# MM 454

# Corrosion and Protection of Materials

Course instructors

Prof. Vijayshankar Dandapani (v.dandapani@iitb.ac.in)
Prof. Smrutiranjan Parida (paridasm@iitb.ac.in)

Department of Metallurgical Engineering and Materials Science
Indian Institute of Technology Bombay

# Course Evaluation

Two quizzes – 10% + 10% (one before and one after midsem)

Mid-sem – 30 %

End-sem exam – 50 % (40% (after midsem) + 10% )

Pass mark – 40% of the highest mark in class

## Attendance [as per institute rule]

Attendance in the class is compulsory and is monitored. The Institute expects 100% attendance. However, due to ill health or other emergency situations, absence up to 20% is considered on case to case basis on production of documentary proof.

**A student not having 80% attendance may be debarred from appearing in the semester end examination and given a "DX" grade**

Such a student is required to reregister for the same course in subsequent semesters. The attendance requirement is applicable to summer courses too.

Students coming 7 min late will be considered absent

All attendance biometric

Manual attendance will be taken time to time

# Miscellaneous

- No make-up test for class test
- Only medical emergency / critical illness will be considered (Midsem and Endsem)
- All announcements will be made via moodle

# Course references

**1. Textbooks:**

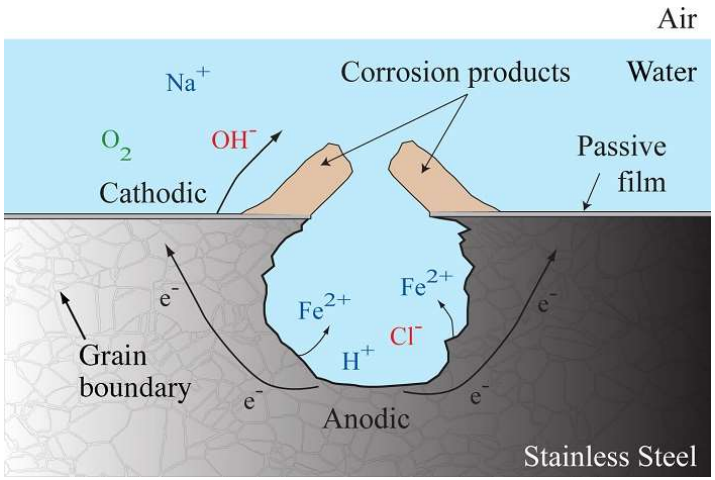
**a)** Corrosion Engineering : *M. G. Fontana*

**b)** Introduction to Corrosion Science: *E. McCafferty*

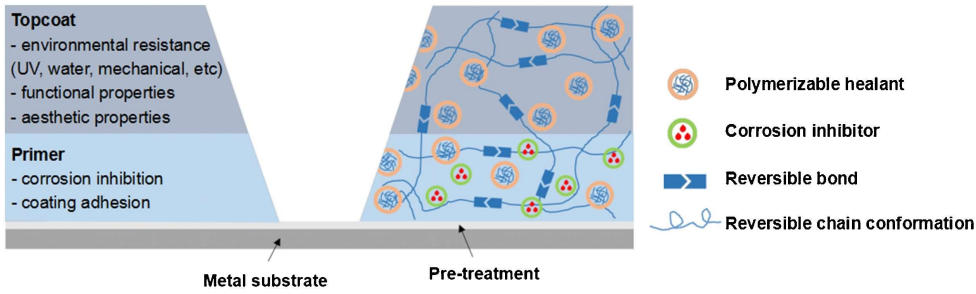
**c)** Corrosion And Corrosion Control – An Introduction to Corrosion Science and Engineering :
*R. Winston Revie & Herbert H. Uhlig*

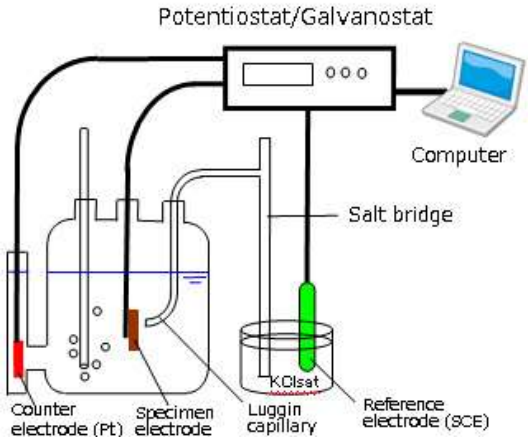
**2. Scientific Articles**

# Course objectives




Provide a basic understanding of corrosion phenomena



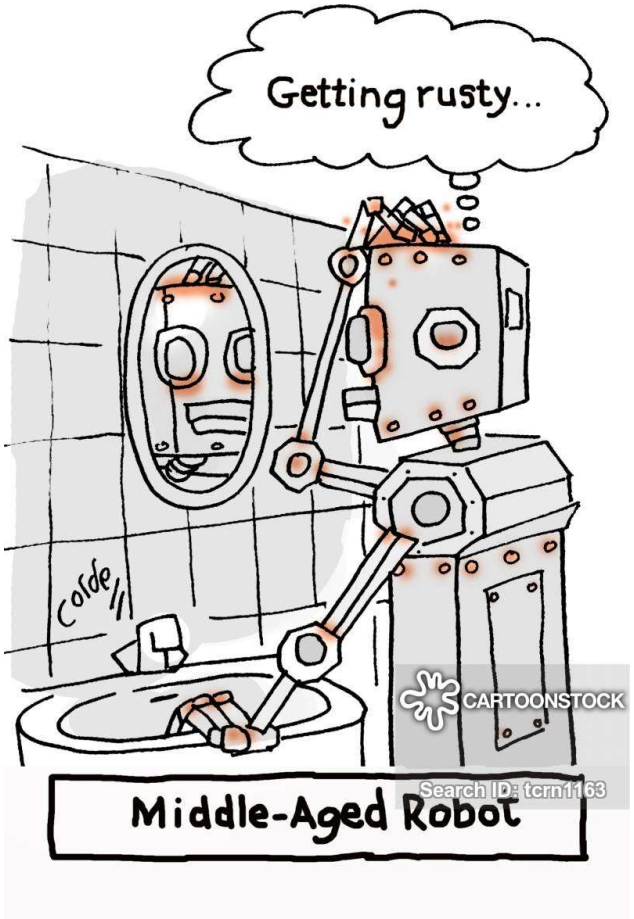




Provide tools to measure, analyse and predict the corrosion behaviour of materials

Provide corrosion prevention and remediation strategies

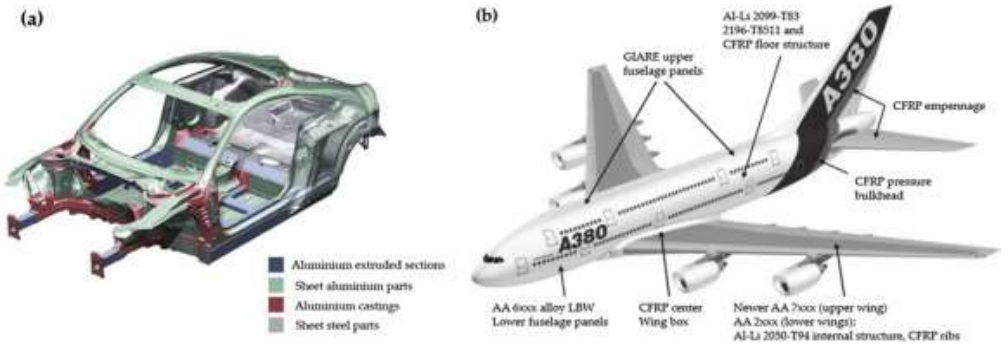
https://www.comsol.com/blogs/strategy-designing-corrosion-resistant-materials/

# What is Corrosion – on a lighter note….




# We live in a metal based society…

- Steel finds use  in bridges, trusses, automobiles, trains, ships, pipelines
- Al alloys – aircraft frames, canned food, electronics
- Copper – water pipes, electrical connectors
- Chromium and Nickel – stainless steel and corrosion-resistant alloys




Applications of aluminium alloy panel structures in an automobile and aircraft: (a) Audi TT coupé and (b) Airbus 380

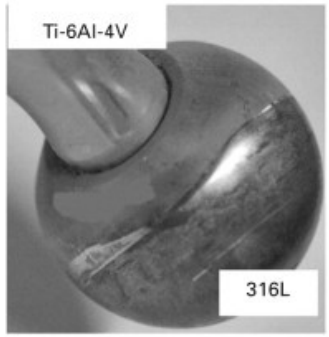
https://www.sciencedirect.com/science/article/pii/S258884041830012X

# We live in a metal based society…corrosion is everywhere

Infrastructure

Automobile/Ship

Hip Implant/Pipeline


*Images from Google*

# Why study corrosion ?

## Human life and safety –

**06/24/2013 Damage of a turbine engine (England)**

During Airbus A330 running at the airport in Manchester, at a speed of 190 km/h, the right engine caught fire. The investigation showed that there had been a fracture of one of the turbine blades. The blade failed due to high cyclic fatigue initiated by corrosion pitting.

**12/12/1999 Sinking of the tanker Erika (Bay of Biscay / France)**

On 12 December 1999, the oil tanker Erika broke in two and sank in the Bay of Biscay. There were no casualties. However, the oil spill led to a great environmental disaster. The main cause of the accident was significant corrosion of the internal structure of the vessel.

https://pdfs.semanticscholar.org/0fc1/925dcfdde69bd1dbc75980fd1de903425211.pdf

# Why study corrosion ?

## Bhopal Gas tragedy - 1984

Union Carbide India Plant Elements in Bhopal

- rush of 500 litres of water into the methyl isocyanate storage tank
- runaway chemical reaction
- high pressure and temperature
- higher levels of chloroform
- iron catalyst presence due to easy corrosion of carbon steel valves in acidic media at high temp. accelerated reaction

# Why study corrosion ?

## Cost of corrosion

### India loses up to $100 billion annually to corrosion: Hind Zinc CEO Sunil Duggal

*"India loses around 4-5 per cent of GDP annually on account of corrosion losses," Hindustan Zinc Ltd (HZL) CEO Sunil Duggal told PTI.*

PTI | Updated: Oct 16, 2016, 12.56 PM IST

NEW DELHI: India with a GDP of around $2 trillion loses as much as $100 billion (more than Rs 6 lakh crore) every year on account of corrosion, which can be checked by using zinc to galvanise steel structures.

"India loses around 4-5 per cent of GDP annually on account of corrosion losses,"

# Why study corrosion ?

Conservation of materials

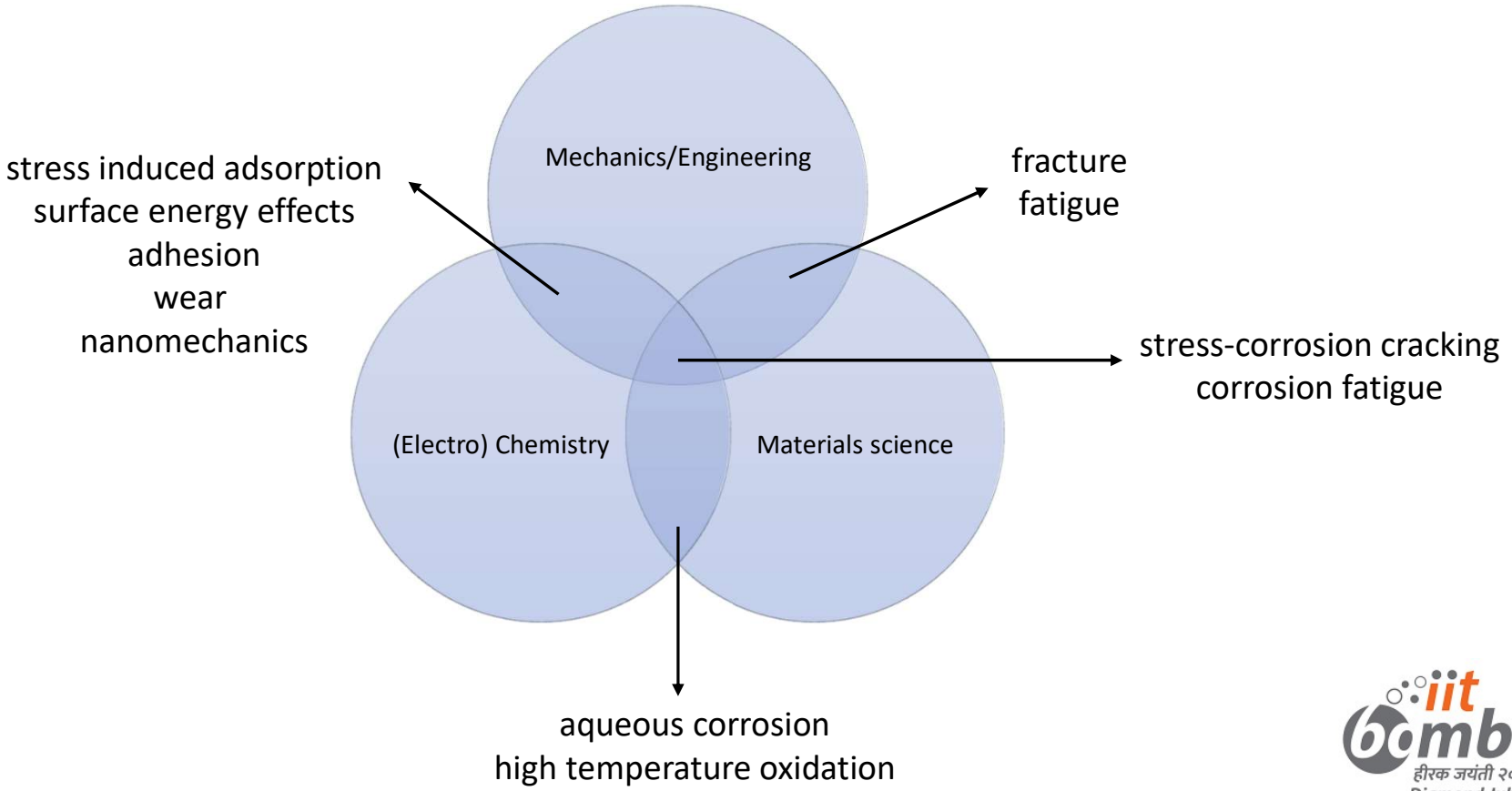
- Limited supply of material reserves on the planet
- Specific geographical location of the ores and minerals
- Wastage of energy and human effort
- Service extension mitigates additional manufacturing
- Development of corrosion and oxidation-resistant alloys

# Corrosion – is it complex ?

Various environments + Various metal systems + Specific conditions = Many different case studies

| Various environments | Various metal systems | Specific conditions |
|---|---|---|
| ocean<br>atmosphere<br>industrial ($SO_2$, $H_2O$)<br>marine ($Cl^-$, $H_2O$)<br>soils<br>chemicals<br>- manufacturing plants<br>- storage tanks<br>- transport lines<br>… | steels<br>stainless steel<br>aluminium alloys<br>titanium alloys<br>copper alloys<br>nickel alloys<br>…..<br>surface alloys<br>metallic coatings<br>organic coatings | concentrations<br>temperature<br>fluid flow<br>stress<br>presence of $O_2$<br>absence of $O_2$<br>pressure<br>organic inhibitors<br>biofilms |

# Corrosion – an interdisciplinary field



# Corrosion – definition

Origin – comes from the Latin root word ***corrodere*** - which means *to gnaw away* or *to eat away*

Corrosion –

- natural phenomenon
- destructive attack of metal by its environment
- causes deterioration of properties of metal

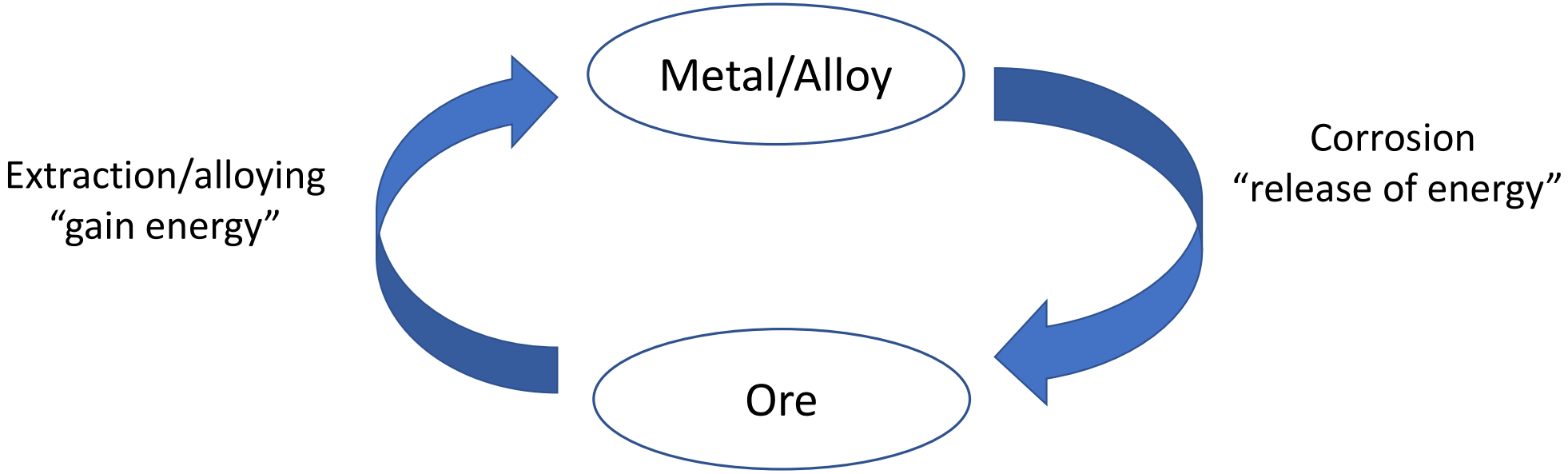
Plastics, concrete, wood, ceramics, composite materials undergo deterioration by environment but don't corrode!

***rusting*** – applies to plain carbon steel and iron
rust – hydrated ferric oxide – red or dark brown color
non ferrous metals- aluminium, copper, zinc corrode but don't rust

https://www.electrochem.org/corrosion-science

# Corrosion – thermodynamic viewpoint

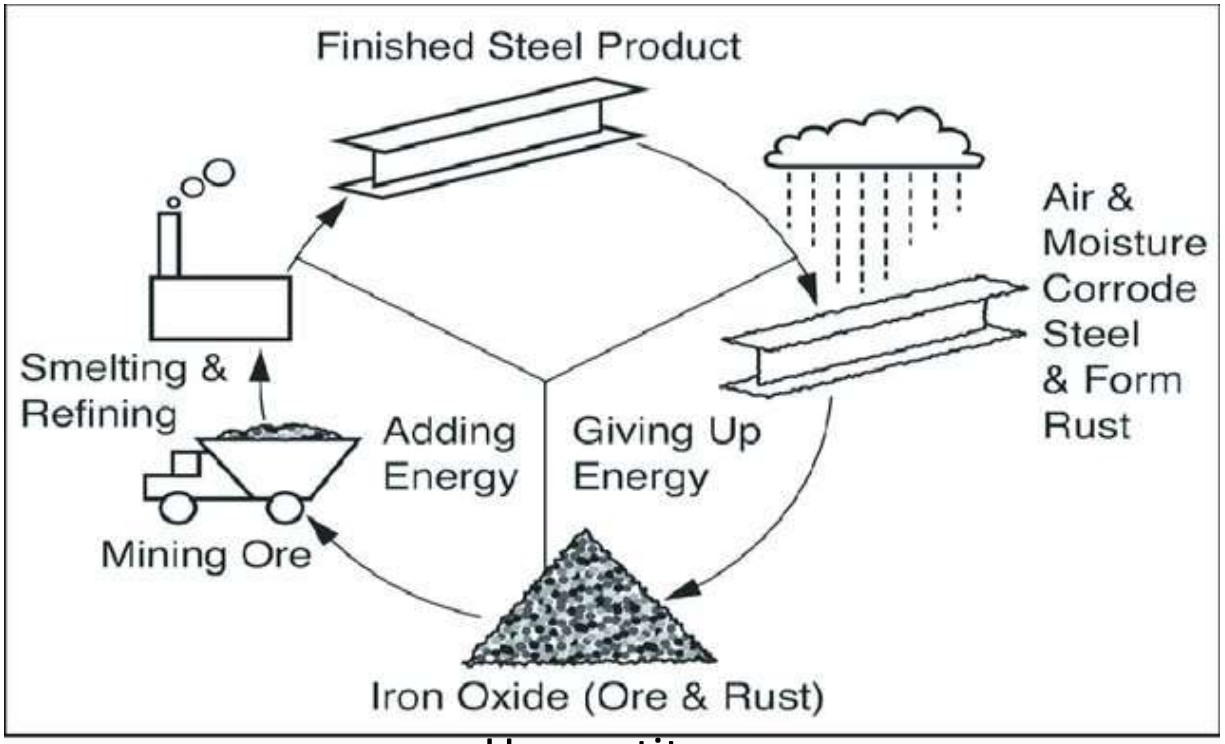
*thermodynamic reaction by which a metal returns back to its natural form as ore*




*corrosion is extractive metallurgy in reverse*

# Corrosion – thermodynamic viewpoint

Fe + C (+ Cr, Ni, Si)




Haematite

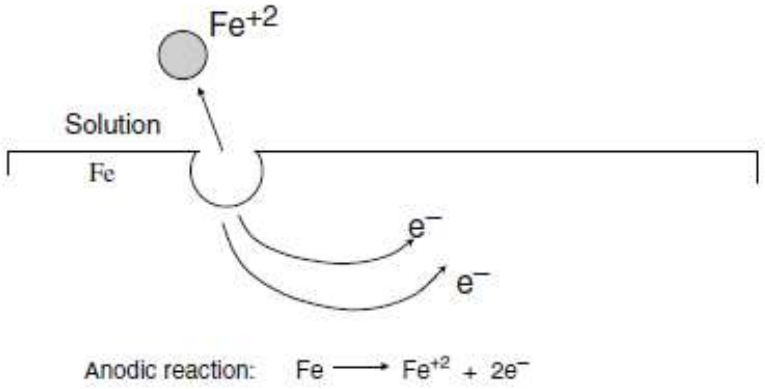
Corrosion Cycle on iron and steel (Adopted from Jenkins, 2005)

# Corrosion – Electrochemical reactions

- Corrosion predominantly an electrochemical process
- Occurs by operation of coupled electrochemical half cell reactions

## Half cell reaction – Anodic

- given species undergoes oxidation ie. increase in its oxidation number
- loss of electrons at anodic site, ie. electrons are produced




$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^-$$

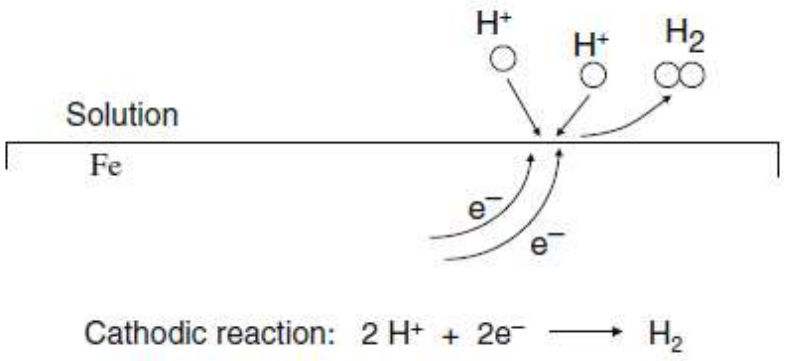
$$2Cu(s) + H_2O(1) \rightarrow Cu_2O(s) + 2H^+(aq) + 2e^-$$

*corrosion is simultaneous transfer of mass and charge across a metal/solution interface*

# Corrosion – Electrochemical reactions

## Half cell reaction – cathodic

- given species undergoes reduction ie. decrease in its oxidation number
- gain of electrons at cathodic site, ie. electrons are consumed

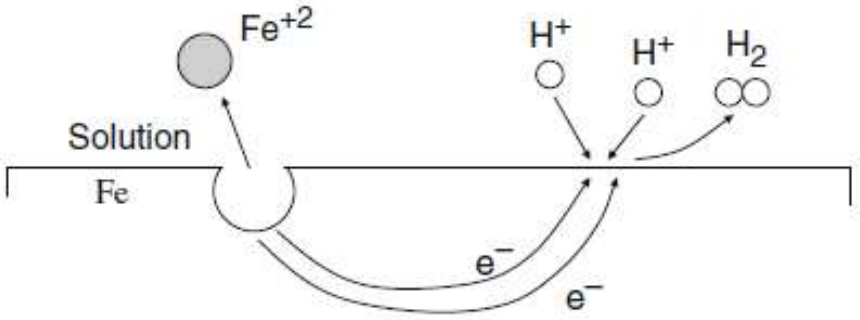



$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$ acidic

$$O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq)$$ basic/neutral

# Corrosion – Electrochemical reactions

## Coupled electrochemical reactions – iron surface immersed in an acidic environment




At anodic sites: $Fe \longrightarrow Fe^{+2} + 2e^-$

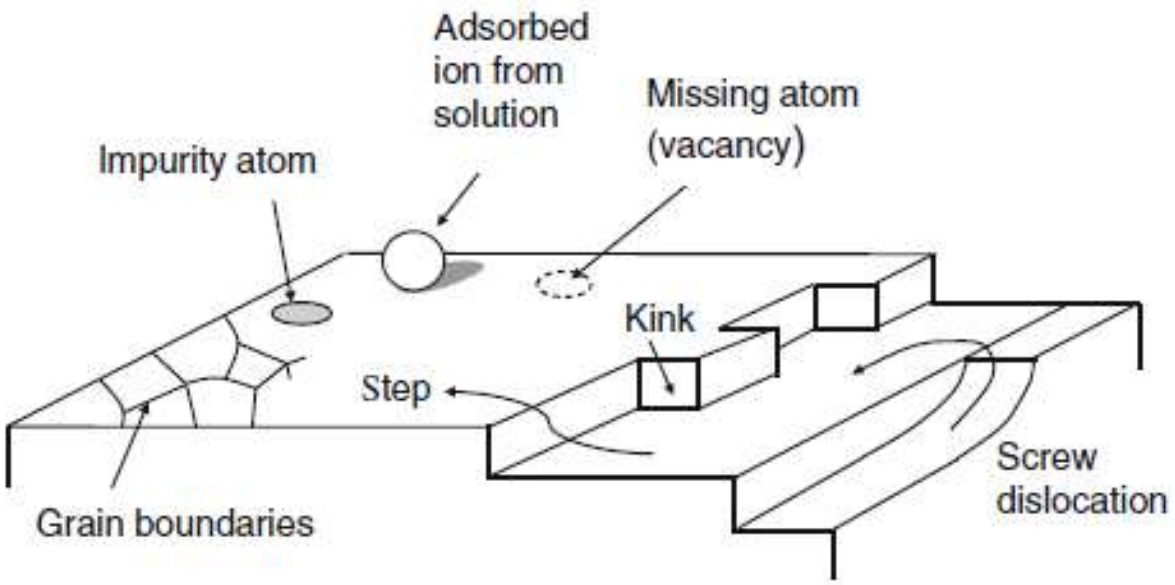
At cathodic sites: $2H^+ + 2e^- \longrightarrow H_2$

Overall reaction: $Fe + 2H^+ \longrightarrow Fe^{+2} + H_2$

1. anodic reaction
2. cathodic reaction
3. electrolyte
4. metallic path of contact between anodic and cathodic site for electron transport

# Corrosion – Electrochemical reactions

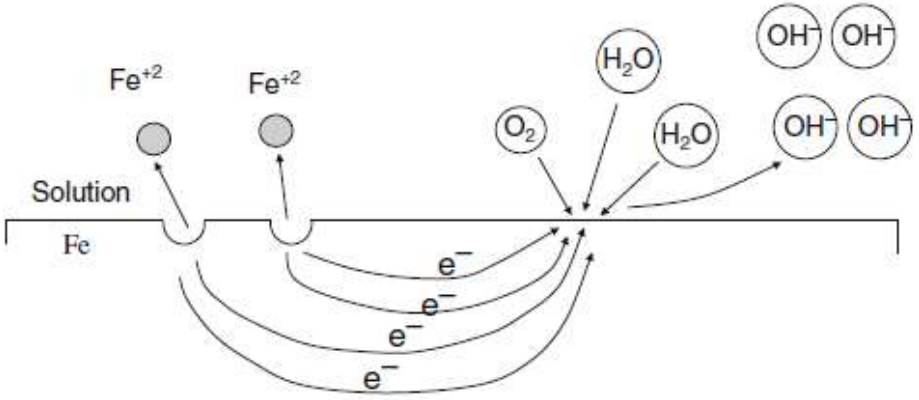
How two different electrochemical reactions occur on same metal surface ?




Heterogeneous nature of metal surface

# Corrosion – Electrochemical reactions

Coupled electrochemical reactions – different sites on same metal surface - iron immersed in a neutral/alkaline environment



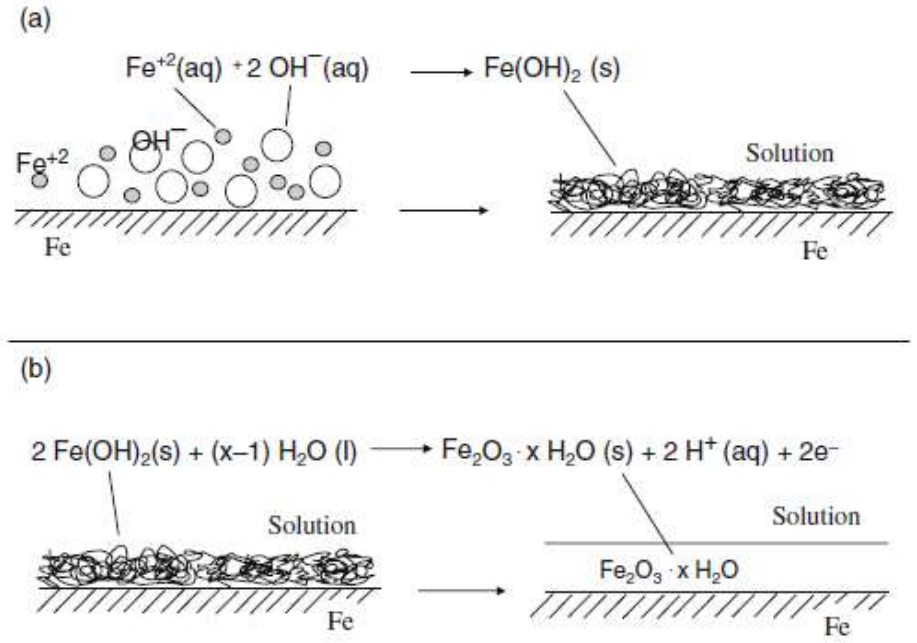

At anodic sites: $2\,[\,Fe\,(s) \longrightarrow Fe^{+2}\,(aq) + 2e^{-}]$

At cathodic sites: $O_2\,(g) + 2\,H_2O\,(l) + 4e^{-} \longrightarrow 4\,OH^{-}\,(aq)$

Overall reaction: $2\,Fe\,(s) + O_2\,(g) + 2\,H_2O\,(l) \longrightarrow 2\,Fe^{+2}\,(aq) + 4\,OH^{-}(aq)$

# Corrosion – Electrochemical reactions

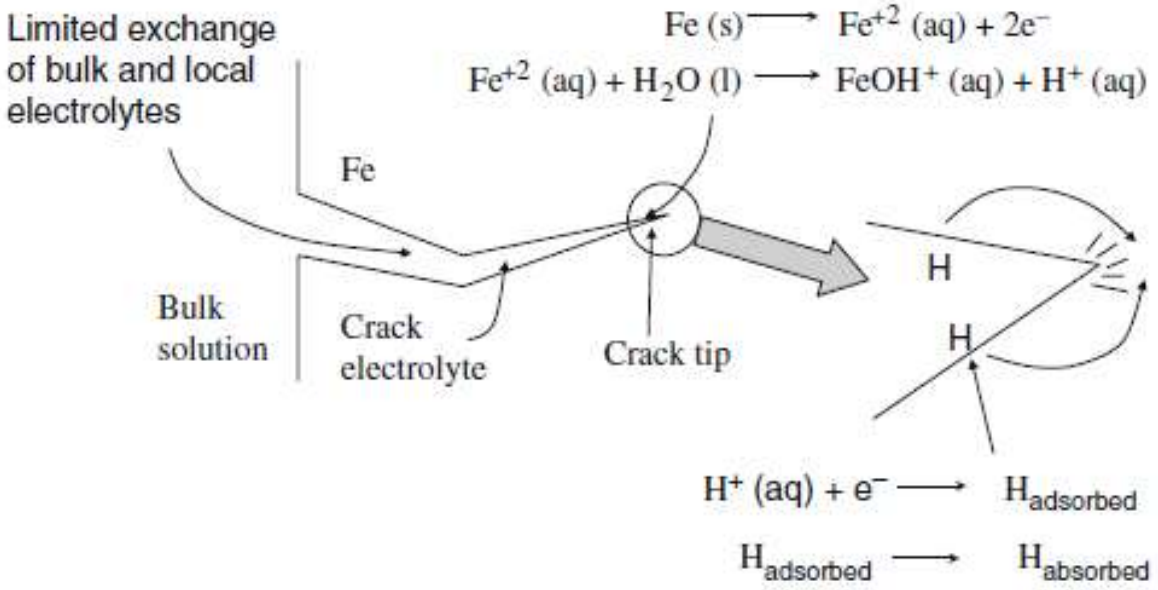
## Coupled electrochemical reactions – iron surface immersed in a neutral/alkaline environment




(**a**) The precipitation of ferrous hydroxide on the iron surface.
(**b**) The conversion of ferrous hydroxide to a hydrated ferric oxide

# Corrosion – Electrochemical reactions

Why are cathodic reactions important ?




*stress corrosion cracking*

# Corrosion – Faraday's law

*Amount of substance produced at an electrode (or liberated from it) during an electrochemical reaction is directly proportional to the amount of charge passing through it*

Faraday connects mass and charge transfer :

$$F \equiv \frac{96,500\,\mathrm{C}}{\text{equivalent}}$$

Faraday's law gives the mass (W) of metal corroded :

$$W = \frac{I\,t\,A}{n\,F}$$

I : current in Amperes
t : time in seconds
A : atomic weight of metal
n : number of equivalents transferred per mole of metal

# Corrosion – Faraday's law

$$\text{Current in amperes} = \frac{\text{charge in coulombs}}{\text{time in seconds}}$$

$$\text{There are } \frac{96,500\ \text{C}}{\text{equivalent}}.$$

$$\text{For the anodic half-cell rection } \text{M} \rightarrow \text{M}^{n+}\text{, there are } \frac{n \text{ equivalents}}{\text{mole M}}.$$

# Corrosion – Faraday's law – Example problem

*Q. The weight loss of an aluminium alloy corroding in a solution of hydrochloric acid was observed to be 0.25 g/cm$^2$ after a 8 hour immersion period. What is the corresponding anodic current density in mA/cm$^2$ assuming all the corrosion is due to the following anodic half-cell reaction :*

$$Al \rightarrow Al^{3+} + 3e^-$$

*The atomic weight of Al is 26.98g/mol*

# Corrosion –Example problem

*Q. Corrosion of copper in water occurs by the following reaction*

$$2Cu(s) + O_2(g) + 2H_2O(l) \rightarrow 2Cu^{2+}(aq) + 4OH^-(aq)$$

*(a) Separate the overall reaction into two half cell reactions*

*(b) If the concentration of dissolved $Cu^{2+}$ ions is 0.001 M and the pH is 9, would the following reaction occur ?*

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$$

*Solubility product for $Cu(OH)_2$ is $K_{sp} = 2.2 \times 10^{-20}$*

*(c) When the reaction in (b) is at equilibrium, what is the effect of decreasing the pH on the precipitation reaction ?*

# Corrosion – Faraday's law - Example problem

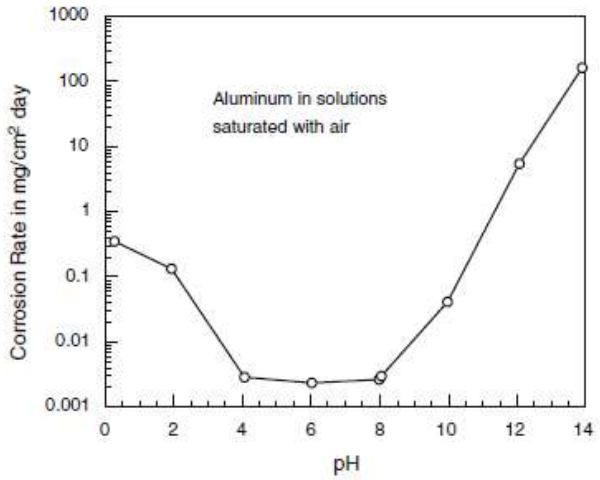
*Q. In the atmospheric corrosion of aluminium, suppose that the cathodic reduction of oxygen*

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

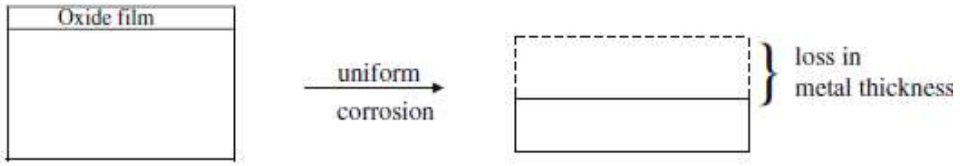
*occurs for a period of 48 h at a current density of 25 $\mu A\ cm^{-2}$ in a thin electrolyte film which is 165 $\mu m$ in thickness.*

*(a) What is the resulting pH in this thin layer of electrolyte if the total electrode area is 2 $cm^2$.*

*(b) If the initial pH was 7.0 would you expect the final pH to cause a change in the corrosion rate ? Answer this part of the question using Fig. below.*



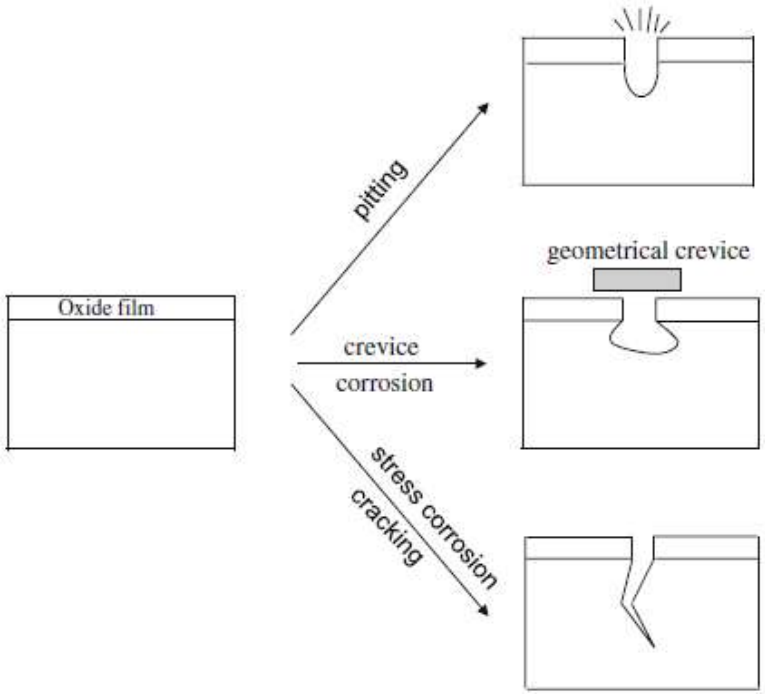
# Corrosion – Uniform vs localised




Uniform corrosion

- metal attacked evenly over entire surface
- no preferential region of attack
- eq: corrosion of zinc in HCl
- existence of localised anode and cathode
- position changes with time
- overall uniform corrosion

# Corrosion – Uniform vs localised

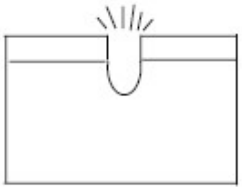



Localised corrosion

- position of local anode and cathode fixed
- corrosion at specific location
- pitting/crevice/stress corrosion cracking

# Corrosion – Uniform vs localised

pitting corrosion



- Pitting corrosion

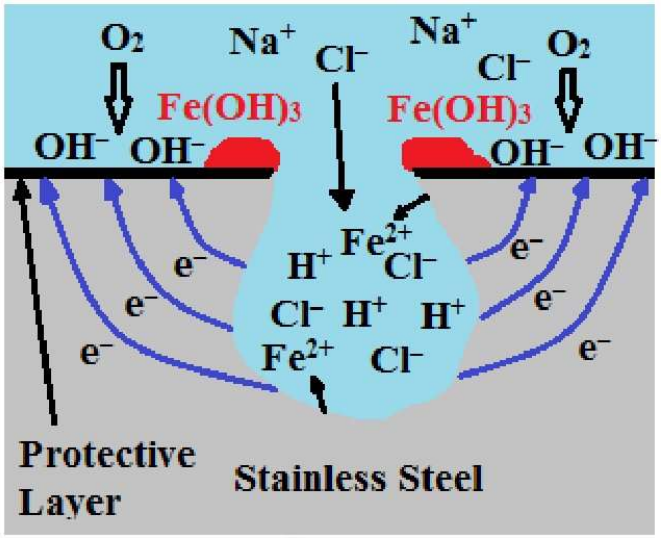
- Halogen species (chloride ions) attack the defects of passive films and locally break the film

- due to attack by chloride ions, certain fixed areas on the metal surface lose their protective oxide layer

- preferential attack at such sites causes loss of metal

- geometrical constraint of cap of corrosion products above propagating pit

# Corrosion – Uniform vs localised




- Pitting corrosion
- once passive oxide layer breaks - metal exposed to electrolyte - undergoes oxidation - becomes local anode
- rest of the electrode where oxygen is available, ORR take place $O_2 + 4e^- + 2H_2O = 4OH^-$ (local cathode)
- continuous oxidation causes excess positive charge accumulation in pit area
- attracts chloride anions and metal M forms MCl
- MCl hydrolyses into MOH + HCl
- HCl dissolves the metal further - auto catalytic