

Corrosion
MM 454 IITB
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<https://somphene.github.io/notes/>

Notes
by
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When Corrosion Engineers don't work, the world rusts.

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This is an **incomplete draft**. Please send corrections, comments, pictures of bad drawings, etc. to somphene1@gmail.com.

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1 Lecture Jan 13

§1.1 Course Logistics

Meets Mon, Tuesday, Thursday Slot 1. 2 Quizzes, 10 marks each. Midsem 30, Endsem 50. 80% attendance.

§1.2 References

- Corrosion Engineering by Fontana
- Introduction to Corrosion Science by McCafferty Corrosion
- Corrosion Control- R. Winston and Herbert H. Uhling
- Specific scientific reports.

§1.3 Course objectives

- Provide a basic understanding of corrosion phenomena.
- Provide tools to measure and analyze and predict the corrosion of materials.

Electrolyte- cathodes and anodes to explain corrosion in Stainless Steel. Pitting corrosion.

Corrosion is degradation of materials. Any big tangible structures like ships or buildings or bridges, you will find steel/ copper. Even in small devices like mobiles, laptops there are copper wires for conducting networks. Car frames and aeroplanes made of Aluminium. What metals undergo corrosion. Examples of corrosion detection- rust in automobiles, titanium in implants (corrodes over a long period of time).

§1.4 Why study corrosion

- Fire on an aircraft Airbus A330 engine (Manchester, 2013) because of fracture of blades via fatigue.
- Bhopal Gas Tragedy also caused due to corrosion. Runaway chemical reaction- starts initiation but doesn't stop, for instance in mobile phones sparks. High temperature and pressure. High levels of chloroform. Carbon steel went corrosion in acidic media at high temperature.
- India loses upto \$100 billion annually (Hind Zinc CEO Sunil Duggal) that's about 4-5 % of the GDP
- Conservation of materials. Limited supply of materials in specific geographical locations. Wastage of energy and human effort. Service extension mitigates additional manufacturing.
- Development of corrosion resistant alloy oxides.

§1.5 Corrosion- Is it complex

Various environments have various unique. For instance- salts are available in Marine environment, Chloride anions from salts is significant. Sulphur dioxide in industrial applications. Sulfate anion in the soil. Materials prone to corrosion are steel, stainless steel, aluminum alloys, copper, nickel, titanium alloys. Complex systems of materials. Different case studies map to different root causes.

§1.6 Corrosion- An interdisciplinary field

Electrochemistry, Mechanics/Engineering, Materials Science Venn Diagram (later). Stress induced adsorption surface energy defects- adhesion, wear, nanomechanics, tribology. Aqueous corrosion- high temperature oxidation.

§1.7 Corrosion- Definition

Origin- comes from Latin *corrodere*- gnaw away or eat away.

Corrosion

- Natural phenomenon
- destructive attack of metal by its environment.

§1.8 Thermodynamic viewpoint

Thermodynamic reaction by which a metal returns back to its natural form as an ore. Extraction/alloying is gaining energy (opposite to spontaneous reaction requires inputting energy). Corrosion is release of energy.

Fe-C (+Cr, Ni, Si) diagram (later)

Fe alloys - Haematite (Fe_2O_3), Wustite (FeO)

Cr_2O_3 layer stops corrosion. Thermodynamics drives corrosion.

§1.9 Electrochemical Reactions

- Corrosion predominantly an electrochemical process.
- Operation of coupled electrochemical half cell reactions.

Half Cell reaction- Anodic

- Species undergoes oxidation
- loss of electrons at the anodic site, ie. electrons are consumed.

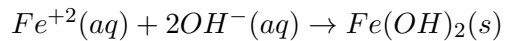
Half Cell reaction- Cathodic

- Species undergoes reduction
- gain of electrons at the cathodic site.

Charge + Mass transport.

How can two different electrochemical reactions happen on the same metal surface. Energy of surface drives reaction. Difference in energies between two points on the metal surfaces. Insert diagram (later). Heterogeneous nature of the surface creates difference in energy.

Half reactions. Insert diagram (later).



In the presence of an acidic media, there is a different reaction leading to Hydrogen embrittlement.

§1.10 Faraday's Law

Simultaneous charge and mass transfer. Charge transfer and Mass transfer related by Faraday's Law.

$$F = \frac{96500 \text{ C}}{\text{Mole equivalent}}$$

The mass of metal corroded is given by: $W = \frac{ItA}{nF}$

2 Lecture Jan 14

§2.1 Corrosion- Electrochemical reactions

§2.1.i Electrochemical Reactions

- Corrosion predominantly an electrochemical process.
- Operation of coupled electrochemical half cell reactions.

Half Cell reaction- Anodic

- Species undergoes oxidation
- loss of electrons at the anodic site, ie. electrons are consumed.

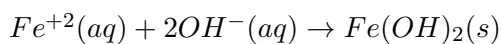
Half Cell reaction- Cathodic

- Species undergoes reduction
- gain of electrons at the cathodic site.

Charge + Mass transport.

How can two different electrochemical reactions happen on the same metal surface. Energy of surface drives reaction. Difference in energies between two points on the metal surfaces. Insert diagram (later). Heterogeneous nature of the surface creates difference in energy.

Half reactions. Insert diagram (later).



In the presence of an acidic media, there is a different reaction leading to Hydrogen embrittlement.

§2.1.ii Faraday's Law

Simultaneous charge and mass transfer. Charge transfer and Mass transfer related by Faraday's Law.

$$F = \frac{96500 C}{\text{Mole equivalent}}$$

The mass of metal corroded is given by: $W = \frac{ItA}{nF}$
where

1. n is the effective mass

Question 2.1.1. The weight loss of an aluminium alloy in a HCl acid soln was observed to be $0.25g/cm^2$ after $8hrs$ immersion. What is the corresponding anodic current density in mA/cm^2 assuming all the corrosion is due to the following anodic reaction: $Al \rightarrow Al^{3+} + 3e^{-}$

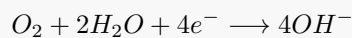
Question 2.1.2. Corrosion of copper in water occurs by the following reaction (later)

- Separate the overall reaction into two half cell reactions
- If the concentration

Answer:

- Anodic : $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Cathodic : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
- $[Cu^{2+}] = 10^{-3}M$, pH

Question 2.1.3. In the atmospheric corrosion of Aluminium, suppose that the cathodic reduction of oxygen



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

- What is the resulting pH in this thin layer of electrolyte if the total electrode area is $2 cm^2$?
- If the initial pH was 7.0 would you expect the final pH to cause a change in the corrosion rate?

Answer:

- Faraday's Law $[OH^-]$

$$W = \frac{ItA}{nF}$$

$$W\left(\frac{g}{cm^{-2}}\right) = \frac{\frac{25\mu A}{cm^2} 48h \frac{3600s}{1h} \frac{17g[OH^-]}{1mol}}{\frac{1equi}{1mol[OH^-]} \frac{96500C}{1equivalent}}$$

$$= 761.03 \times 10^{-6} \frac{g}{m^2}$$

-

$$pH = 14.4$$

§2.1.iii Corrosion- Uniform vs localised

Two basic forms of corrosion.

Uniform Corrosion: cathode and anode spots keep dancing around. Energy of the surface keeps on changing. Local cathode and anode changes with time causing a same rate of metal loss throughout the surface.

- metal attacked evenly over the 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

Local corrosion

- position of anode and cathode is fixed

Pitting corrosion

- 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.
- insert figure (later) $NaCl$ in H_2O electrolyte. Cl^- ions attack the oxide film.
- 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 at the bottom of the pit area.
- Attracts chloride anions (OH^- has lesser mobility than Cl^- towards the pit bottom).
- Reacts to form metal chloride.
- MCl hydrolyses into $MOH + HCl$
- HCl further dissolves the metal-autocatalytic.

Next time crevice corrosion. Electrical Double layer.