

Oilfield Corrosion

The image shows a complex industrial oilfield facility. Large, thick-walled metal pipes, heavily corroded to a reddish-brown rust, dominate the foreground and middle ground. These pipes are connected by various fittings and valves. In the background, several large, vertical cylindrical storage tanks are visible, also showing signs of weathering and corrosion. The overall scene is one of industrial decay and the effects of harsh environments on metal infrastructure.

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Production Chemistry & Corrosion Control

Surface Operations

- Significance of Corrosion
- Why and How Corrosion Occurs
- Manifestations of Corrosion
- Corrosion Control Techniques
- Corrosion Monitoring

Oilfield corrosion can be considered under the following headings:

Significance - what it costs.

Why it occurs - the mechanism.

What it looks like.

The last two items, “How to control it” and

“How to measure it” are covered in the next section

Why is Corrosion Important

Significance

- Operating Costs
- Health & Safety
- Environmental Impact

All three of the above will appear in most asset goals.
Corrosion can prevent the attainment of these goals on one or more of these criteria

The costs fall into three categories:

Financial

Risks to Health and Safety

Possible Environmental Problems

Each is important in today's business and political environment.

Operating Costs

- Direct (Money Spent)
 - Replacement
 - Installation
 - Maintenance
 - Clean up of spillages
- Indirect (Money Not Saved)
 - Unplanned shutdowns
 - Loss of product (oil or gas)
 - Overdesign (“corrosion allowances”)
 - Loss of efficiency (e.g. thermal efficiency of corroded heat exchangers)
 - Bad publicity

Indirect costs are often considerably higher than direct costs, BUT are difficult to quantify

Bad publicity can lose a company business. It is difficult to determine how much business is lost.

Opportunity Costs

Shell

- Estimated costs of corrosion at \$100MM in 1992
- Estimated 70% was avoidable

Another Major Oil Company

- Estimated costs of \$320MM due to corrosion in a recent 3 year period
- Equivalent to 6.5% of net asset value/yr
- 67% Repairs, 33% Lost Production

Health & Safety

- Leaks caused by corrosion
 - Can release hydrocarbons/other chemicals
 - risk of injury from fire, explosion
 - risk of exposure to hazardous materials
 - Can cause equipment malfunction
 - risk of injury to personnel
- Mechanical failure caused by corrosion
 - Can cause process upsets
 - risk of injury from operating outside normal envelope
 - Can occur catastrophically
 - risk of injury

Environmental Impact

- Pollution of environment from corrosion leaks
- Depletion of non-renewable resources

In most countries environmental concerns can no longer be ignored. This is especially true for large multi-national companies like Shell, which must avoid upsetting the 'neighbours'.

It is not just the cost of clean-up; often leaks lead to financial penalties from local and national regulatory bodies.

Once the oil is spilled, it is usually not recoverable.

Why and How Corrosion Occurs

A brief look at the mechanisms that lead to oilfield corrosion problems.

What is meant by “Corrosion”?

Definition

- NACE International has defined “CORROSION” as:-

“... the deterioration of a substance (usually a metal) or its properties because of a reaction with its environment”

NACE - the National Association of Corrosion Engineers.

Does this definition really help us? Let us analyse what it means in a practical sense.

- All corrosion processes are chemical reactions
- Chemical reactions only occur spontaneously if there is a net decrease in the energy of the system as a result

ΔG must be negative

What is the main metal used for construction in the oil industry?
Carbon steel, otherwise known as mild-steel.

- Metals of importance in engineering generally exist in their “natural” state as compounds e.g. iron oxide
- Refining of metals consumes energy - “stored” in the pure metal
- Refined metals are generally unstable and tend to revert to a lower energy state, as a chemical compound, by reacting with their environment, i.e. they CORRODE

Iron oxide is heated (energy input) to convert it to pure iron, then a small amount of carbon is added during the process to form mild-steel.

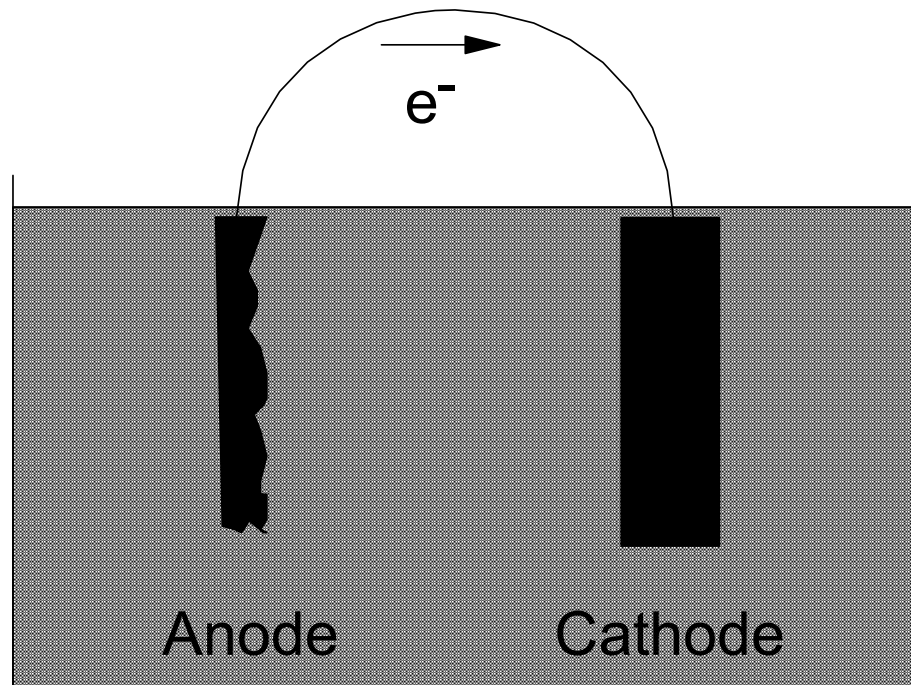
It is this stored energy that is the driving force for the metal to react with its environment (e.g. oxygen in air) and revert to the more stable iron oxide.

How Do Corrosion Reactions Occur?

- Oilfield corrosion is almost entirely electrochemical in nature
 - This means that an electrochemical cell is in operation
 - flow of electrical current (electrons)
 - chemical reaction
- } Occur in conjunction

Electrochemical Cell

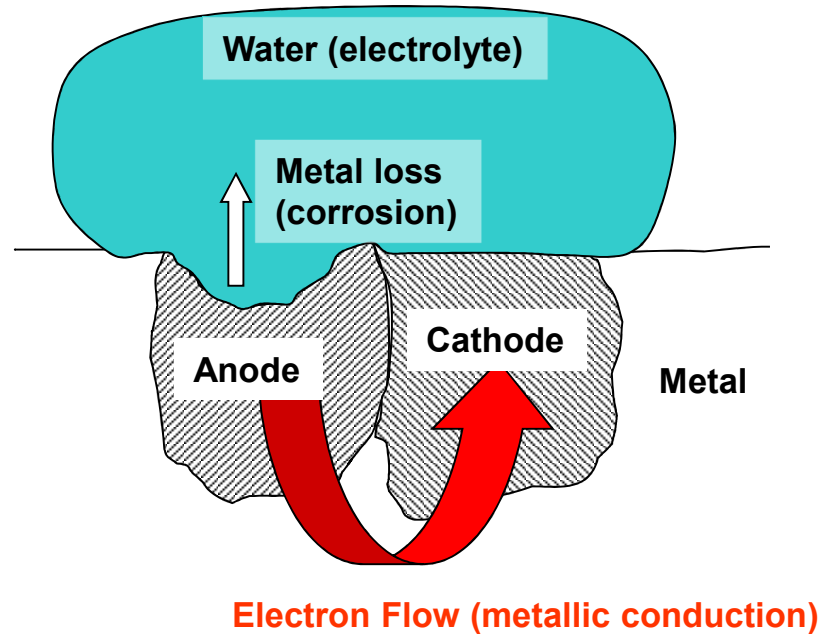
- MUST have 5 components
 - anode
 - electrolyte (ionic conductor)
 - metallic conductor
 - cathode reactant (electron acceptor)



We need electrical contact between the anode and cathode, in the presence of an electrolyte and cathode reactant (which accepts the electrons from the anodic reaction).

Electrochemical Cell

- In practice microscopic cells can be generated where 3 of the cell components are provided by a single piece of metal



- In practice cells are often microscopic, they move location and often overlap one another

Carbon steel has a crystalline structure consisting of iron (Fe) and iron carbide grains. The iron carbide acts as the cathode and the iron grains as anodes. Since these grains are adjoining, there is electrical contact. Hence the 3 components automatically present are the anode, cathode and metallic conductor.

How Fast Will Corrosion Occur?

- Factors which can influence corrosion rates
 - temperature
 - pressure
 - velocity
 - pH
 - dissolved solids

Effect of Temperature

- Generally as $T \uparrow$, corrosion rate $\uparrow$
- But not always
 - as $T \uparrow$ solubility of corrosive gases $\downarrow$
 - as $T \uparrow$ protective scales may form

Effect of Pressure

- **Main effect is on solubility of corrosive gases**
- **As $P \uparrow$ more gas goes into solution so corrosion rate $\uparrow$**

Chemical reaction rates usually increase with increasing temperature and corrosion is a chemical reaction.

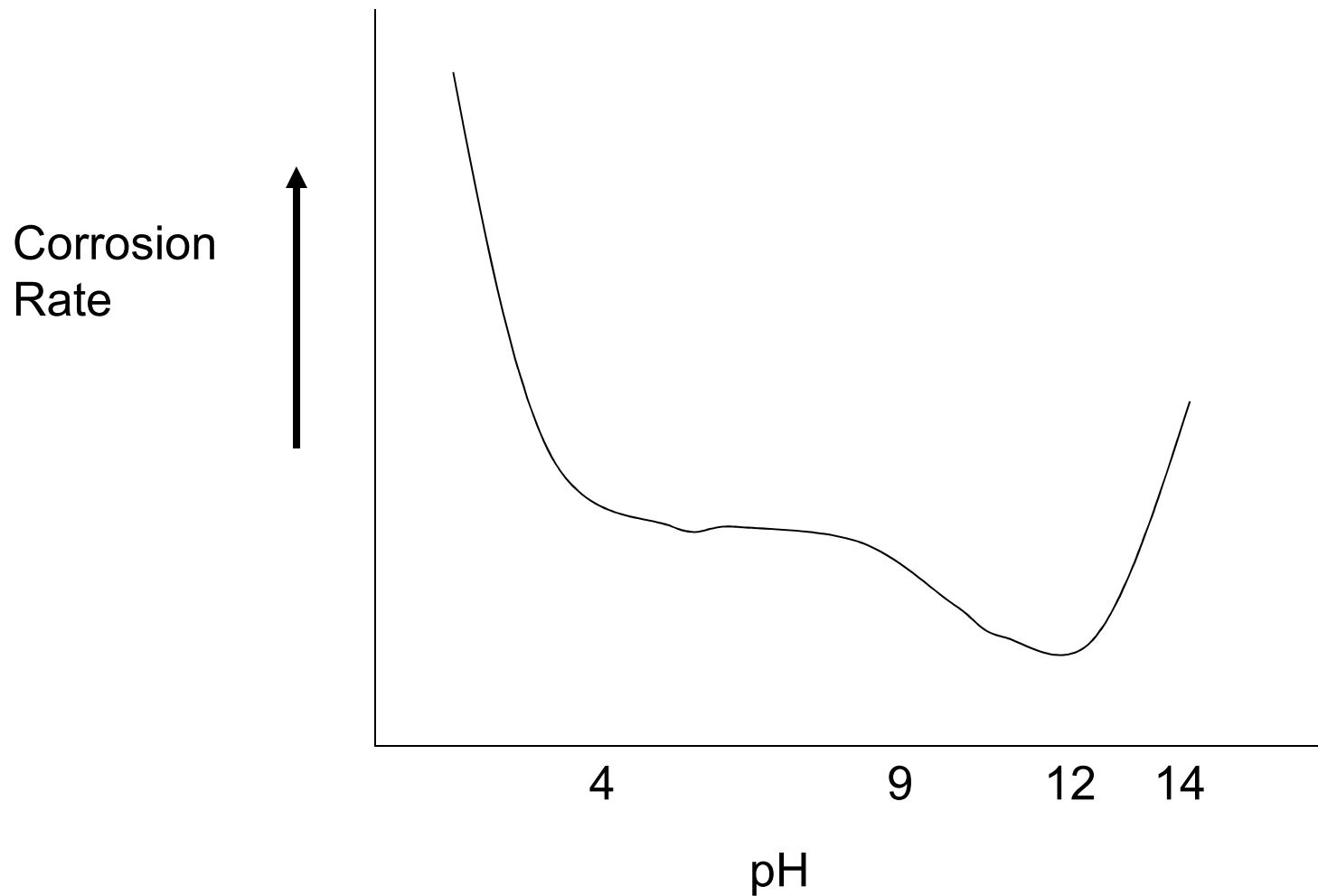
Increasing temperature will drive corrosive gases out of solution in the water, thus reducing the corrosion rate. This may also lead to the deposition of mineral scales, that may partially protect against corrosion.

Effect of Velocity

- Complex
- Usually as $V \uparrow$, corrosion rate $\uparrow$
 - improved mass transfer
 - protective film of corrosion product removed
 - erosion corrosion at very high velocity
- But sometimes as $V \downarrow$ corrosion rate $\uparrow$
 - suspended solids deposit on surfaces - “under deposit” corrosion
 - bacteria prefer “stagnant” conditions to colonise surfaces

Increased flow rate keeps the concentration of oxidising agent high at the corrosion site. When solids are present, such as sand, scale, or corrosion by-products, a reduction in velocity allows them to deposit on surfaces.

Effect of pH



Oilfield water systems are typically in the range of pH 4.0 to 8.3. Hence, the severe corrosion likely at lower pH is only possible when excess mineral acids enter the system e.g. from well stimulation work.

Effect of Dissolved Solids (Salts)

- Complex
- Usually as Concentration $\uparrow$ corrosion rate $\uparrow$
 - increased conductivity of electrolyte
 - increased flow of current in basic electrochemical cell
- BUT sometimes as Concentration $\uparrow$ corrosion rate $\downarrow$
 - solubility and diffusivity of dissolved gases $\downarrow$
 - precipitation of protective scales

The effect of increased conductivity and hence higher current flow in the electrochemical cell, increases the speed (or rate) of the chemical reaction.

- The solutes which cause most oilfield corrosion:
 - Carbon dioxide (“sweet”)
 - Hydrogen sulphide (“sour”) - may be of bacterial origin
 - Oxygen (not normally present)

A solute is any material dissolved in a solvent, in this case water.

Carbon Dioxide is usually present in % levels, whereas hydrogen sulphide is only at ppm levels. However, there are some oilfield systems where H_2S can reach 1-2%.

The presence of oxygen is normally due to leaky equipment and the most effective treatment is to find and repair the leak.

- Oilfield corrosion can be divided into external and internal (process side). The principles involved are the same for both but emphasis here will tend to be on the internal (process side) corrosion issues

Electrochemical Attack

Manifestations



- This process is called oxidation (electron donation) and always occurs at the anode

To maintain the charge balance another reaction must occur:



- This is reduction (electron gain) and occurs at the cathode

Oxygen Corrosion



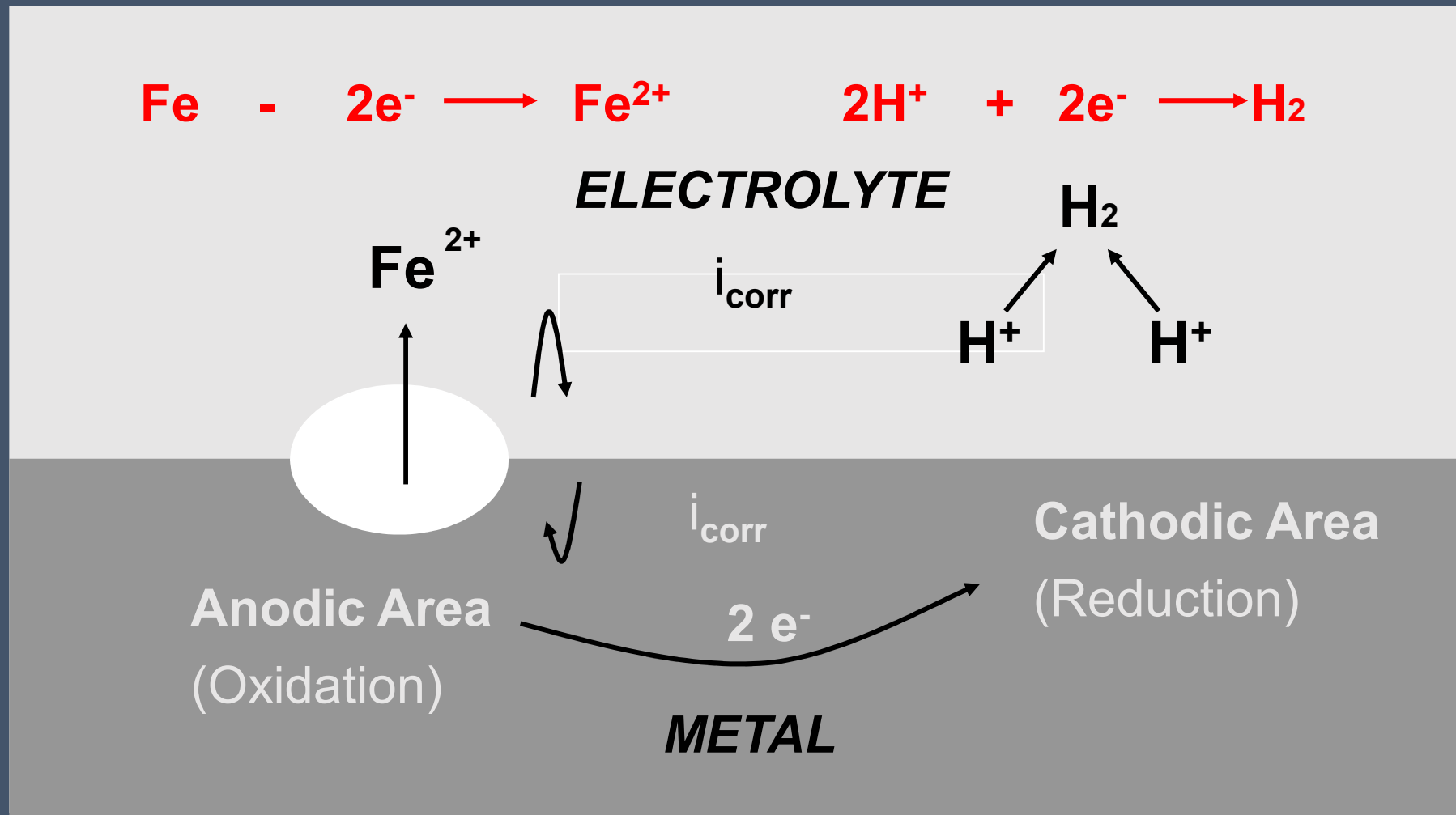
Appearance:

Large, shallow pitting.

O_2 contamination due to air drawn in.

Fatigue cracks may initiate if enough metal removed

The above corrosion cell illustrates the electrochemical reactions taking place at the anode and cathode under acidic conditions.

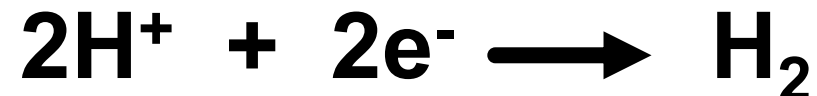
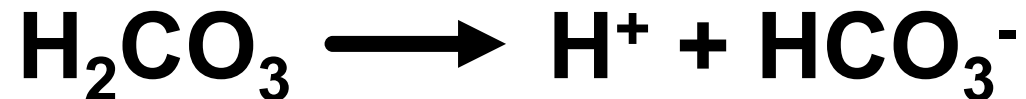
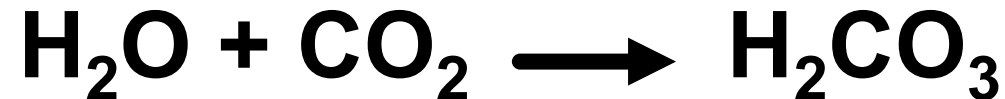


Corrosion Mechanism

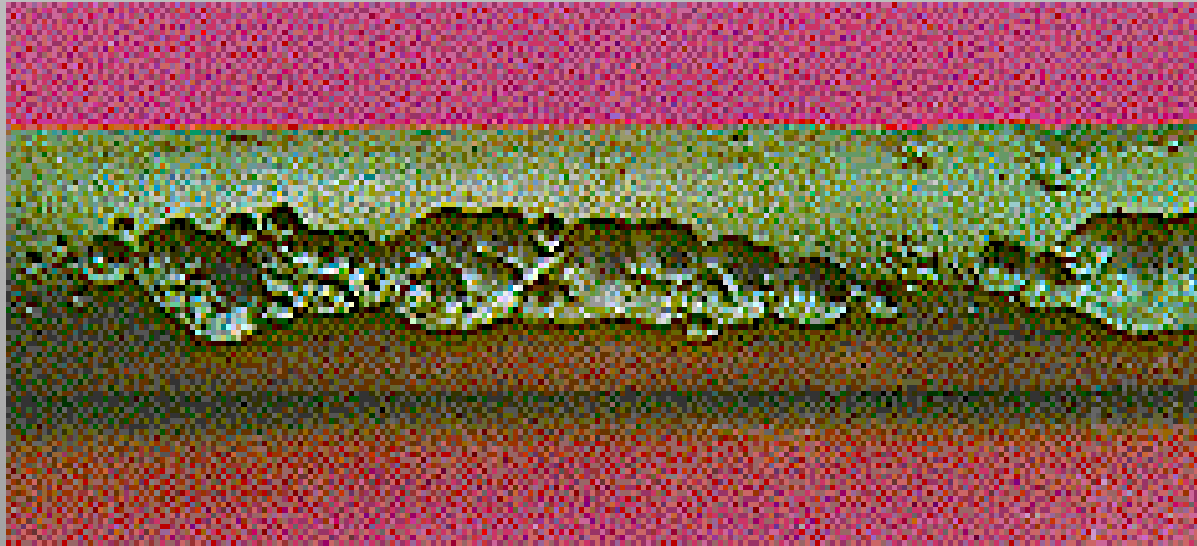
H_2CO_3 is carbonic acid. The higher the pressure, the more CO_2 dissolves in the water and the stronger the resultant carbonic acid.

Carbonic acid then gives rise to acid attack on mild steel structures.

The Carbon Dioxide cathodic reaction is associated with hydrogen ions:



CO₂ Corrosion



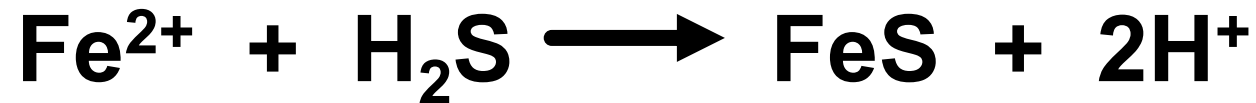
Appearance:

Round-bottomed pitting with sharp sides

This example is a section of sucker-rod from a reciprocating-rod pumped well.

Corrosion Mechanism

Hydrogen Sulphide acts as a corrosion rate accelerator

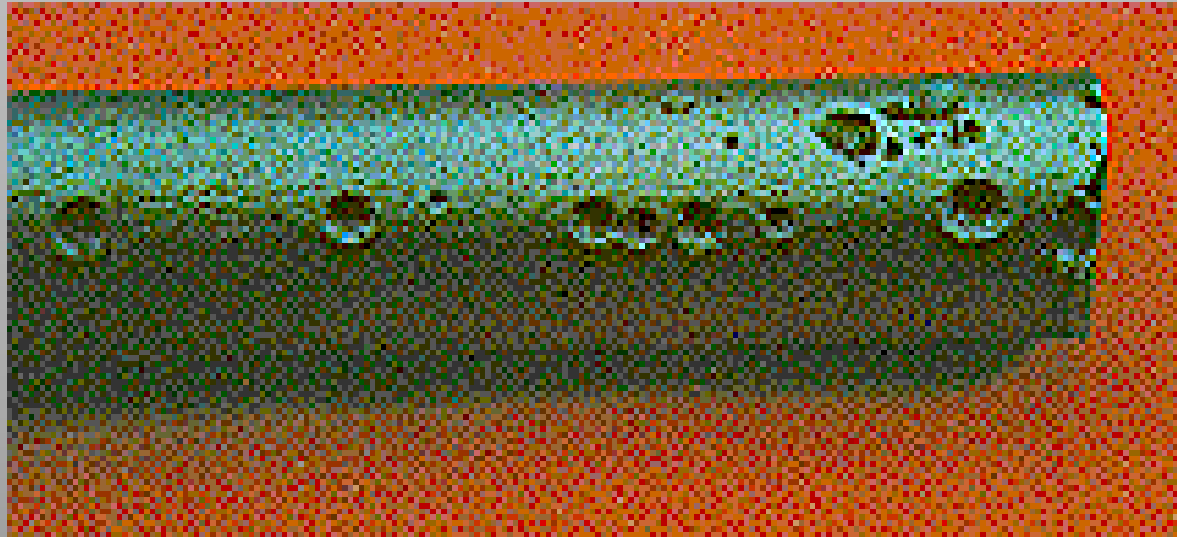


There is much misunderstanding about H_2S and its role in the corrosion process. While thermodynamically it is an acid, its ionisation is dependent upon the pH of the solution. As a result, the rate of reaction in typical oilfield waters is relatively slow in comparison to the corrosion rate due to carbon dioxide.

However, the reaction with iron ions (shown above) is extremely fast.

Pitting damage often occurs since FeS is cathodic to steel.

H₂S Corrosion



Appearance:

Small, steep-sloping pits

May contain fatigue cracks

H embrittlement also possible

Manifestations

- Classification
 - Uniform
 - Pitting
 - Crevice (under deposit)
 - Galvanic
 - Includes selective leaching
 - Intergranular
 - Erosion corrosion
 - Includes:-
 - cavitation
 - Microbiologically Influenced (MIC)
 - Environmental Cracking
 - Stress corrosion cracking
 - Hydrogen damage
 - Corrosion fatigue

This is about what the corrosion looks like when it does occur and how it affects the corroded metal.

General (Uniform) Corrosion

Manifestations

- Most common form of corrosion
- Electrochemical reactions proceed uniformly over the entire exposed surface over a large area
- Represents the greatest destruction of metal on a tonnage basis
- Life of equipment can be accurately estimated from corrosion tests

Simply put, this is where the corrosion takes place evenly over the whole metal surface.

Design engineers take into account the expected general corrosion rate and determine the metal thickness based on maintaining equipment integrity over the design life of the system.

System failures do not normally occur as a result of uniform corrosion.

Pitting Corrosion

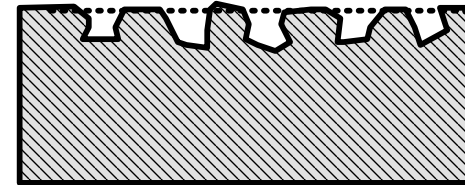
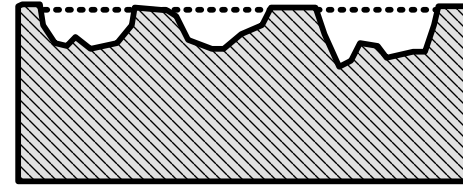
Manifestations

- More destructive than uniform attack - due to prediction difficulties
- Alloys that rely on passive films are particularly susceptible e.g. 13 Cr stainless pits rapidly in presence of chlorides and oxygen
- Can be isolated or clustered giving appearance of uniform attack
- Slower rate if more pits
- Changes in velocity can be both beneficial and detrimental

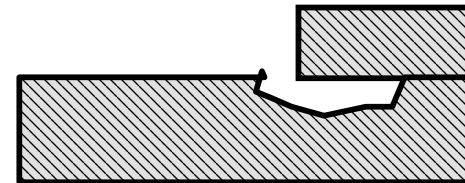
Pitting corrosion rates can be 10-50 times the general corrosion rate. Hence, holes in the metal can appear within times much shorter than the system's design life.

Pitting/Crevice Attack

Pitting Corrosion



Crevice Corrosion



Pitting corrosion occurs when the corrosion reaction takes place in localised areas, leaving much of the surface relatively corrosion free.

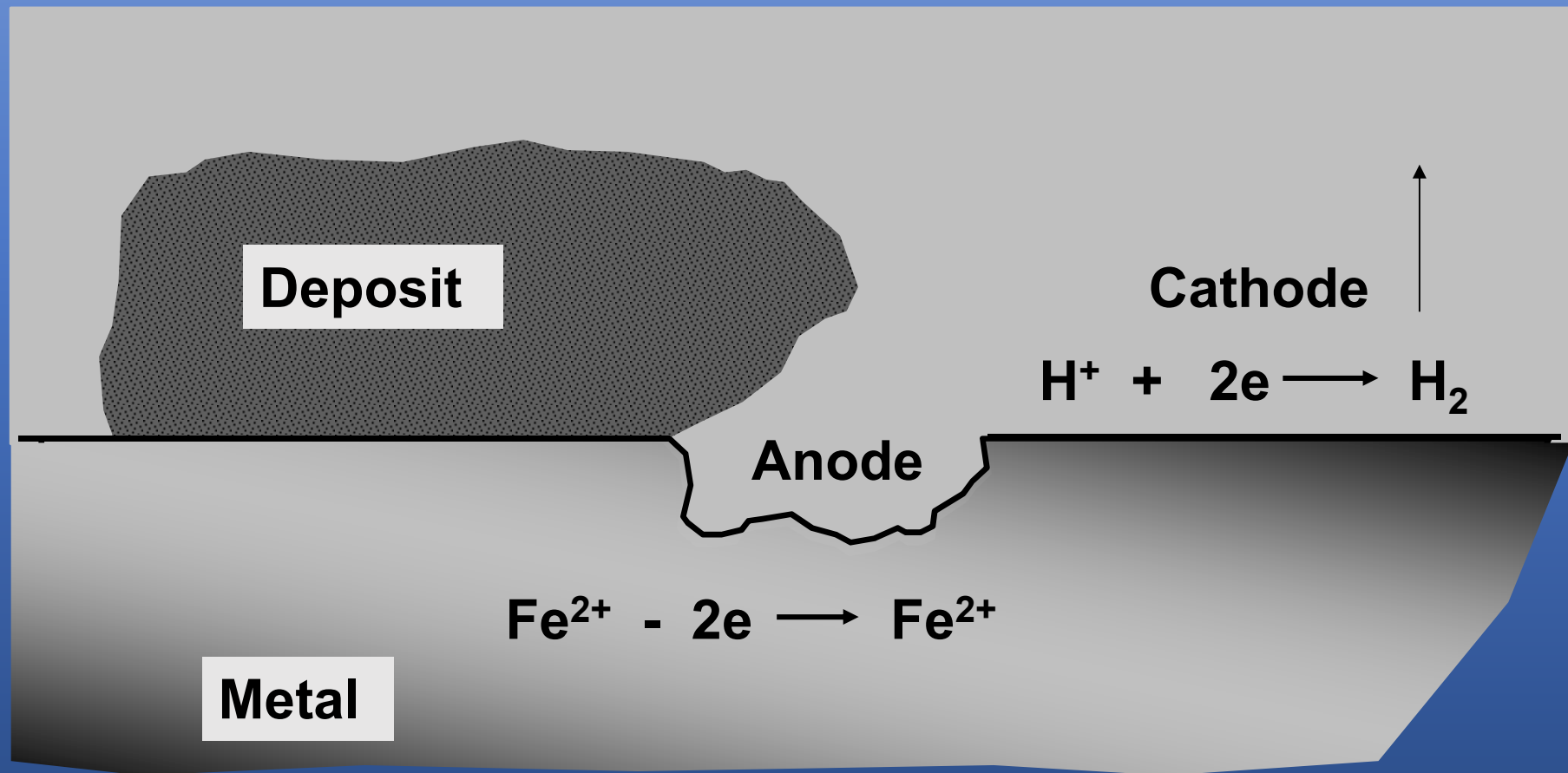
Since the corrosion reactions are concentrated at a few points, the metal loss is greater at those locations. Hence, pits are formed.

Crevice (Under Deposit) Corrosion

- Occurs in constricted areas where free access of the surrounding environment is restricted
- Crevice corrosion caused by metal-to-metal or metal to non-metal surfaces, e.g. gaskets, couplings and joints
- Under deposit corrosion - crevice formed from discontinuous deposit, can be inert (e.g. sand) or electrochemically active (e.g. FeS)
- Under-deposit corrosion is often the cause of failures in oilfield systems.

How Corrosion Occurs

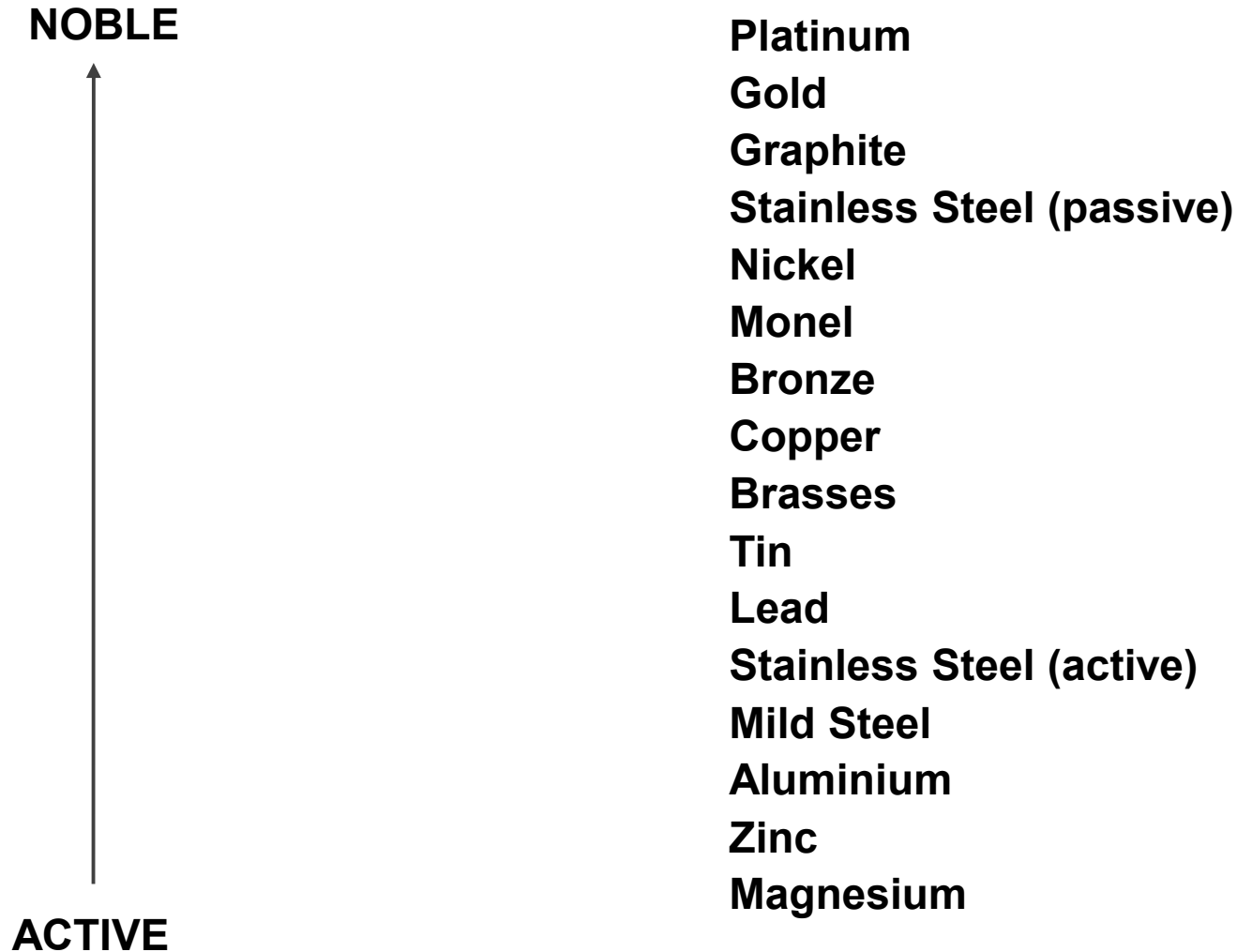
In the crevice between the edge of the deposit and the metal surface, a differential concentration cell develops. Here the concentration of corroding species becomes less compared to the bulk fluid covering the rest of the surface. This location then becomes anodic to the rest of the surface and pitting corrosion results.



Galvanic Corrosion

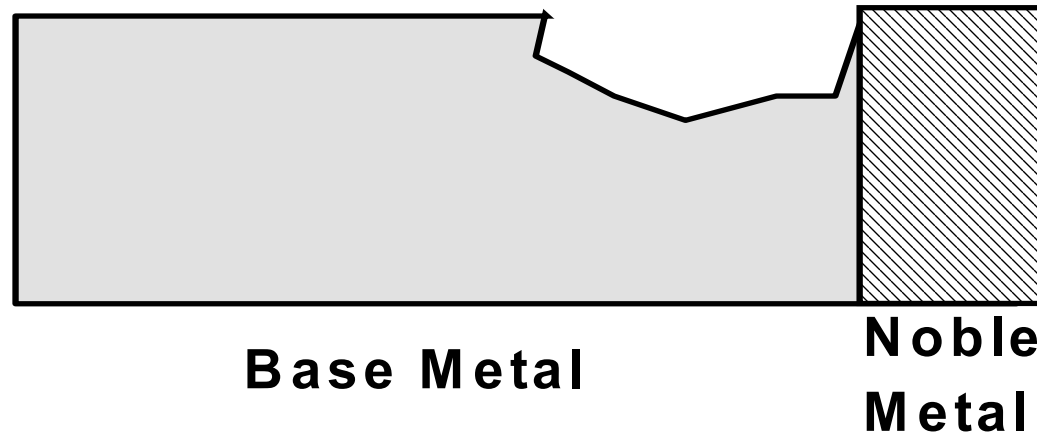
- A potential difference usually exists between two dissimilar metals
- Corrosion of less resistant metal is increased and more resistant metal is reduced
- Less resistant metal is anodic and more resistant metal is cathodic
- To predict corrosion can use galvanic series
- Particular problem with threaded connections between dissimilar metals
- A number of simple guidelines exist concerning galvanic corrosion. Surface area differences and the relative position in the Galvanic Series of the two adjoining metals, effect the corrosion rate.

Galvanic Series in Seawater



In simple terms, the Galvanic Series can be regarded as the decreasing order of the amount of energy required to process the pure metal from its natural state. That is, the more active the metal the more energy is 'stored' in that metal and the greater the driving force for it to revert to its natural low energy state.

Galvanic Attack



Such connections as these can lead to rapid and drastic failures.

Factors Effecting the Rate of Galvanic Corrosion

- The degree of potential difference between the two metals
- Distance effect - greatest near the junction
- Area effect - better to have large anode, small cathode
- Corrosiveness of the environment

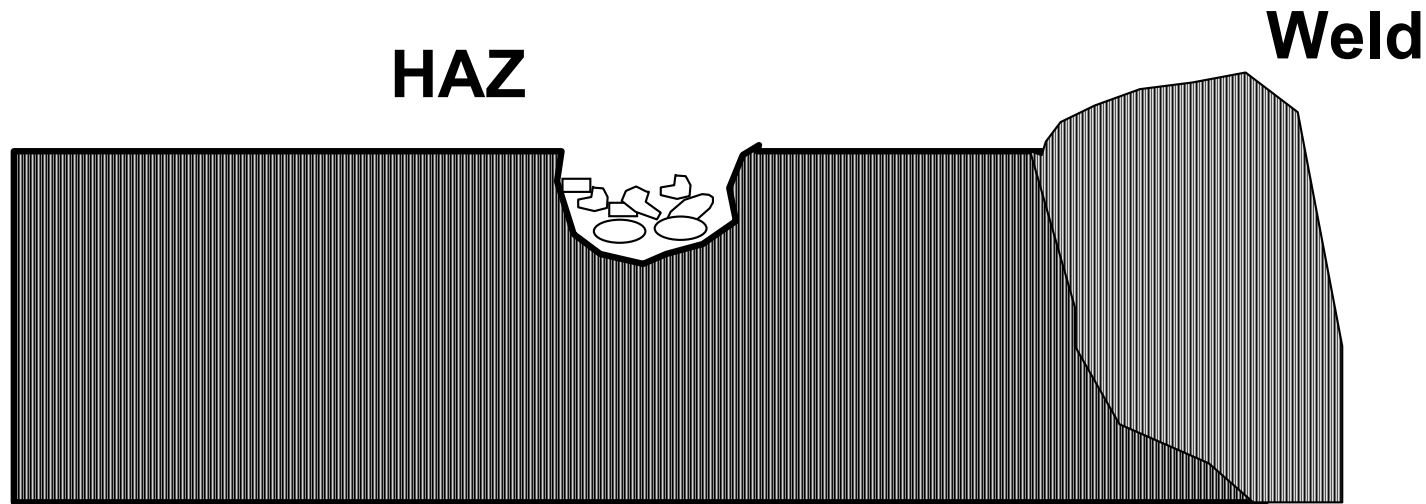
For example, if the more active metal surface area is smaller than that of the noble metal, the corrosion rate is higher. Likewise, if active metal has a much larger surface area, the corrosion rate will be lower.

Referring to the table in the next slide, the corrosion rate rate would be lower if copper and steel were connected (the steel would corrode) compared to the corrosion of magnesium when connected to copper.

Intergranular Corrosion

- Localised attack of grain boundaries with relatively little corrosion of the grains
- Caused by more reactive grain boundaries
- The metal has a granular structure. In circumstances where the grain boundaries become anodic with respect to the grains themselves, the corrosion reaction will preferentially occur along the lines of those boundaries. This will obviously affect the strength / integrity of the metal.

Intergranular Attack - Weld Decay

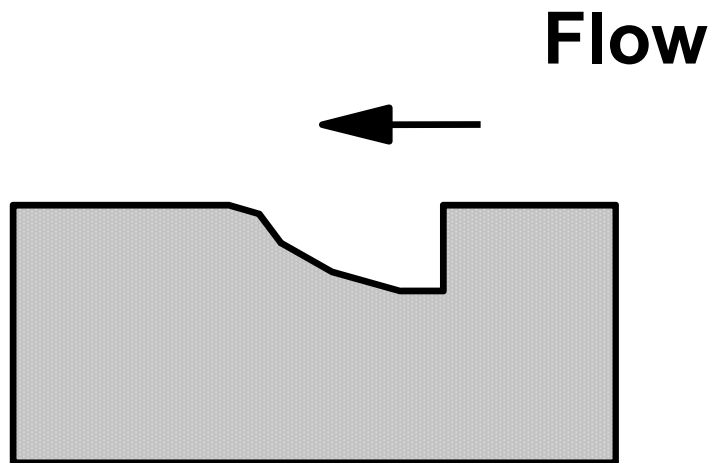


HAZ - heat affected zone.

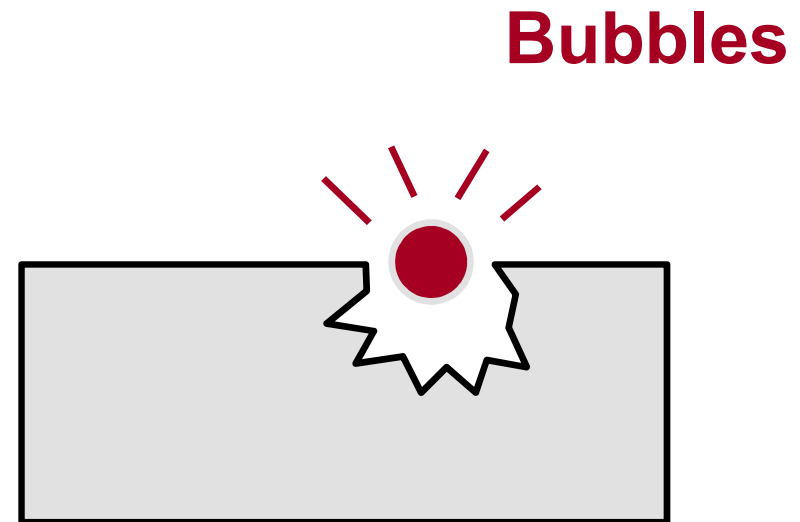
When weld areas have not been (or poorly) stress relieved by annealing, intergranular corrosion can occur in the HAZ. Often this appears as a corroded groove / channel all the way round the internal circumference of the pipe.

Velocity Phenomena

Erosion



Cavitation

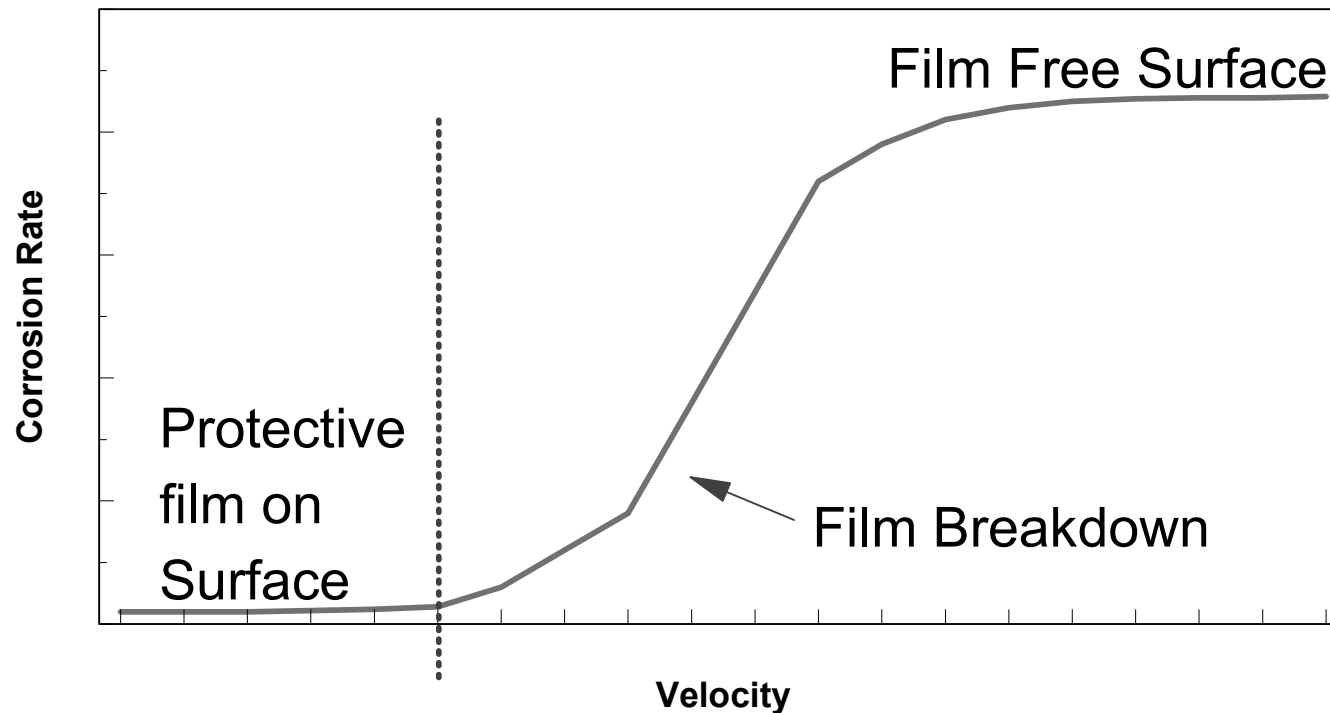


Erosion is due to the 'wearing' effect of high velocity fluid streams, usually containing solid particles. This is NOT a corrosion effect.

Similarly, cavitation is the implosion of vapour bubbles (created by forced evaporation due to pumping effects) as a higher pressure region is reached. The implosion on metal surfaces can result in metal loss.

Velocity Effect

- Velocity of the flow is sufficient to remove weakly adherent corrosion products from metal's surface
- Breakaway velocity determined by alloy and environment system



Erosion corrosion is a velocity effect that disrupts a partially protective corrosion product layer, opening the metal surface to further corrosive attack.

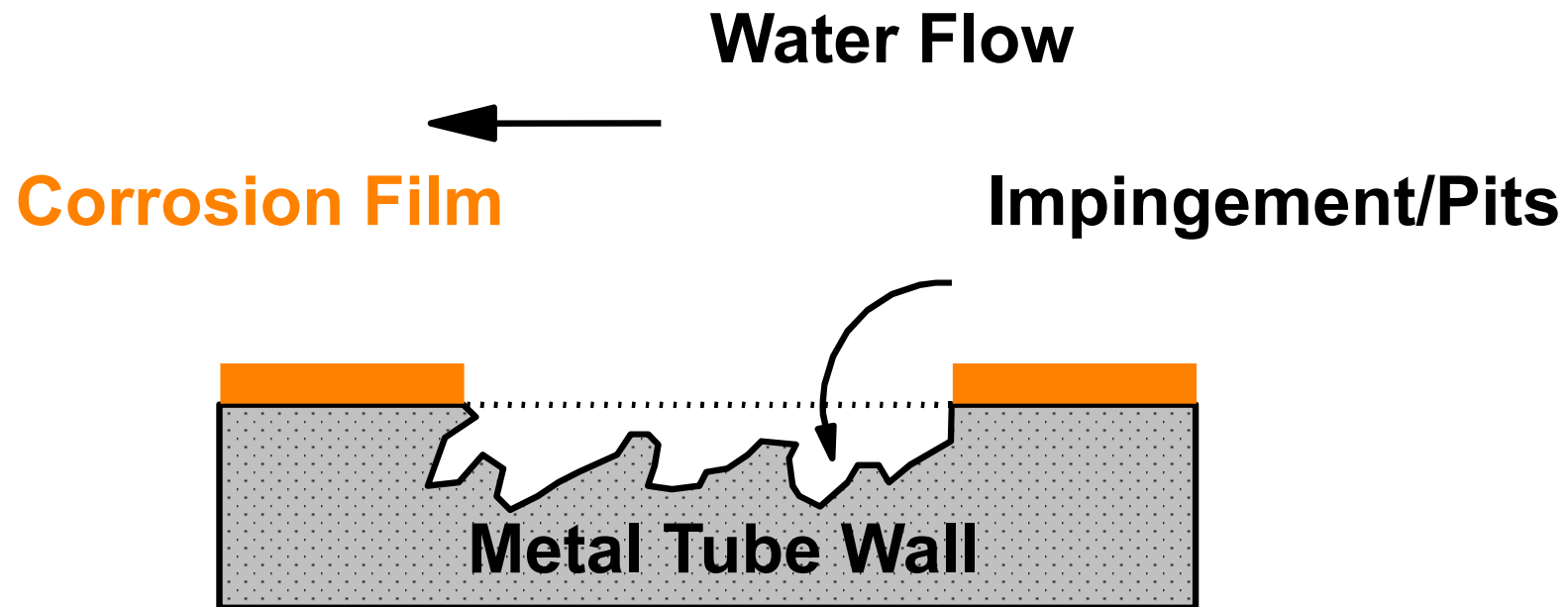
Erosion - Corrosion

- High velocity - film removal and corrosion
 - Suspended solids assist
 - Areas of turbulence susceptible
 - section changes, elbows, etc.
- Damage follows flow direction
- Corrosion inhibitors can reduce damage

Continued stripping of the corrosion product layer leads to a higher overall corrosion rate, but in a localised area.

The major difference between erosion and erosion corrosion is that corrosion inhibitors can reduce the damaging effects of the latter, but not erosion.

Erosion - Corrosion : Condenser Tube Wall

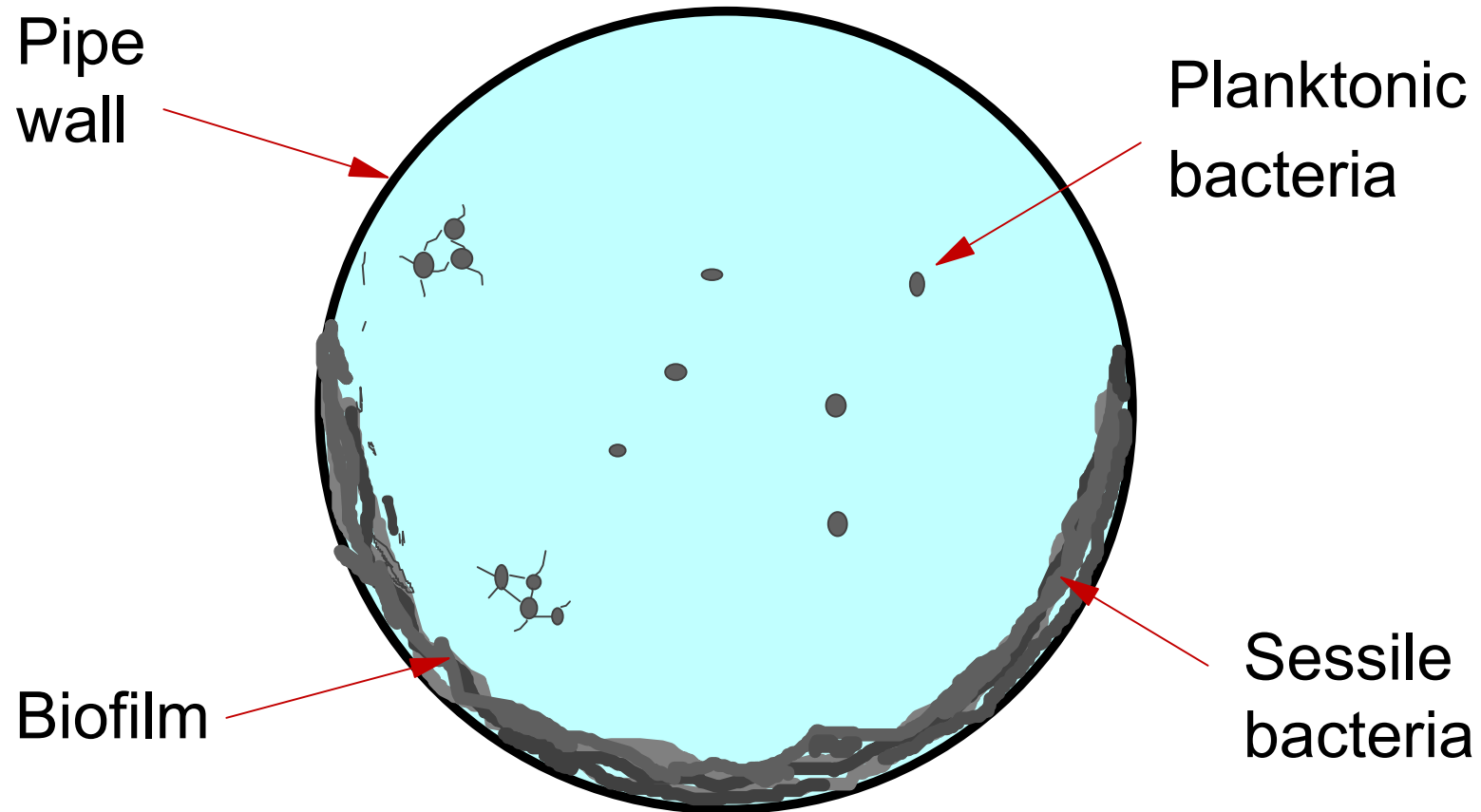


Cavitation

- Also occurs during fluid flow
- Rapid changes in pressure
 - Formation and collapse of gas bubbles
 - Repeated action wears away metal
 - Example : pump impellers
- Often design problem, but can inhibit
- Where the metal loss is mainly due to cavitation impact removing the corrosion product layer, inhibition can reduce the amount of damage.

Bacteria in Oilfield Systems

- Section of pipe indicating bacterial growth



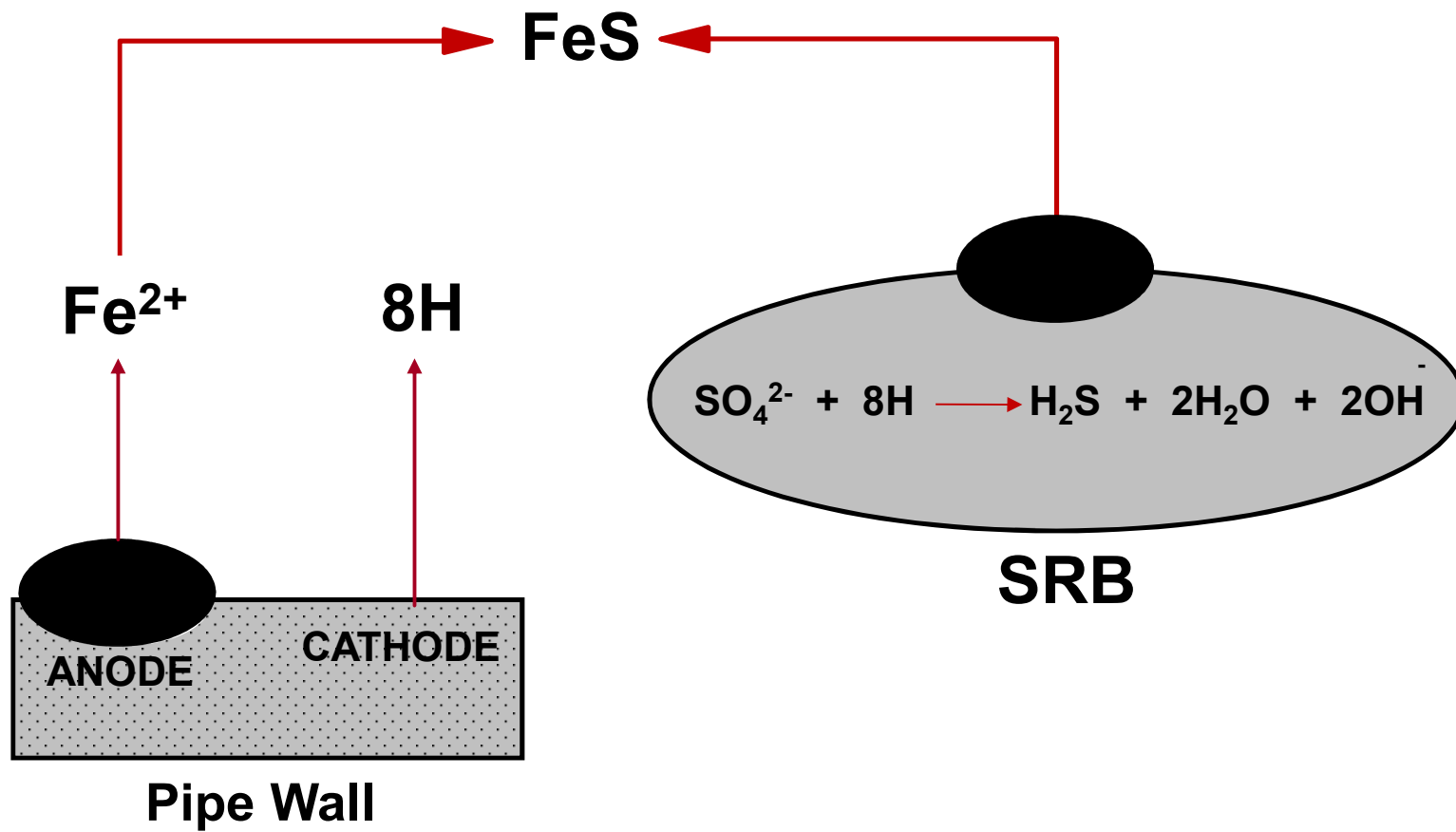
The next five slides are a brief introduction to oilfield microbiological problems, which is covered in more detail immediately after this topic (Corrosion).

Bacterial Corrosion

Certain types encountered:

- Sulphate reducing bacteria (SRB) cause most problems
 - Exist in anaerobic conditions
 - Metabolise by reducing inorganic sulphate to sulphide
 - $4\text{H}_2 + \text{SO}_4^{2-} \rightarrow \text{S}^{2-} + 4\text{H}_2\text{O}$
 - FeS deposits associated with black bacterial slimes
 - Pitting problems
 - Anaerobic conditions - in the absence of oxygen

Sulphate Reducing Bacteria

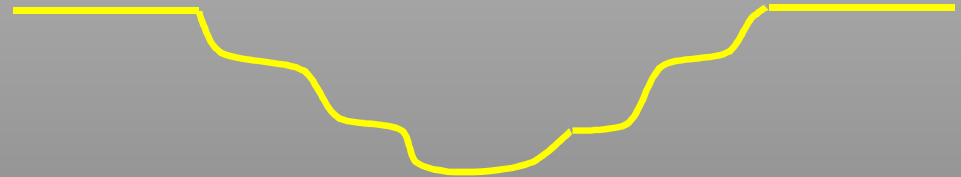


Bacterial Corrosion SRB

These sketches show the typical form of SRB induced pitting corrosion.



PLAN



SIDE

Appearance:
Shallow pits within pits

Bacterial Corrosion SRB



This pit was in a section of a failed oil pipeline. Note the smoothness of the pit sides and the hole. The remaining pipe surface was almost untouched by corrosion. The red-brown rust seen on the remaining surface occurred after removal of the section from the pipeline (i.e. it was due to atmospheric oxidation).

Environmental Cracking

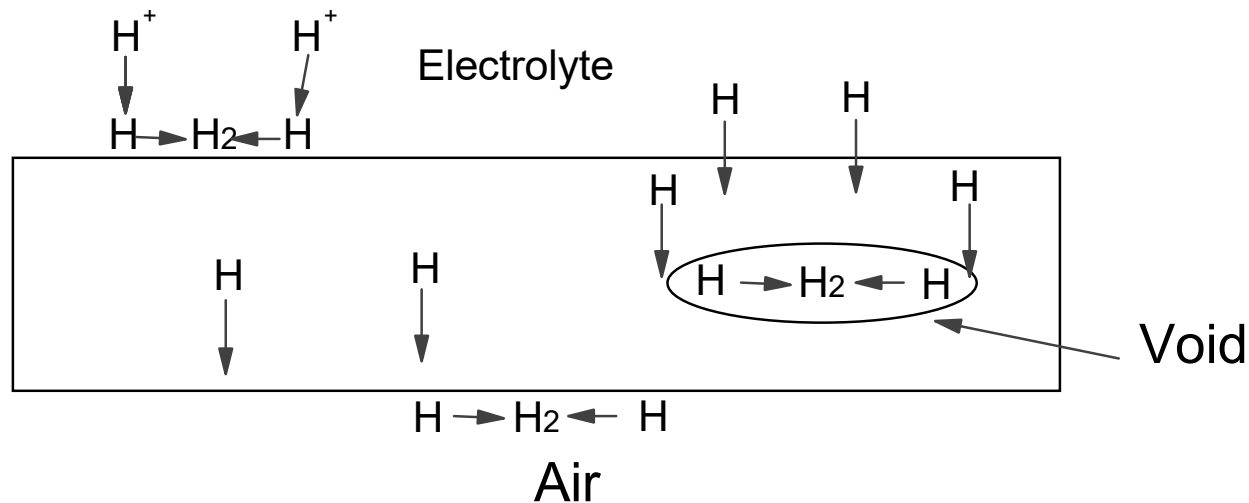
- Environmental cracking is the brittle failure of an otherwise ductile material as a result of the combined action of corrosion and tensile stress
 - Stress Corrosion Cracking (SCC)
 - Hydrogen Induced Cracking (HIC)
(and Hydrogen Blistering)
 - Corrosion Fatigue
 - Liquid Metal Embrittlement (LME)

Stress Corrosion Cracking

- Stress Corrosion Cracking is the brittle failure in an otherwise ductile metal from combined action of tensile stress and specific corrosive environment
- Carbon steel : caustic
- Stainless steel : chlorides
- Copper alloys : ammonia

Hydrogen Blistering

- Hydrogen blistering results from the penetration of atomic hydrogen into a metal
- More prevalent in softer metals, the harder metals usually suffer from hydrogen embrittlement
- Blistering is the local deformation and in extreme cases complete destruction of vessel wall



This effect usually happens only where high pressures, or high concentrations (% levels) of hydrogen sulphide, exist.

The hydrogen atom combination to form molecular hydrogen (H_2), is an extremely rapid reaction. However, some hydrogen atoms can enter the metal lattice before the reaction takes place. When H_2 is then formed within voids in the metal, the molecule is too large to exit the metal lattice. As the pressure of hydrogen builds in the void, the metal becomes distorted.

Hydrogen Induced Cracking

- Hydrogen embrittlement results from the penetration of atomic hydrogen into a metal
- Embrittlement results in a loss of ductility and tensile strength
- Potentially more damaging than Hydrogen Blistering
- When hydrogen enters harder steels, the pressures exerted cannot distort the metal and cracking tends to be the result.

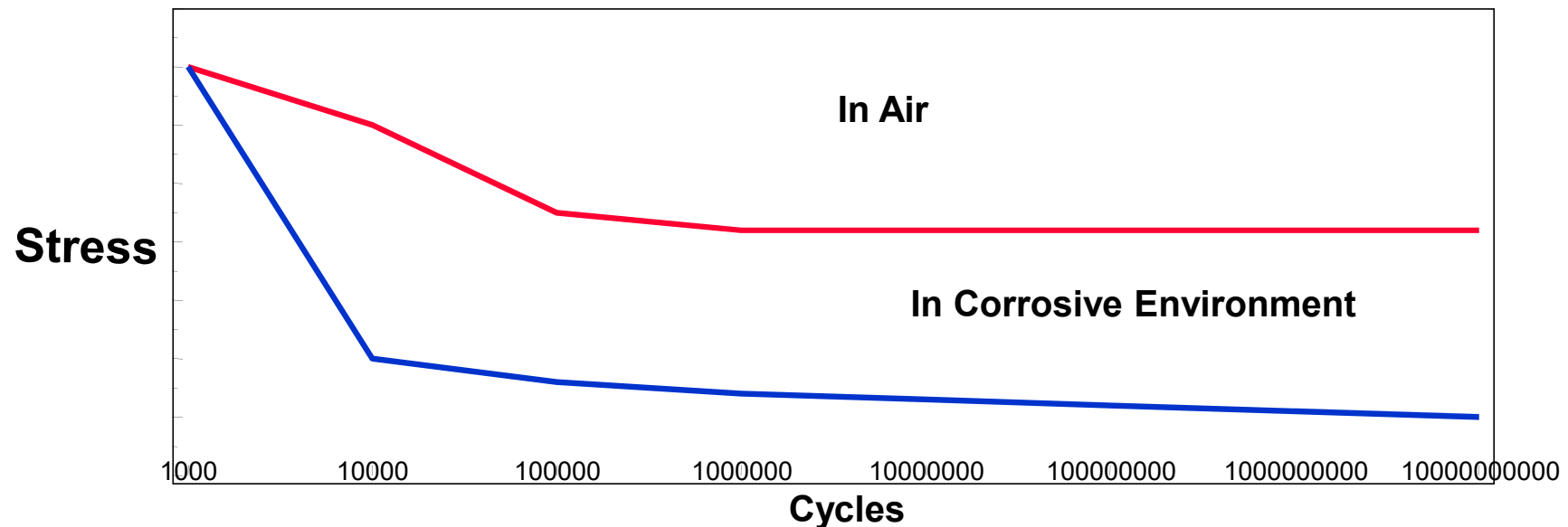
Sulphide SCC

- Sulphide is a poison to the reaction of the formation of molecular hydrogen from its atomic form
- Greater concentration of atomic hydrogen on the metal surface
- Therefore accelerates Hydrogen Blistering or Embrittlement
- In the presence of sulphide films on the metal surface the H-H combination reaction is slowed down to the extent that far more hydrogen atoms can enter the metal lattice structure.

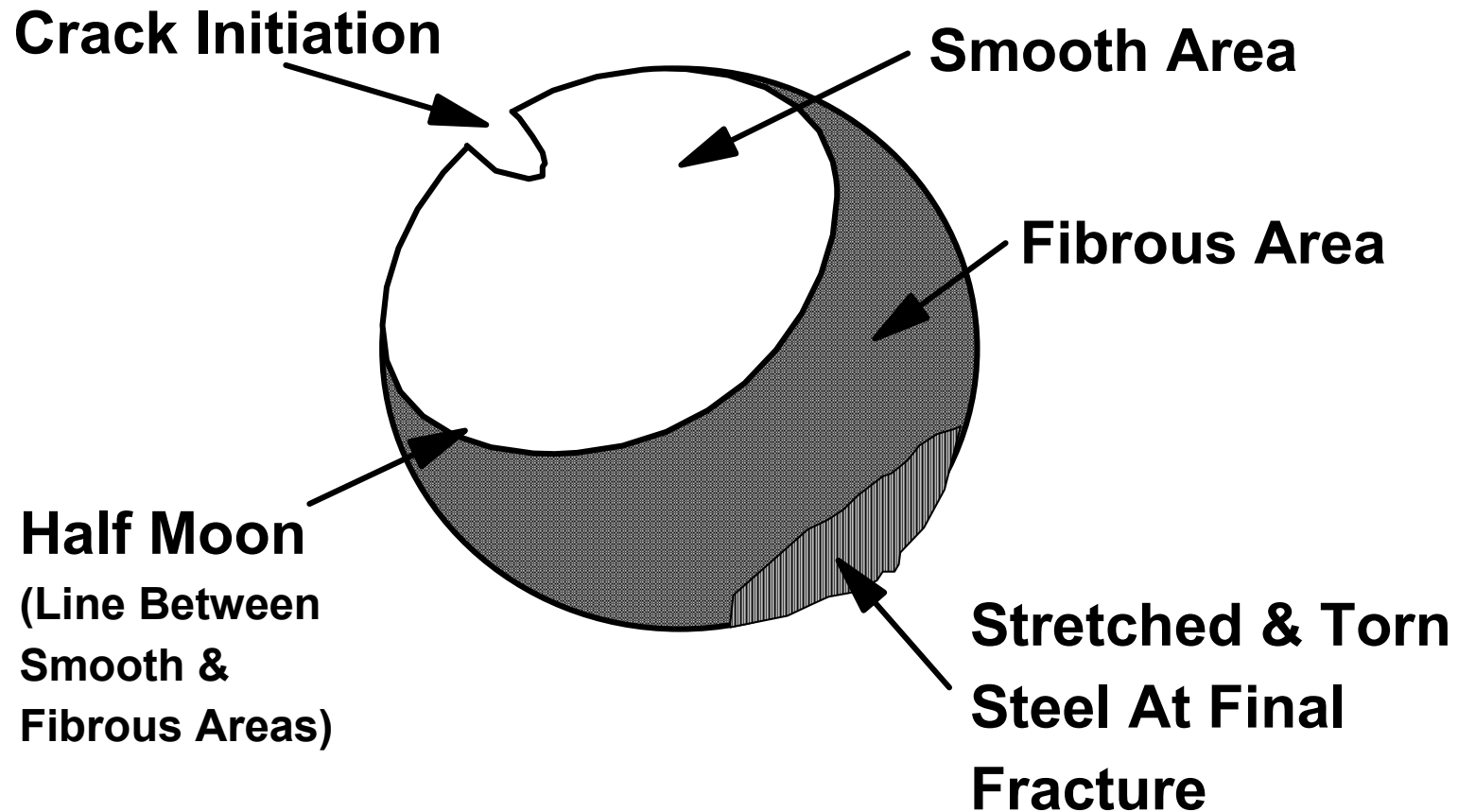
Corrosion Fatigue

- Metal fatigue
 - Repeated cyclic stressing causes cracking failure
- Corrosion fatigue
 - Fatigue life much reduced in corrosive environment

The shorter failure time is due to corrosion, where the resultant pits provide weak points in the metal.

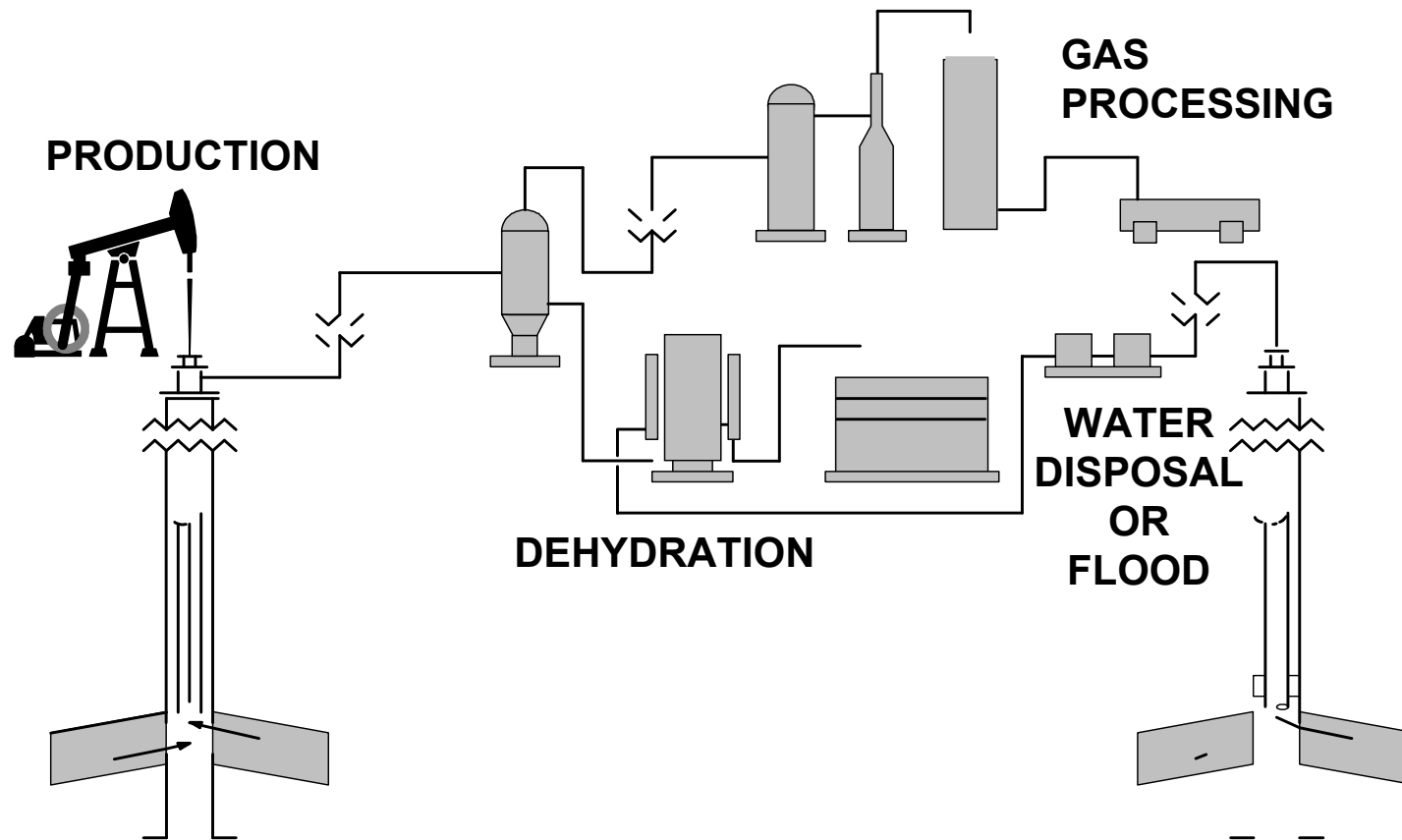


Typical Face of a Corrosion Fatigue Break in a Sucker Rod Body



The corrosion pit causes the eventual failure.

- Where will corrosion occur?
- Almost anywhere where liquid water is present either continuously or intermittently



How fast will corrosion take place?

- Very difficult to predict accurately
 - systems constantly changing
 - mechanism complex and not well understood

How fast will corrosion take place?

- Prediction of CO₂ Corrosion

- DeWaard - Milliams relationship (1975)

$$\log(\text{C.R.}) = \frac{5.8 - 1710 + 0.67 \log (P_{\text{CO}_2})}{273+t}$$

- Since revised to account for:-

- corrosion product films
 - pH
 - systems pressure
 - effect of methanol or glycol
 - effect of crude oil
 - effect of velocity

This equation was developed by these two Shell employees and is used world-wide for system design. It is not a day-to-day practical tool.

How Fast will Corrosion Take Place

- Prediction of H₂S Corrosion
 - no simple models
- Estimated corrosion rates in oil wells

$$\text{Blank Rate} = \frac{1/25 [(\text{CO}_2 + 1/2 \text{H}_2\text{S}) + (\text{HCO}_3^- + 1/2 \text{H}_2\text{S})]}{10}$$

Where all concentrations are in ppm and where O₂ = 0 ppm