

Principles of Corrosion

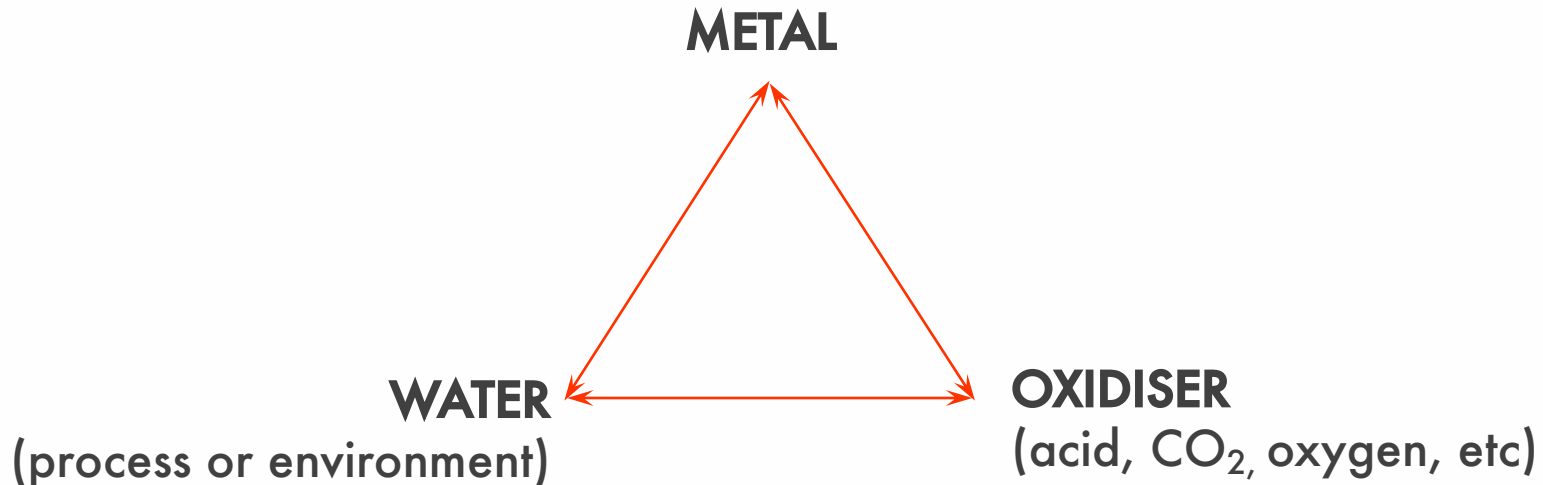
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Content

- Fundamentals of corrosion and electrochemistry
- Types of corrosion and common corrosion mechanisms
- Corrosion control and management
- Costs and significance of corrosion

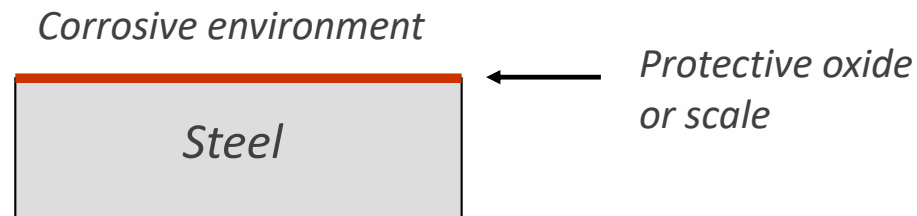
What is corrosion?

- Degradation of a material, starting at the surface, due to an (electro-)chemical reaction with a component in its environment
- Dry corrosion - usually high temperature e.g. oxidation, sulphidation
- Wet corrosion - requires an aqueous phase (water)



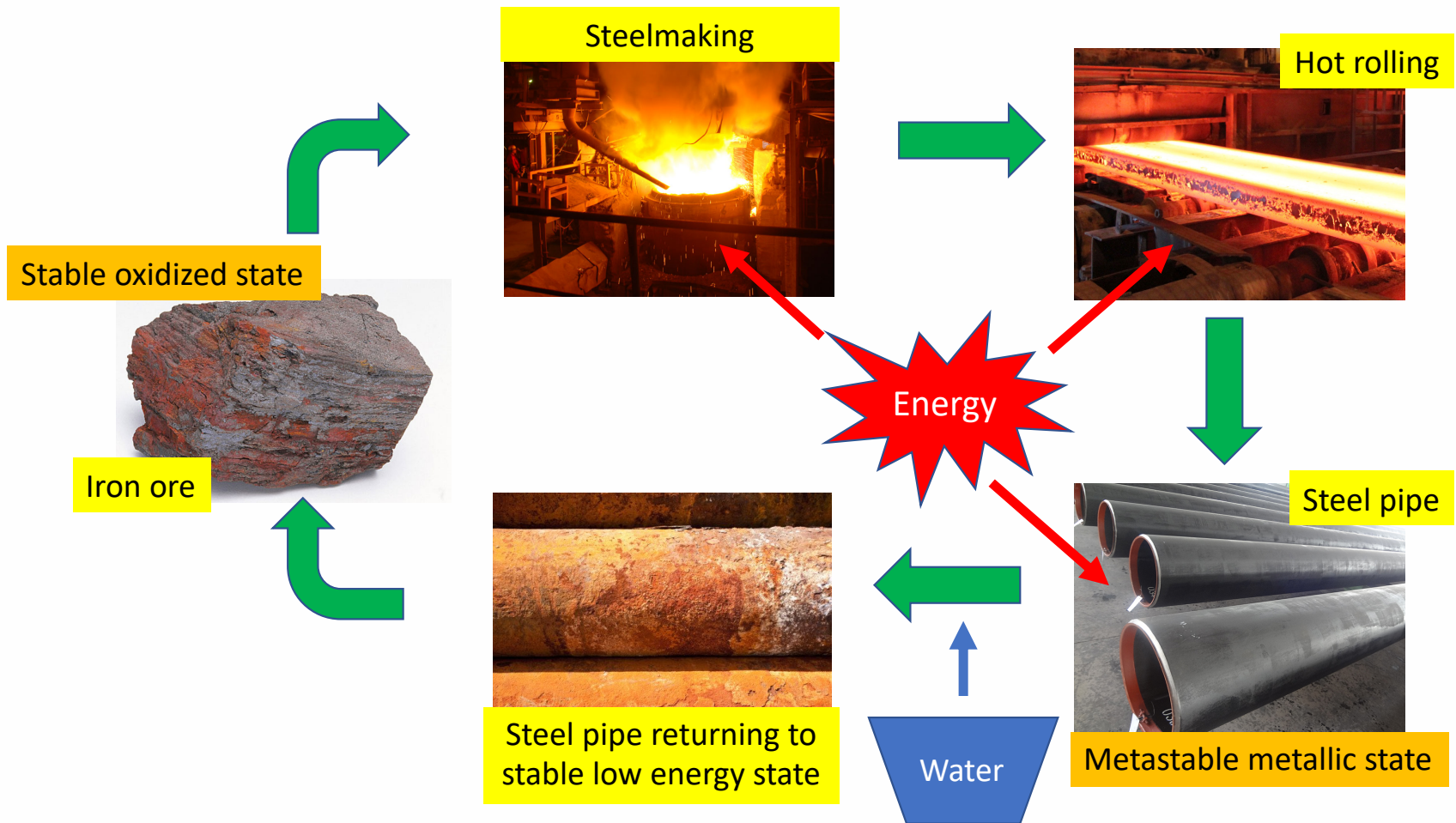
Corrosion drivers

- Driving force: Thermodynamics
- Reaction rate (kinetics) is influenced by...
 - Concentration of reacting components
 - Temperature
 - Conductivity of the environment
 - Protection by a barrier between the metal and the environment



- Stimulating factors, e.g. chlorides, biofouling, flow effects

Thermodynamic corrosion cycle



Corrosion process of metals

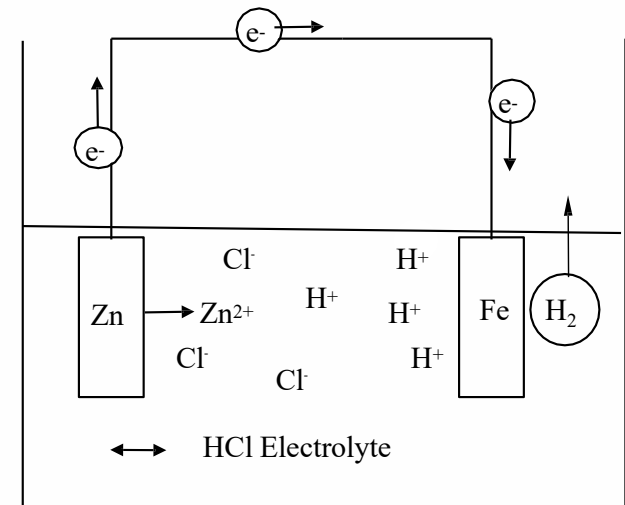
- Corrosion of metals is a natural process that seeks to reduce the overall energy state of the system
- The result of corrosion involves a metal atom **M** being oxidized in which it loses one or more electrons and forms an ion in the solution, e.g.:
 Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$ $Fe \rightarrow Fe^{2+} + 2e^-$ $Cu^{2+} \rightarrow Cu^{3+} + e^-$
Note: oxidation does not mean that formation of an oxide occurs or that oxygen is required
 The site where metal atoms lose electrons is referred to as the Anode
- The electrons produced in the oxidation reaction move through the metal to another site where they reduce (i.e. combine with) a non-metallic element or another metallic ion X^{n+} that is in contact with the metal, e.g.:
 Reduction: $2H^+ + 2e^- \rightarrow H_2$ $X^{n+} + ne^- \rightarrow X$ $Fe^{3+} + e^- \rightarrow Fe^{2+}$
 The site where electrons are transferred to the reducing species is referred to as the Cathode
- **OIL RIG**: Oxidation is loss (of electrons), Reduction is gain (of electrons)

Electrochemical process

- Electrochemical corrosion involves two half-cell reactions and exchange of electrons:
 - an oxidation reaction occurs at the **anode**
 - a reduction reaction occurs at the **cathode**
- For corrosion of zinc connected to iron in an acidic solution (electrolyte)
 - Anodic reaction:

$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$$
 - Cathodic reaction:

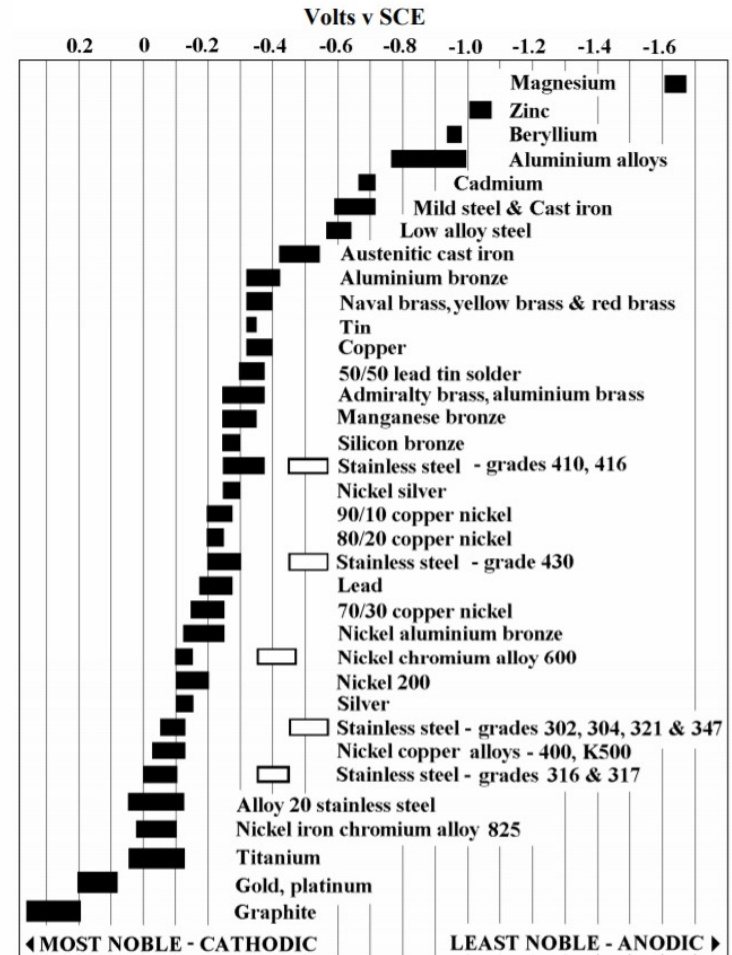
$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$$



- With the anode connected externally to the cathode, current flows from the anode to the cathode to make a galvanic cell
- Potential of the galvanic cell can be calculated using the electrode potentials of the voltages of each half-cell
- Electrochemical reactions only take place in a (conductive) water phase

Galvanic series in seawater

- The standard electrode potentials in seawater of various metals, alloys and graphite have been listed to form the galvanic series
- This series acts as a guide for selecting metals or alloys that will be connected together in an aqueous environment
- Metals or alloys which are more anodic (or active) will corrode preferentially if connected to one that is cathodic or more noble, e.g. aluminium will corrode preferentially if connected to steel in seawater and hence protect it (cathodic protection)
- The further apart the materials are in the galvanic series, the higher the risk and rate of galvanic corrosion
- Materials that are close together in the series may not suffer significant galvanic corrosion



Stimulating factors

Also factors that are not directly responsible for the corrosion mechanism but can stimulate the corrosion (or stress corrosion) in some way:

- Temperature: Increasing temperature can significantly increase the reaction rate
 - rule of thumb: the corrosion rate doubles for every 10°C rise in temperature
- Conductivity: The presence of ions significantly increases corrosion rate
 - corrosion rates in seawater are much higher than in potable water
- Flow rate: A high rate of flow increase the transport of the corrosive species to the metal surface thus increasing the corrosion rate
- pH: A low pH (<4) increases the hydrogen ion concentration which promotes corrosion reactions and can destabilise any protective passive layers
- Chlorides: Presence of chlorides can affect the stability of passive film allowing pitting corrosion or stress corrosion to occur
- Biofouling: The presence of bacteria can move the potential on the metal surface to a region where corrosion or stress corrosion can occur
 - biofilms can shift the potential by ca. 300 mV creating conditions for pitting or SCC
- Galvanic effects: A galvanic couple can significantly increase anodic corrosion rate

Key mechanisms in Oil & Gas

Internal

- Acid gas corrosion ($\text{CO}_2/\text{H}_2\text{S}$)
 - CO_2 (sweet) corrosion
 - Preferential weld corrosion
 - H_2S (sour) corrosion
 - Mixed sweet & sour corrosion
- Sulphide stress cracking (SSC)
- Hydrogen induced corrosion (HIC)
- Hydrogen embrittlement
- Chloride pitting/crevice corrosion
- Oxygen corrosion
- Microbial induced corrosion (MIC)
- Sand erosion

External

- Atmospheric corrosion
- Corrosion under Insulation (CUI)

Internal/External

- Galvanic corrosion
- Chloride stress corrosion (SCC)

Key mechanisms in Renewables

CCS

- CO₂ corrosion
- Acid corrosion (HNO₃, H₂SO₄)
- Chloride stress corrosion
- Oxygen corrosion
- Microbial induced corrosion
- Non-metallic degradation

Wind

- Atmospheric corrosion
- Seawater corrosion
- Microbial induced corrosion

Geothermal

- Acidic corrosion (CO₂ / H₂S)
- Sulphide stress cracking
- Chloride stress corrosion
- Caustic cracking
- Oxygen corrosion
- Microbial induced corrosion

Hydrogen

- Hydrogen embrittlement
- Hydrogen induced corrosion
- Effect on non-metallics??

Corrosion control

- Allow to corrode, monitor, and replace when necessary
- Mitigate corrosion by:
 - Materials selection
 - Dehydration
 - Process or environmental control
 - Chemical treatments
 - Coatings and linings
 - Anodic/Cathodic protection
- Establish an active corrosion management system to control corrosion threats
- Risk based inspection is not “active” corrosion management!
 - “You cannot inspect integrity into a product or system”



Control options

- Most effective is to select appropriate material that removes corrosion threat completely (e.g. CRA/Non-metallic material)
 - selecting CRA may introduce other threats such as SCC
- Very effective approach is to remove water by dehydration
- Chemical treatment (e.g. corrosion inhibitor, biocide or oxygen scavenger) is most common corrosion mitigation method for internal protection of carbon steels
- Coatings and cathodic protection can be used for external protection
- Coatings can also be used for internal corrosion mitigation
- Control of process parameters/environment, e.g. by limiting temperature and chloride content can reduce the risk of SCC

Process/environment control

Control Parameter	Effect
Temperature	Keeping temperature below certain limits can reduce corrosion reaction rates, or avoid crossing threshold temperature for pitting crevice or stress corrosion
Pressure	Lowering the pressure e.g. through use of separators can reduce the CO ₂ corrosivity or in the case of H ₂ S avoid sensitivity to sulphide stress cracking.
Flow-rate	High flow rate (>1.5 m/s) in multiphase oil systems can result in mitigation due to continuous oil wetting of steel surface especially if water cut is less than 40%
Flow-rate	Reducing flow-rate (e.g. by increasing pipe diameter) can reduce the corrosion reaction rate, or the effect of erosion and erosion/corrosion mechanisms.
Velocity	High velocities can decrease effectiveness of film forming inhibitor. In cupro-nickel alloys in seawater significant corrosion can occur above 2.5 m/s
Desalination	Removal of salts can lower the risk of some corrosion threats.
Mixing of process streams	E.g. from different wells. Reduce overall concentration of corrosive constituent
Demisters	Removal of liquid droplets from gas streams reduces the risk of liquid carryover
Hydrocyclones	Removal of sand or solids with hydrocyclones reduces the risk of erosion
Water washing	Injection of water can reduce concentration of salts and lower the risk of some corrosion threats.
Filtration	Removes solids that could be sources for microbial or under-deposit corrosion

Approach to tackling corrosion

- Appreciate that all materials corrode under some conditions
- Recognise and understand the mechanisms causing corrosion
- Prevent corrosion through appropriate materials selection and/or control of the environment
- Manage corrosion actively through **systematic** mitigation and control of threats
- Implement focussed inspection and preventative maintenance
- Create transparency of integrity management performance
- Ensure corrosion awareness and understanding at all levels from senior management to operators, technicians, painters, etc.

Cost of corrosion

- A NACE study in 2016 estimated the global cost of corrosion to be US\$2.5 trillion/year, equivalent to circa 3.4% of global GDP (Gross Domestic Product)
- For the UK equates to £60 billion per year
- The NACE study found that implementing corrosion prevention best practices could result in savings of between 15% and 35%
- Clearly there is a motivation for corrosion engineers to contribute in achieving such savings and to the associated improvement in integrity of facilities and infrastructure and protection of the environment



Relevance to energy sector

- Carbon steel is normally the material of choice:
 - 95% of upstream oil and gas facilities
 - Essential to make most renewable projects economic (CCS, Wind, Hydrogen, Low enthalpy Geothermal)
- Without corrosion control integrity can be compromised:
 - In low-pressure systems can have leaks (exposure of personnel to toxic and hazardous fluids), release of hydrocarbons (fire and explosion risk), environmental impact
 - In high-pressure systems can have ruptures (usually more severe consequences than leaks – including business and reputation)
- Project economics, i.e. the balance between the cost savings of selecting carbon steel versus CRA (CAPEX), and the increased costs associated with requiring more operational intervention, maintenance and inspection (OPEX) if carbon steel is chosen
- Need to consider lifecycle costs at the project definition phase
- But assurance of integrity for the lifetime is essential!

Satartia (Mississippi) incident

- Delhi pipeline ruptured in Satartia on 22nd Feb 2020 causing evacuation of entire town and sending 45 people to hospital
- Periods of intense rain resulted in a landslide that caused heavy strain and rupture of a girth weld in the pipeline
- Concluded that the Delhi pipeline released 31,405 barrels of CO₂ with concentrations as high as 28,000 ppm, well beyond the permissible exposure limit of 5,000 ppm
- The 45 people had various symptoms and effects related to CO₂ poisoning
- Pipeline operator fined nearly \$4M
- Pipeline Safety Trust Executive:
“As the failure in Satartia demonstrates, CO₂ releases can be incredibly hazardous to our communities”



Hydrogen in homes

- Hy4Heat programme explored use of hydrogen in homes with testing done at the Fire Service College
- Structural damage and overpressures three times higher than for methane
- Hydrogen transitioned from deflagration (confined to enclosure) to a detonation type explosion (rupture of enclosure) when hydrogen concentrations near the ignitor were above 20%
- UK Government recommended fitting:
 - automatic shut-off valves in homes to prevent significant leaks of hydrogen
 - hydrogen detectors
 - always-open air vents to ensure any leaking hydrogen escapes into the atmosphere rather than accumulate in enclosed spaces
- https://www.youtube.com/clip/Ugkxh_g27enUsROYDtQD8vu0eSq0MMNPobsL



