

ENGINEERING CHEMISTRY

UNIT - 4

CORROSION

Vibha Masti

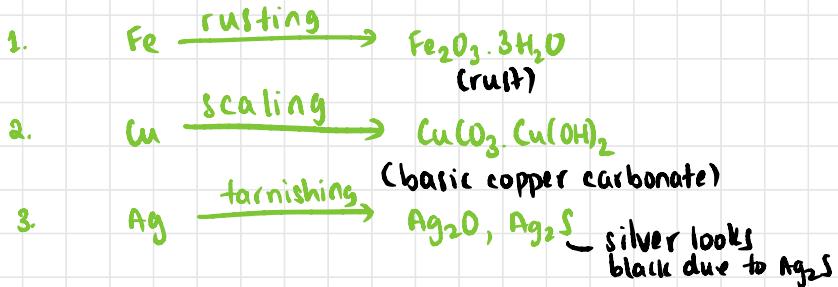
corrosion

DEFINITION

- Destruction or deterioration and consequence loss of metal through chemical or electrochemical attack by the environment
- It is a surface phenomenon
- 2 lakh crore rupees spent annually to curb corrosion in India
- Most metals undergo corrosion

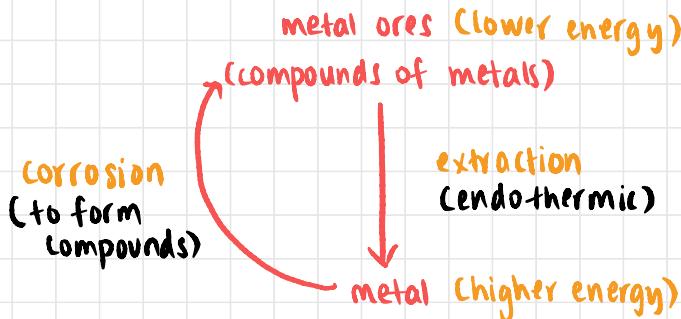
ILLUSTRATIONS

pure metal → undesirable products



WHY CORROSION IS SPONTANEOUS

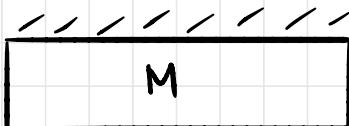
In nature, ores exist (compounds of metals)



types of corrosion

DRY CORROSION

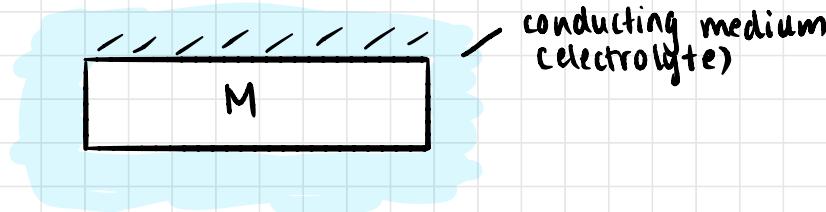
- Absence of moisture/conducting medium
- Due to chemical attack of environment on the surface of metal



affinity for gases
 O_2 , H_2S , NH_3 , F_2

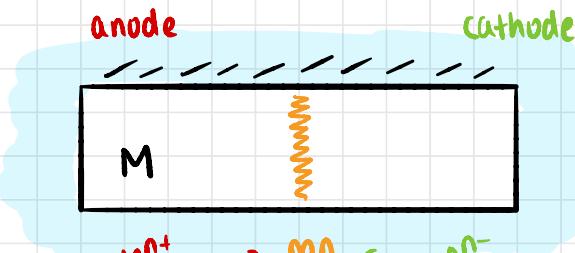
WET CORROSION

- Presence of moisture/conducting medium
- Due to electrochemical attack of environment on surface of metal
- Formation of galvanic cell



conducting medium
(electrolyte)

ELECTROCHEMICAL THEORY OF CORROSION



anode

cathode



Anode



- metal gets destroyed
- cations formed

Cathode



- environment gets reduced
- anions formed

theory

- Corrosion current: very small amount
- Anode and cathode formed at the surface of the metal
- Metal gets deteriorated at the Anode
- Cathode unaffected by corrosion
- To curb corrosion, make metal the cathode

REACTIONS

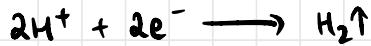
ANODE



CATHODE

— Liberation of H_2

(a) Acidic medium

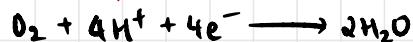


(b) Alkaline medium



— Absorption of O_2

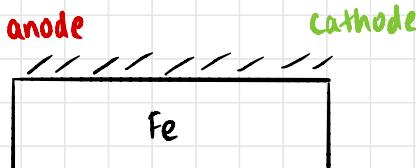
(a) Acidic medium



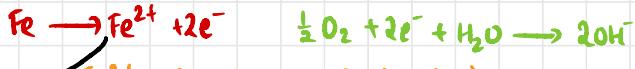
(b) Alkaline medium



corrosion of iron

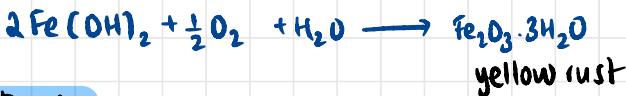


Fe^{2+} gets further oxidised to Fe^{3+} in the presence of O_2 (like FeAs , FeSO_4)

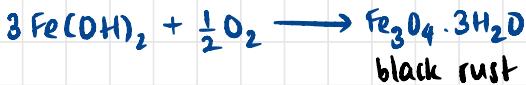


(corrosion product)

PLENTY OF O_2



LIMITED O_2



SUMMARY OF ELECTROCHEMICAL THEORY

1. A number of tiny galvanic cells are formed due to formation of separate anodic and cathodic regions on the surface of the metal.
2. Corrosion takes place at the anode and electrons liberated at the anode are consumed at the cathode producing a small corrosion current.
3. While anodic area is corroded, cathodic area remains unaffected.
4. Metal ions liberated at anode and anions from the cathode diffuse through the conducting medium and form corrosion product.
5. Anode: $\text{M} \rightarrow \text{M}^{n+} + n\text{e}^-$
Cathode: $\text{A} + n\text{e}^- \rightarrow \text{A}^{n-}$
6. High level of O_2 in the corrosion environment accelerates corrosion rate.
7. Anodic and cathodic areas are formed on the same metal surface due to presence of metal impurities, difference in O_2 concentration on the metal surface, cracks and crevices on the surface and residual stress.

TYPES OF WET CORROSION

(1) DIFFERENTIAL METAL CORROSION

anode

cathode



$E^\circ_{M_1}$ more -ve than $E^\circ_{M_2}$

Anode:



Cathode:



- More active metal undergoes oxidation, cathode completely unaffected
- Driving force: difference in electrode potentials

illustrations

(a) Fe, Cu

-0.44 V	+0.34 V
Fe	Cu

Anode:



Cathode:



(a) Zn, Fe

-0.76 V	-0.44 V
Zn	Fe

Anode:



Cathode:



- As long as there is a metal more active than the structure, the structure can be protected

- Examples

(1) Iron/ steel screws in Cu sheet: Cu is unaffected.

(2) Steel pipe connected to Cu plumbing

(3) Nuts and bolts should always be made of same metal.

(2) DIFFERENTIAL AERATION CORROSION

- Different $[O_2]$ on the same metal surface



Anode:



Cathode:



- O_2 involved in cathodic reaction
- more O_2 at cathode \rightarrow cathode rxn more \rightarrow forces anode rxn more

DEFINITION

Corrosion arising as a result of formation of an O_2 concentration cell due to uneven supply of air on the metal surface

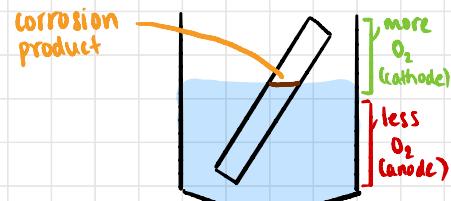
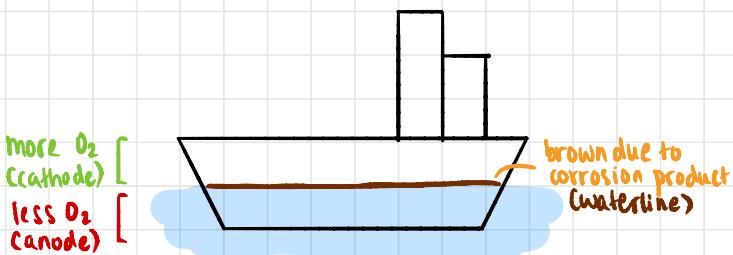
• Examples

- (1) Nail pulled out from wall - part inside is corroded, not outside ($Fe_2O_4 \cdot 3H_2O$)
- (2) Paper clip on paper for a long time - paper gets rust due to inside
- (3) Barbed wire - insides are corroded.
- (4) Paint peeled off from metal, metal under paint gets corroded.

/ less O_2 , black rust

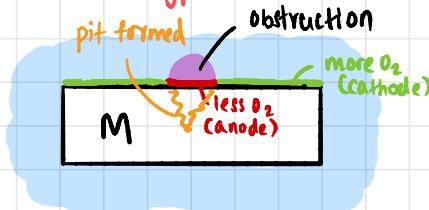
waterline CORROSION

- Special case of differential aeration corrosion (part inside water is more corroded)
- Water flowing through a steel pipe - no waterline corrosion.



(3) PITTING CORROSION

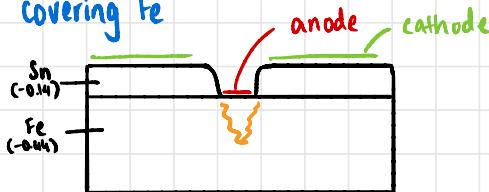
- Localised and accelerated corrosion resulting in formation of pits or pinholes around which the metal is relatively unattacked.
- One of the most destructive types of corrosion



- Anode much smaller than cathode
- Demand for e⁻ very high
- Anode becomes like a pit

illustrations

(1) Sn covering Fe

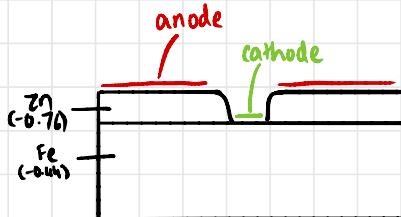


If Sn peels off, pitting corrosion

(2) Steel screws in copper sheets.

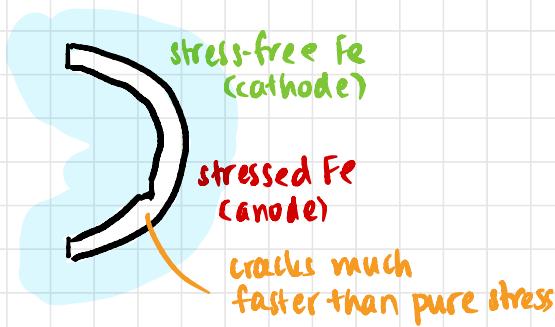
Note

Zn covering Fe is NOT pitting corrosion (small cathode, large anode)



(ii) STRESS CORROSION

- Also known as stress corrosion cracking and is caused by the combined effect of
 - (i) tensile stress
 - (ii) specific corrosive environment
- Stress causes cracks to form
- Crack deepens → breakdown of structure



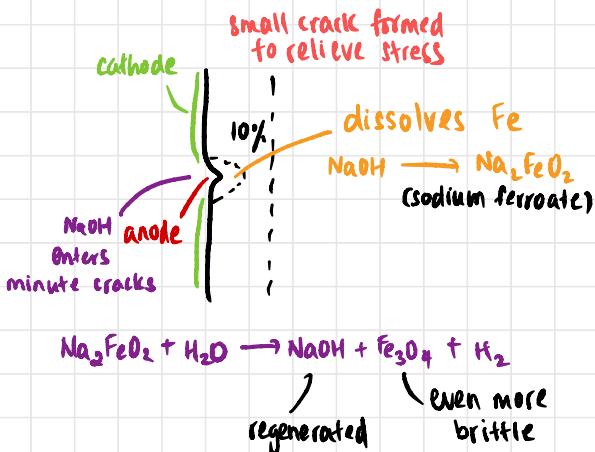
specific environment

Metal	Environment
mild steel	NaOH
brass	ammonical sol/ ammonical vapours

illustrations

1. Horse dung-NH₃ Vapours - brass got cracked in summers in stables (British)
2. U in disinfectant affected steel roof over indoor swimming pool
3. Bridge collapsing (H₂O, salts)
4. Boiler explosions

STRESS CORROSION IN BOILERS (Caustic embrittlement)



- Made of mild steel (requires NaOH)
- Use soft H_2O (scaling prevented)
- Na_2CO_3 formed while softening H_2O



brittle Fe_3O_4
comes in contact with
atmosphere \rightarrow diff in
pressure \rightarrow explosion

CORROSION CELL

stressed Fe | conc. NaOH | dil NaOH | stress-free fe

- corrosion inhibitors added to prevent corrosion
- example: tannin, lignin, phosphates (organic compounds)

FACTORS AFFECTING EXTENT OF CORROSION

(1) NATURE OF THE METAL

- More active metal — more corrosion (very -ve E°)
- Example: Na (-2.71 V), K (-2.93 V), Mg (-2.70 V), Fe (-0.44 V), Zn (-0.76 V)
- Noble metals — less corrosion
- Example: Ag (+0.80 V), Au (+1.83 V), Pt (+1.19 V)
- Exceptions: Al (-1.66 V), Cr (-0.74), Ti (-1.37 V) — highly +ve E° , passive to corrosion

GALVANIC SERIES

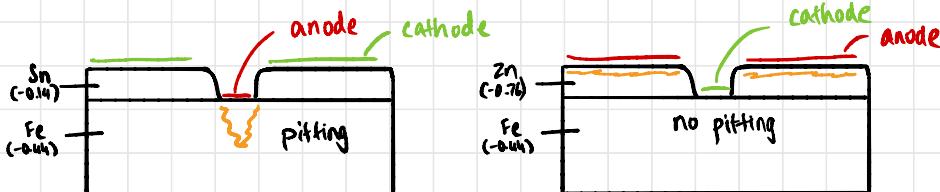
- An arrangement of metals and alloys in order of their corrosion resistance in a given environment.
- Experimentally found (not for ideal conditions)
- How a metal/alloy behaves in a specific environment
- Most common environment — sea water

(2) DIFFERENCE IN E° OF ANODE AND CATHODE

- Galvanic corrosion, differential metal corrosion
- Driving force: diff. in E°
- Example: Fe (-0.44 V) in contact with Cu (+0.34 V) will undergo more corrosion than Fe (-0.44 V) in contact with Sn (-0.14 V)

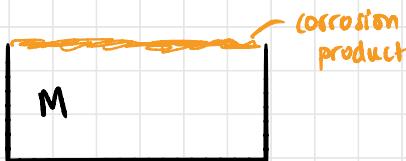
(3) RATIO OF ANODIC TO CATHODIC AREAS

- If anodic area is very small, extent of corrosion more (pitting)
cathodic area
- Demand for e^- in cathode more \rightarrow anode rxn more



(4) NATURE OF CORROSION PRODUCT

PASSIVE LAYER

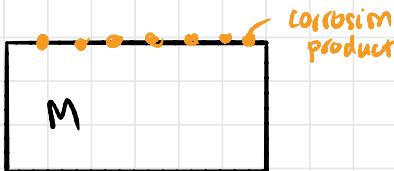


- Corrosion product forms passive layer on the surface of metal
- Arrests further corrosion, becomes passive
- Example: Al, Cr, Zn (protective oxide layer)
in stainless steel (Cr_2O_3)

CHARACTERISTICS OF CORROSION PRODUCT

- insoluble in the medium
- uniform, non-porous
- Stable

ACTIVE PRODUCT



- Corrosion not uniform
- Not protective
- Example : Fe, Zn

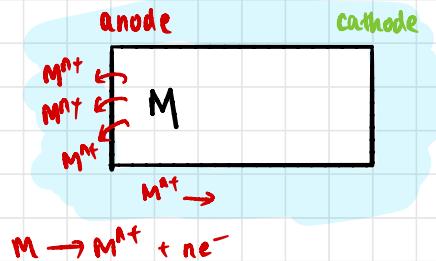
stainless steel

- Cr added to Fe, forms Cr_2O_3 (passivates)
- Does not corrode

(5) POLARISATION (CONCENTRATION POLARISATION)

- Desirable to curb corrosion
- Undesirable for electrolysis and galvanic cells

ANODIC POLARISATION



- Rate of formation of metal ion faster than rate of diffusion
- Due to accumulation of metal ions at anode, extent of corrosion reduced, metal protected
- E° value becomes less -ve

CATHODIC POLARISATION

- Due to depletion of O_2/H^+ ions in cathodic region, which in turn reduces extent of anodic reaction
- E° value becomes less +ve

Methods to Reduce Polarisation in cells

1. Agitation: Stir solution to move ions

both of the electrodes continuously agitated (electroplating)

2. Increase in temperature

3. Adding conducting salts.

(6) OVERVOLTAGE

- Extra voltage over the theoretical voltage of an electrode required to carry out a particular process at the electrode.

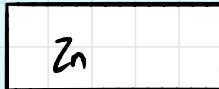
hydrogen OVERVOLTAGES

Pt: 0.09 V, Cu: 0.33 V, Zn: 0.70 V, Platinised Pt: 0.00 V

will not liberate H_2 ;
Cu acts as rxn surface

Zn rod dipped in HCl

(0.70 V) H^+



liberation of H_2 on Zn surface

(0.09 V) Zn | $Zn^{2+} \parallel H^+ | H_2 \uparrow$ Pt

liberation of H_2 on Pt

ELECTROLYSIS OF H_2O

Theoretical value: 123 V

Pt. electrode: 1.70 V

Pb electrode: ~2 V

ELECTROLYSIS OF BRINE

- O_2 not liberated at anode
- Reason: overpotential

Steps for liberation of H_2



- If liberation of H_2 more, cathode rxn more, anode rxn more
- Overvoltage high \rightarrow helps curb corrosion
- To control corrosion, use surface with high H_2 overvoltage (reduces extent of corrosion).

EXAMPLE

- Zn in 1 M H_2SO_4 , slow dissolution.
- 1-2 drops of CuSO_4 , rapid dissolution



- Cu deposited on surface
- Liberation of H_2 on Cu surface faster (0.33 V vs 0.70 V)
- Cathode rxn faster \rightarrow anode rxn faster

(7) pH

- Low pH \rightarrow more $[\text{H}^+]$
- Cathode: $\text{H}^+ + \text{e}^- \longrightarrow \frac{1}{2} \text{H}_2 \uparrow$
- most corrosion products soluble in H^+

EXCEPTIONS

- Al is found to corrode more in alkali
- Al_2O_3 is more soluble in base



(8) TEMPERATURE

- High temp \rightarrow high corrosion

REASONS

1. Increase in rate of reaction.
2. Increase in conductance
3. Decrease in polarisation
4. Increase in solubility of corrosion product
5. Breakdown of protective film

CORROSION CONTROL

- Steps taken to reduce / stop the extent of corrosion on metals.

(I)

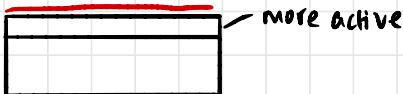
PROTECTIVE coating

(a) METALLIC COATING

Deposition of a protective metal on the surface of the metal to prevent corrosion of the underlying metal.

ANODIC COATING

- When the base metal is coated with a more active metal.



- Example: Fe coated with Zn (Galvanization)

ADVANTAGES of ANODIC COATING

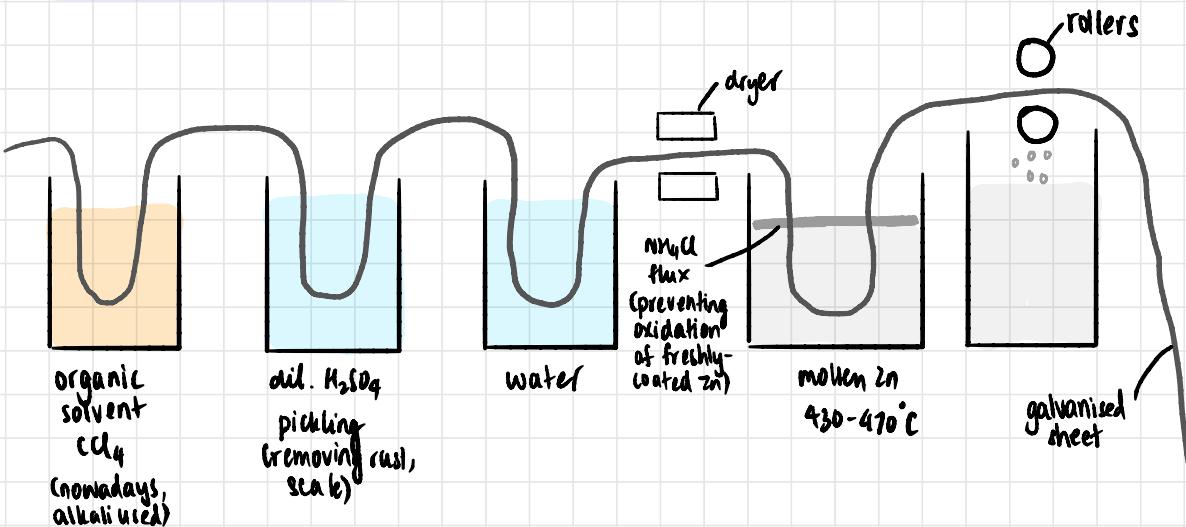


1. No possibility of pitting corrosion, even if the coating ruptures (sacrificial coating)
2. Ease of application: even if coating is rough, metal is protected.

galvanisation

- Coating of the base metal with Zn.
- Zn is cheap; cost is low

HOT DIPPING METHOD



DISADVANTAGES OF GALVANISATION

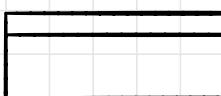
- Galvanised sheets cannot be used to make containers to store food.
- Reason: Zn dissolves in acids, producing toxic Zn compounds and H_2

USES

- Used in building construction material
- Fencing wires
- Nuts, bolts, pipes etc.

CATHODIC COATING

- When the base metal is coated with a metal which is more noble (less active) so that it is cathodic w.r.t the base metal.



- less active

DISADVANTAGES



- Pitting corrosion can take place (old tins)
- No ease of application

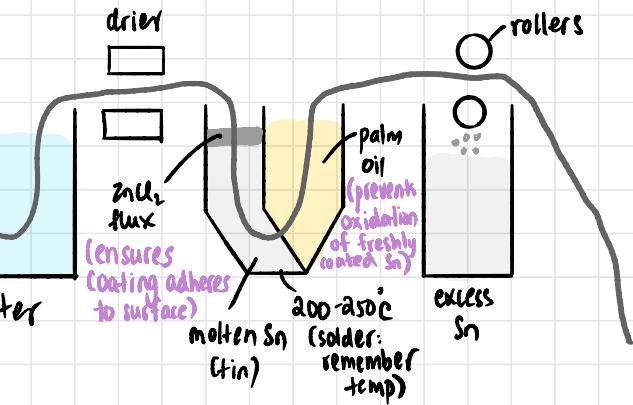
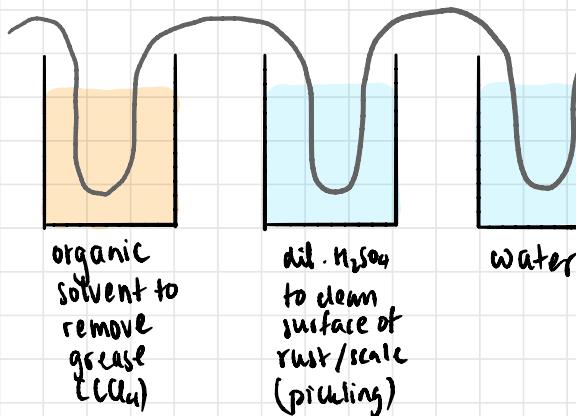
ADVANTAGES

- Can be used for food containers; the largest use for tinned sheets is for manufacturing containers used for storing foodstuff, such as instant food, food products, pickles.
- Soft drink cans are called tins.

TINNING

- Coating of Fe with Sn

HOT DIPPING PROCESS



(b) INORGANIC COATING / CHEMICAL CONVERSION COATING



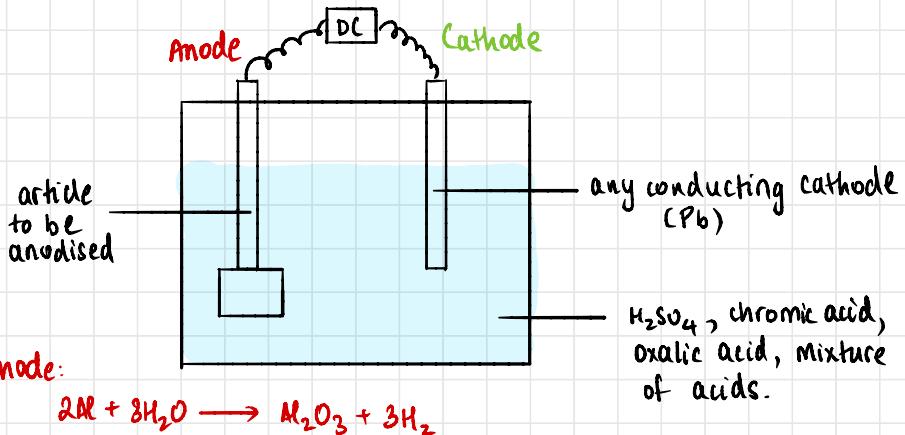
- Chemical conversion coating is where a surface layer of the metal is converted into a compound by chemical or electrochemical reactions, which forms a barrier between the underlying metal surface and the corrosion environment
- Coating not external; inherent part of metal
- Much more strongly held

ANODISING



- Applicable only to nonferrous metals
- Applicable to only those metals that passivate
- Example: Al, Cr, Ti
- The method of developing an oxide layer on the surface by induced oxidation in an oxidising environment by making the object the anode (hence the name anodising) and passing a current.
- Done to control thickness of protective layer formed.
- Thickness due to induced oxidation of metal ($\sim 18\text{ - }25\ \mu\text{m}$) as opposed to natural corrosion ($\sim 0.1\text{ - }0.5\ \mu\text{m}$)

ANODISING TANK



- First few layers of oxide: very dense
- Next few layers: porous — not very useful
- Cannot be used directly

SEALING

- Anodised article placed in boiling water for 15-20 minutes
- $$Al_2O_3 + H_2O \longrightarrow Al_2O_3 \cdot H_2O$$
- hard, transparent solid
- Occupies more volume, seals all the pores and makes the material more robust
 - Articles have a dull finish.

COLOURING THE ARTICLE

1. Organic colouring

- To colour it, dip it in an organic dye before sealing
- Absorbed into pores of Al_2O_3

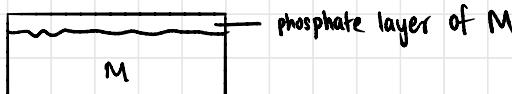
2. Electrolytic colouring

- Deposit metals like Ni, Co etc into the pores (Electroplating)
- Make article the cathode; from coloured salts.
- Seal after; $Al_2O_3 \cdot H_2O$ deposits on top of deposited metal.
- Can still see shine of Ni, Co etc. because hydrated oxide is transparent.

APPLICATIONS OF ANODISED Al, Ti

1. Architecture
2. Aerospace (fairings on space shuttles — extremely strong)
3. Cookware (alternative to Teflon; Al known to cause Alzheimer's)
4. Household articles
5. Titanium jewellery
6. Bronze-coloured Al in bathrooms.

PHOSPHATING



- Development of phosphate layer on the surface by reaction of metal with dilute phosphoric acid.
- It is done by dipping the article in the phosphating solution
- It is a chemical rxn, not electrochemical.

PHOSPHATING BATH

Compounds

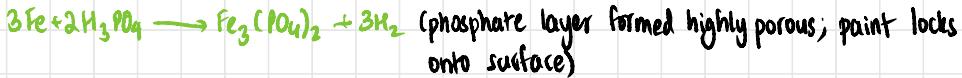
1. Free H_3PO_4
2. Mn, Zn phosphates (metal phosphates) decrease porosity, increase adhesion
3. Accelerator: H_2O_2 , NO_2^- not catalyst, accelerator

Conditions

pH: 1.8 - 3.2

temperature: $\sim 35^\circ C$

Reaction



CORROSION CONTROL FOR AUTOMOBILE BODIES

- Automobile bodies are pre-treated with phosphate (dipped into phosphate bath - primer)
- Paint locks onto surface after phosphating.
- Done for all steel articles (refrigerators, washing machines)
- Coastal areas: low resale of cars due to moisture

(II)

CORROSION INHIBITORS

- Substances which, when added in small concentrations to a corrosion environment decrease the corrosion rate by inhibiting the reactions at anode and cathode.
- It should be in a closed environment / should be contained for corrosion inhibitors
- Particular amount required; unlimited environment → not possible
- Examples: inside boilers, antifreeze, automobiles etc

ANODIC INHIBITORS



- Large anions like chromate (CrO_4^{2-}), tungstate (WO_4^{2-}) are used. (sodium salts)
- These anions react with M^{n+} ions, form a precipitate, which gets adsorbed on the surface of the anode, which prevents further reaction (oxidation) at anode.
- Creates a barrier between anode and environment (reduces corrosion)
- Anions need to be large because they should form precipitate

- If they form soluble salts, they will promote corrosion (depolariser)
- For example, if you add Cl^- , it combines with M^{n+} , forms soluble salt, and drives reaction in the forward direction.
- Anodic inhibitors need to be added in sufficient quantities because otherwise, not enough precipitate will form; only part of the anode will be covered and localised/pitting corrosion occurs (only part of anode covered).

CATHODIC INHIBITORS

Liberation of H_2

(1) Retard the diffusion of H^+ to the cathode

- Example: urea (NH_2CONH_2), thiourea (NH_2CSNH_2) → organic compounds containing N, S
- They are adsorbed over the surface of the cathode and prevent H^+ ions from coming in contact with cathode
- Therefore, H_2 liberation is reduced and hence anodic rxn is also reduced.

(2) Increase H_2 overvoltage of the surface

- Example: arsenic oxide (As_2O_3), antimony oxide (Sb_2O_3)
- As_2O_3 and Sb_2O_3 get reduced at the cathode

$$\text{As}^{3+} + 3\text{e}^- \longrightarrow \text{As}$$
- As/Sb will coat the surface of the cathode (adsorbed), which has H_2 overvoltage → liberation of H_2 becomes slower → cathodic rxn reduces → anodic rxn reduces

Absorption of Oxygen

(1) Removal of O₂

- Using Oxygen scavengers

Example: hydrazine (N₂H₄), sodium sulphite (Na₂SO₃)



- They remove O₂ from environment → O₂ absorption is less → cathodic rxn less → anodic rxn less

(2) Retard the diffusion of O₂ to the cathodic surface

- Using large cations like Mg²⁺, Zn²⁺, Ni²⁺ (rxn produces -OH)

cannot use
Na⁺ (NaOH is soluble in H₂O)



- This precipitate will get adsorbed on the surface of the cathode, not allowing O₂ to come close to cathode

LIMITATIONS OF USING CORROSION INHIBITORS

- It can be used only in systems in which corrosion environment is either contained or regenerated
- They contaminate the environment
- Many of these inhibitors are toxic and cannot be used in systems that come in contact with humans (eg: As₂O₃)

(III)

CATHODIC PROTECTION

A method of protecting a metal by converting it completely into cathode and no part of it is allowed to act as anode.

SACRIFICIAL ANODE METHOD

- The protected metal structure is converted to cathode by connecting it to a more active metal
- Commonly used anodes: Mg, Zn
- These metals, being more active, act as anode and undergo preferential corrosion, thereby protecting the metal structure.
- Since the anodic materials are sacrificed, this method is called sacrificial anode method.
- Exhausted anode needs to be replaced:
 - (a) A small block of Mg connected to buried pipelines by new ones.
(1 Mg bar can protect upto 8km)
 - (b) Mg bars fixed to the sides of ocean-going ships

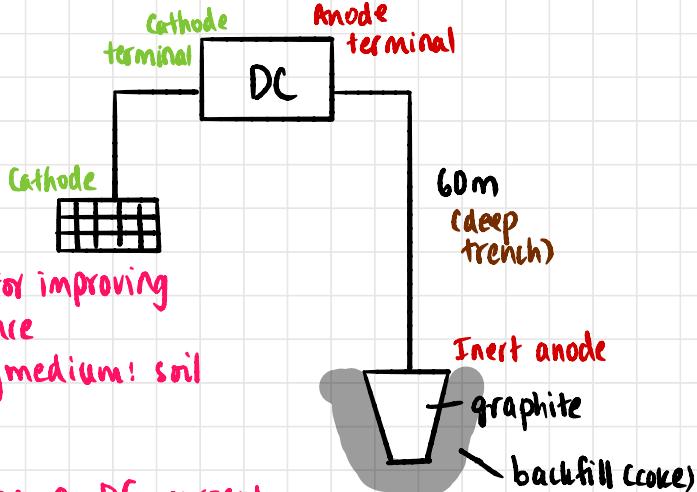
ADVANTAGES

1. Installation is simple
2. Does not require power supply

DISADVANTAGES

1. Involves recurring expenditure because exhausted anodes need to be replaced periodically
- Al is not used as sacrificial anode (protects itself & not structure)
- In a poorly conducting medium, anodes need to be placed closer

IMPOSED CURRENT METHOD (ICCP)



- Backfill: for improving conductance
- Conducting medium: soil

SCIVP

- By applying a DC current, the protected metal is made cathode by connecting it to the cathode terminal of the external source.
- The anode of the source is connected to an inert electrode, usually graphite.
- A backfill of gypsum or coke is used to improve conductance.

WORKING

- The metal structure, being cathode, does not undergo corrosion.
- The anode, being inert, remains unaffected.

ADVANTAGES

1. One installation can protect a large area of the metal.
2. Corrosion rate reduced to zero.

LIMITATIONS

1. Expensive method since it needs high current for safe protection of the structure.
2. If impressed current non-uniform on the entire surface, local anode and cathode will be formed and localised corrosion can take place.
3. Hydrogen embrittlement: if formation of H_2 main rxn at cathode, H gets into lattice of metal \rightarrow pressure buildup \rightarrow blisters formed.

APPLICATIONS

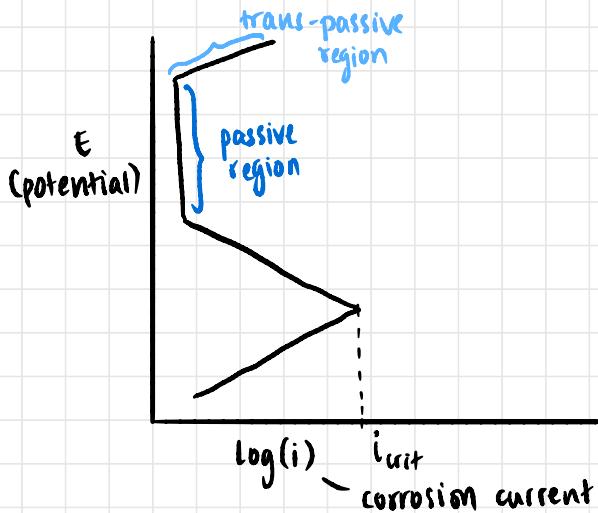
1. Bridges over rivers (look for power)
2. Offshore structures (oil rigs)
3. Oil pipelines

(IV)

ANODIC PROTECTION

IMPOSED CURRENT METHOD

- For metals that show active-passive behaviour

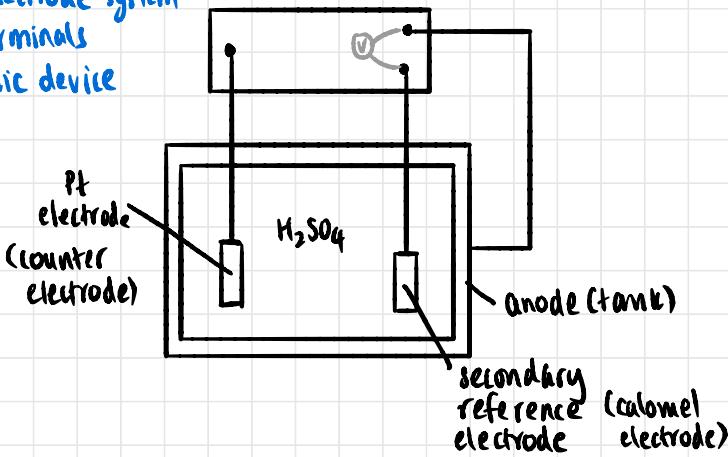


SETUP

- Relatively new method; used sparingly
- Only for severe cases of corrosion.
- Eg: transportation of conc. H_2SO_4 in steel containers.
- Should maintain potential at passive region
- Using potentiostat.

POTENTIOSTAT

- Three electrode system
- Three terminals
- Electronic device



- Find passive region by changing E
- Reference electrode continuously measures potential
- Very small corrosion current (due to passive layer)

- Anodic protection is protection by developing a protective film by applying anodic current continuously from an external source using a potentiostat
- Potentiostat is an electronic device which maintains the protected metal at constant potential with respect to the reference electrode.
- It has three terminals
 - Anode: connected to storage tank (WE)
 - Cathode: connected to Pt electrode (CCE)
 - Third terminal: connected to calomel electrode (RE)
- During operation, potentiostat maintains a constant potential between the tank and the reference electrode corresponding to the passive range.

ADVANTAGES

1. Applicability in extremely corrosive environment
2. Low current demand.

LIMITATIONS

1. Installation cost is high.
2. Only for those metals that show active-passive behaviour.
3. Cannot reduce corrosion rate to zero.

APPLICATIONS

1. Steel containers used in transportation of concentrated acids.