FACTORS INFLUENCING CORROSION

Key concepts

- Corrosion as an electrochemical process
- Four key elements for corrosion
- Corrosion of dissimilar metals

Introduction

Metals are essential materials used in all aspects of our daily life, such as communication devices to transportation goods, energy, and food. Like other materials, metals can lose their properties due to the interaction with the environment by a process called corrosion. For most metals, corrosion is inevitable and is a natural process. However, by understanding it, we can protect the metals from corrosion while they are being used.

The vast majority of the metals we use can only be found in the environment as minerals (ores), and they need to be transformed to the metallic state to be employed. The life cycle of metal starts from mining metal-containing minerals (oxides, sulphides, etc.), smelting and processing to the metallic state, and forming metals to required shapes (pipes, bars, plates, etc.). Over time, metals corrode and return to their original form, i.e., minerals. Corrosion scientists study this last step of the lifecycle and design strategies to reduce its rate, so the metals remain in the metallic state to achieve their purpose for the remaining design life.

Figure 1: Metal life cycle

Electrochemical (galvanic) corrosion of metals

Metals corrosion is an electrochemical process (Redox reaction) that requires 4 components:

- **Cathodic reaction (Reduction, positive polarization)**: A reaction that gains electrons. As a result, the oxidation number decreases. For instance, hydrogen and oxygen reduction reactions are common in acidic and aerated solutions, respectively. The site where the cathodic reaction occurs is called the cathode.
    - $\mathbf{2H^+ + 2e^- \rightarrow H_2}$ (The oxidation state goes from +1 to 0)

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- $\mathbf{O_2 + H_2O + 4e^- \rightarrow 4OH^-}$ (The oxidation state goes from 0 to -2)

- **Anodic reaction (Oxidation, negative polarization):** A reaction that loses electrons. As a result, the oxidation number increases. Generally, this is the metal dissolution reaction. A metal in metallic form, which has an oxidation number of zero, loses electrons, becoming metal cations. Metal cations can dissolve away or further react with the surroundings, such as with oxygen to form oxide scales. The site where the anodic reaction occurs is called the anode.
  - $\mathbf{Fe \rightarrow Fe^{2+} + 2e^-}$
  - $\mathbf{Zn \rightarrow Zn^{2+} + 2e^-}$
- **Electrolyte**: a conductive solution to carry ions. Seawater is an effective electrolyte for corrosion due to its high salt concentration and low resistivity. Coastal regions are more susceptible to corrosion than areas further in land due to deposition of salt aerosols.
- **Electrical conductor**: an electrically conductive medium to transport electrons. For instance, an electrical wire connecting two metal pieces, a direct contact between dissimilar metals, or the metal itself.

In short, a metal will corrode (oxidise) if another substance can be reduced. The overall electrochemical (redox) reaction is spontaneous according to thermodynamics if both an electrolyte and electrical conductor are available. We use the standard reduction potentials (E^o) to determine if a redox reaction is spontaneous. For that, we calculate the potential of the redox reaction as per Equitation 1. If the potential (E_{Redox}) is positive, the redox reaction is thermodynamically favoured. We call this type of reaction a "galvanic cell". In contrast, if the redox potential is negative, the redox reaction will not be spontaneous. In some applications, we can force this reaction to occur. An electrochemical cell that requires additional help is referred to as an "electrolytic cell".

$$E_{Redox} = E^o_{red} - E^o_{oxi} \quad (1)$$

The lower (i.e., the more negative) the E^o of the metal, the more reactive the metal is.

Corrosion can be minimised or accelerated by altering at least one of the four components described above. For instance, removing oxygen from the electrolyte reduces the consumption of electrons and, consequently, metal dissolution rates. We can visualise cathodic and anodic reactions as demand and supply of electrons. When the demand increases (e.g., acidic electrolytes, i.e., low pH), the supply has to keep up, leading to an accelerated corrosion rate and vice versa.

When a metal corrodes, local cathodes and anodes are developed within the metal surface. If the metal is homogeneous, the preferential locations of the anodes and cathodes are defined by geometry to minimise the energy of the system (e.g., separate the oxidation and reduction reaction as much as possible due to polarisation while maintaining electrical neutrality). However, there are often heterogeneities within the metal, such as inclusions or defects formed during the manufacturing or machining processes. These areas are more prone to corrosion and will preferentially act as anodes or cathodes. For instance, Figure *2* illustrates an iron-based metal with two phases, one of which is more susceptible to corrosion. The phase more prone to corrosion will preferentially act as an anode and dissolve faster than the more resistant phase, which will support the cathodic reaction(s).

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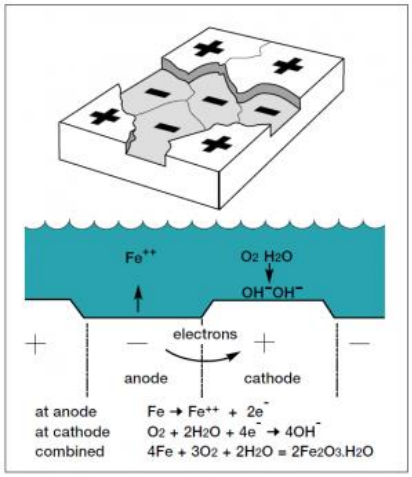

Figure 2: Local anode and cathode sites in a metal with two phases. The phase is more prone for the anodic reaction will be negatively polarised and preferentially corroded. Simultaneously, the more resistant phase will preferentially act as a cathode and be positively polarised. Link

Cathodic protection (Sacrificial anode)

When two metals are electrically and electrolytically in contact, the metal more susceptible to corrosion will preferentially oxidise (i.e., corrode). We can use the standard reduction potential (E^o) or electromotive force (emf) series to determine which metal is more likely to be oxidised (i.e., corroded). A metal with a lower standard reduction potential is more susceptible to oxidation.

Corrosion specialists use this form of preferential corrosion as a method to protect a metal of interest. For instance, if we need to protect a steel (an iron-based alloy) structure, we can electrically connect it to other metals with lower E^o, e.g., zinc, aluminium, magnesium, etc., that are more susceptible to corrosion. In the Steel-Zn pair, zinc will be the anode and corrode, reducing the corrosion rate of the iron-based alloy. In contrast, the cathodic (reduction) reaction will predominantly occur on the iron by being in contact with zinc. Because Zn is "sacrificed" to protect steel, we referred to this form of corrosion protection as sacrificial cathodic protection and zinc as "sacrificial anode."

Equipment and materials (details of the materials)

- Bright steel nail (non-galvanised)
- Agar
- Non-insulated copper wire or strips
- Zinc strip
- DI water
- Salt (e.g., NaCl, KCl) (optional)
- Phenolphthalein
- Potassium hexacyanoferrate(III)
- Heater
- Beakers
- Container (e.g., petri glass)
- Tools to bend a nail (e.g., clamp and hammer)
- Sanding paper #120 (optional)

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Experimental observation

Nail – Copper

Observation: Areas surrounding copper wire turned pink, while the exposed nail showed a blue colour. In this pair, copper acts as the cathode while the nail as the anode. The nail is made of steel, which consists mainly of iron. Iron is more reactive compared to copper, thus preferentially corroded. As iron corroded, ferrous ions (Fe^{2+}) were produced, which then reacted with the ferricyanide indicator, turning blue.

At cathode (copper surface):

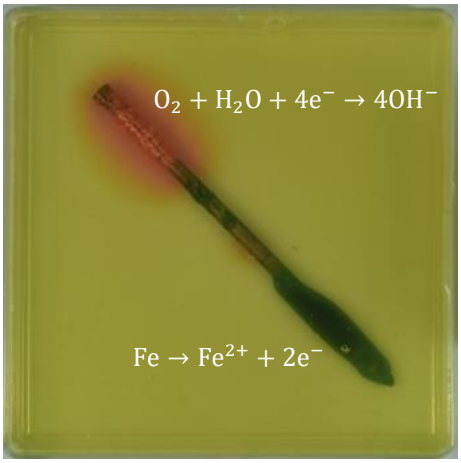
$$O_2 + H_2O + 4e^- \rightarrow 4OH^-$$

$$HInd + OH^- \rightarrow H_2O + Ind^- \textit{ (Pink)}$$

At anode (steel nail surface):

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$Fe^{2+} + Fe(CN)_6^{3-} \rightarrow Fe[Fe(CN)_6]^- \textit{ (Blue)}$$



Time = 3 min

Time = ~ 24 h

Nail - Zinc

Observation: Initially, the area adjacent to the nail immediately turned pink, while no visible change was observed on the zinc surface. As the test duration increased, the pink colour migrated further away from the nail and the area adjacent to zinc gradually became white and cloudy. Zinc is more readily oxidised compared to iron. Thus, when zinc was in contact with the nail, it became the anode, and zinc dissolution was the primary anodic reaction. Zinc corrosion products gradually formed, resulting in the agar mixture turning white and cloudy.

Zinc oxide (ZnO) generally forms rapidly and is hydrolysed to hydroxide ($Zn(OH)_2$). Subsequent reaction with the environment leads to $Zn_5(CO_3)_2(OH)_6$, which forms the white precipitates.

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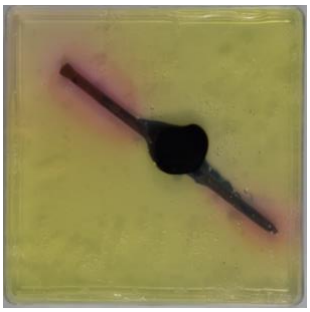
Time = 3 min	Time = 24 h

Nail – straight

Observation: Changes were not immediate. The natural corrosion reaction of the nail is slower than when it is electrically connected to a dissimilar metal. When connected to copper, the dissolution of the nail was accelerated. On the contrary, when connected to zinc, the nail was cathodically polarised, and the cathodic reaction occurred on its surface.

Sites for cathodes and anodes for a uniform corrosion process can appear random. The colours may also develop at different locations (other examples are given with the hyperlinks). In this demonstration, the anode appears to be more prominent at the centre.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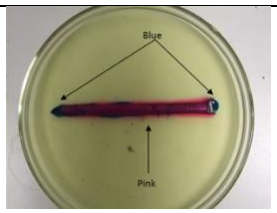 *Link*	 *Link*

Nail – Bent

Observation: Deformation and "cold work" (i.e., the plastic deformation of a metal at low temperatures) introduced stresses and surface defects, causing it to be more susceptible to corrosion. When the nail was bent a couple of times, the centre of the nail became the preferential anode. The blue indicator colour was prominent at the bent area, indicating that this area was an anode.

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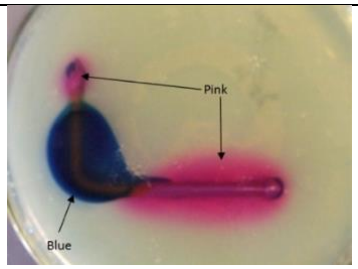
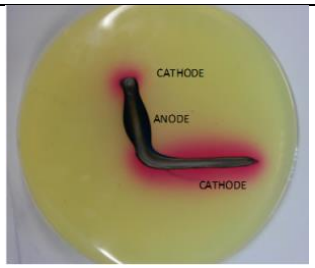
Time = 3 min	Time = 24 h
 Link	 Link

Experimental troubleshooting

Agar does not solidify

Most likely, the agar did not fully dissolve. After adding the agar to the boiling water, keep the solution boiling for a few minutes until the agar solution is homogeneous and no particles are evident.

No colours developed

If no colours are developed after 15-30 min of purring the agar solution, there might be a problem with the indicators, or the corrosion rate of the nail is too slow. Try increasing the concentration of indicators, add salt to increase the conductivity and corrosivity of the electrolyte or both.

"Incorrect" colours developed

If white products appear instead of blue colour in the nail section with copper or nail straight or nail bent, probably the nail is galvanized (i.e., the nail has a zinc coating). Once the zinc is consumed, the nail will start to corrode, and blue colour will eventually appear. However, this may take time. You can try a different nail or roughly grind the external surface of the nail with sandpaper.

If you see the colour of only one indicator (e.g., either pink or blue), try reducing the concentration of that indicator and increasing the other one. The reactivity of the indicator might be affected if the chemicals are old.

If you see blue colouring in the Nail – Zinc couple, which indicates that the nail is corroding and iron is being oxidised, try tightening the zinc strip to the nail to increase the contact with the nail and cover more area of the nail with zinc.

Colour developed all over the nails – no clear distinction of anode and cathode

Zinc (or copper) needs to be wrapped tightly around the nails and covered the nail fully, as shown in the figures. The steel nail under the zinc (or copper) should not be exposed.

Bent nail does not preferentially corrode at the bend

Introduce significant deformation in the nail and, if possible, bend it back and forth multiple times.

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Keywords

Alloys: Metallic material consisting of a base metal and one or more alloying elements partially or completely dissolved in the base metal.

Standard reduction potential (E°): value that indicates the tendency for a given chemical species to be reduced.

EMF series: The electromotive force series is a list of elements and reactions ordered by their standard reduction potential to compare inherent reactivity.

Cathode: Sites where the cathodic (reduction) reaction occurs.

Anode: Sites where the anodic (oxidation) reaction occurs.

Electrolytic cells: An electrochemical cell that requires external energy to facilitate the reaction to happen. Examples are electroplating (for jewellery, etc) and electrolysis (separation of water to form oxygen and hydrogen)

Galvanic cells: An electrochemical cell that does not require external energy to facilitate the reaction to happen. Examples are batteries and corrosion.

Explanations

Corrosion of dissimilar metals

The tendency for a metal to be reduced is determined by the standard reduction potential. A metal with a low standard reduction potential is not readily reduced. In other words, it is prone to corrosion. A table of standard reduction potential can be found from various sources, such as here and here. In these tables, the potentials of reduction reactions of metallic elements are listed. Thus, it can be used to crudely estimate which metals are more prone to corrosion, should they connect electrically.

The concept of dissimilar metal corrosion (or commonly known as galvanic corrosion) is utilised in one of the common corrosion control strategies, i.e., cathodic protection using a sacrificial anode.

Effects of residual deformation/stresses on corrosion

Local areas with residual deformation or stresses, such as the bend in the nail, are areas with a higher disorder and energy, and contain a larger amount of surface defects. These areas will require less energy to oxidate the metallic atoms and, thus, they will be more susceptible to corrosion.

Additional questions (To brainstorm during session) – and *model answers*

Following questions may be used to further engage with students

1. Identifying the components of a corrosion cell

Four components are required for any corrosion process to occur. In this experiment, four scenarios were simulated, namely nail-copper, nail-zinc, straight nail, and bent nail. What are the corrosion cell components in each of these scenarios?

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Cell	Electrolyte	Electrical conductor	Cathode site	cathodic reaction	Anode site	Anodic reaction
Nail-Copper	*Agar*	*Contact between Nail and copper*	*Copper*	*Oxygen reduction*	*Nail*	*iron dissolution*
Nail-Zinc	*Agar*	*Contact between Nail and Zinc*	*Nail*	*Oxygen reduction*	*Zinc*	*zinc dissolution*
Nail-straight	*Agar*	*Nail itself*	*Nail*	*Oxygen reduction*	*Nail*	*iron dissolution*
Nail-Bent	*Agar*	*Nail itself*	*Nail*	*Oxygen reduction*	*Nail*	*iron dissolution*

2. What are other dissimilar metal couples might we observe in real life and in what scenarios?

Cathodic protection by sacrificial anodes (or sacrificial cathodic protection) utilises the principles of dissimilar metals corrosion. Zinc anodes can be seen attaching on a ship hull or aluminium anodes on offshore oil and gas structures.

3. Can you provide an example of how to prevent galvanic corrosion?

Eliminating electrical contact between two metals, appropriate material selection, coating, or adding corrosion inhibitors.

4. Did the nail coupled to zinc corrode compared to the nail coupled to copper? Why?

*The nail coupled to zinc corroded **less** than when it was coupled to copper. As zinc is more active than iron (nail), it preferentially corrodes, reducing the corrosion rate of the iron nail.*

5. What colour(s) do you expect to see if you immerse the zinc strip alone (without the nail)? Can you do a prediction for the copper?

Without the nail, galvanic corrosion is not possible, and the reactions will be slower. In the absence of the nail, ferrous ions will not be generated to react with the ferricyanide indicator. Thus, blue colour will not develop. White zinc corrosion products can be visible (see the photo in the nail-zinc experiment).

If only copper is present, the reaction may be very slow, as copper is not as reactive as iron. Thus, colour change may not be visible.

6. Compare the nails after the tests with your classmates, do they look the same? Can you stipulate why?

Open discussion

Additional resources

Articles

- Definition of corrosion: https://curtin-corrosion-centre.com/knowledge/resources/what-is-corrosion/
- Materials and corrosion trends in oil and gas production: https://curtin-corrosion-centre.com/knowledge/resources/materials-and-corrosion-trends-in-oil-and-gas-production/

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- O. Wallinder and C. Leygraf, "A Critical Review on Corrosion and Runoff from Zinc and Zinc-Based Alloys in Atmospheric Environments," CORROSION (2017) 73 (9): 1060–1077, (*open access).*

Impacts of corrosion

- Economic impact of corrosion:
  - North America study: http://impact.nace.org/economic-impact.aspx
  - Australia study: https://membership.corrosion.com.au/wp-content/uploads/2021/07/Impacts-of-Corrosion-in-Australasia-3.6.pdf
- Flint (2020): A Netflix documentary based on five years of research into a Michigan auto town where tens of thousands were drinking water which poisonous lead had leached, and how officials failed to respond.
- Oil spills due to corrosion https://www.theguardian.com/environment/2011/may/04/bp-25m-north-slope-oil-spill

Industry

- https://www.ampp.org/home
- https://membership.corrosion.com.au

Terminologies

- https://www.ampp.org/resources/what-is-corrosion/corrosion-terminology-glossary

Careers in corrosion and materials

- https://newengineer.com/blog/corrosion-engineering-a-fascinating-little-known-career-option-1506659
- Corrosion career survey (job opportunities, salary, etc.): https://www.materialsperformance.com/articles/material-selection-design/2015/09/nace-internationals-annual-corrosion-career-survey-results-for-2015

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