corrosion occurs in various forms in the refining process, such as **pitting corrosion from water droplets, *embrittlement from hydrogen,* and stress corrosion cracking from sulfide attack.**

Hydrogen embrittlement
Hydrogen Induced Cracks (HIC)

Hydrogen embrittlement is the process by which metals such as steel become brittle and fracture due to the introduction and subsequent diffusion of hydrogen into the metal.

This is often a result of accidental introduction of hydrogen during forming and finishing operations



Refinery corrosion is sometimes separated into two classifications:

(1) low-temperature corrosion and

(2) high temperature corrosion.

The dividing point is usually 260 º C.

i-Perhaps, water can exist below 260 º C, and the mechanism of aqueous corrosion apply.

ii-The high temperature mechanism takes over above260 º C.

iii-Perhaps another reason for the division at 260 º C is that ordinary carbon steel is economical for handling most crudes and naphtha's up to this temperature, but alloy steels and other materials must be used at higher temperature.

Corrosion Problems Split into two categories

Low temperature (below 260 ^oC)

Corrosion mostly by pitting and stress corrosion cracking.

Always in the form of aqueous or other liquid solutions.

Caused by two sources:

I-Contaminants in crude oil process stream

1-Air and water,

2- Hydrogen sulfide,

3- Sour water ,

4- combination of water with ammonia

5-hydrogen cyanide

6- organic sulfides.

II Chemicals introduced, such as

1-solvents 2-neutralizers3- catalysts 4-Caustic .

Corrosion mostly by uniform thinning, local attacked, and erosion-corrosion.

Generally in the absence of water, taking the form of liquid or gaseous hydrocarbons

Most dangerous form of corrosion

High temperatures and high pressures can cause ignition

Primarily caused by sulfur compounds in the crude oil in concentrations of 0.1% to 5.0%

Corrosion occurs when sulfides react with metal to form metal sulfides and H_2S.

Metal corrodes faster on the heated side of furnace tubes

Dependent on the metal surface temperature, rather than the stream temperature

Carbon steel is resistant to the most common forms of corrosion, particularly from hydrocarbon impurities at temperatures below 205 °C, but other corrosive chemicals and environments prevent its use everywhere. Common replacement materials are low alloy steels containing chromium and molybdenum, with stainless steels containing more chromium dealing with more corrosive environments.

More expensive materials commonly used are **nickel**, **titanium**, **and copper alloys**. These are primarily saved for the most problematic areas where extremely high temperatures and/or **very corrosive chemicals are present.**


Thank You