Corrosion of Iron

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Corrosion

• deterioration of metal caused by loss of metal to solution by oxidation - reduction reaction

• electron transfer
Corrosion

anode-cathode electrical connection

anodic area ← corrosion → cathodic area

electrolyte that connect anode-cathode
Corrosion

- Anodic area
  - Oxidation reaction
  - Crack in the oxides coating
  - Boundaries between phases
  - Around impurities

\[ M \rightarrow M^{n+}(aq) + ne^- \]
Corrosion

• Cathodic area
  – Reduction
  – Metal oxides coating
  – Less reactive impurities
  – Round other metal compound (sulfides)
The mechanism of the corrosion of iron

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \]
Corrosion of iron in gel medium

reduction  oxidation
Corrosion of Iron

• rate of corrosion of anodic >> cathodic
• corrosion is controlled by cathodic process
• preventing
Corrosion of Iron

• anodic reaction:
  – oxidation of iron & electron are produced
  – $M \ (s) \rightarrow M^{n+} \ + \ n \ e^{-}$
Corrosion of Iron

• cathodic reaction:
  – depends on:
    • acidity of the surrounding solution
    • the amount of oxygen presence
Corrosion of Iron

- cathodic reaction:
  - electron are consumed by any or all of several possible half reaction

\[
2H^+(aq) + 2e^- \rightarrow H_2(g) \\
2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g) \\
O_2 + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)
\]
Corrosion of Iron

1. In the absence (little) of free oxygen and \( \text{H}_2\text{O} \)

- E.g., iron nail buried in moist clay
  
- \( \text{H}_3\text{O}^+ \) & \( \text{H}_2\text{O} \) are reduced
Corrosion of Iron

1. in the absence (little) of free oxygen and H₂O

- Reactions
  - anode:
    \[ \text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \]
  - cathode:
    \[ 2\text{H}_2\text{O}(\ell) + 2\text{e}^- \rightarrow 2\text{OH}^- (\text{aq}) + \text{H}_2(\text{g}) \]
  - net reaction:
    \[ \text{Fe(s)} + 2\text{H}_2\text{O}(\ell) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq}) + \text{H}_2(\text{g}) \]
Corrosion of Iron

1. in the absence (little) of free oxygen and water

\[ \text{Fe}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{Fe(OH)}_2 (\text{s}) \]

- \( \text{Fe(OH)}_2 \) :
  - insoluble precipitate
  - precipitate on metal surface & inhibit further corrosion
Corrosion of Iron

1. in the absence (little) of free oxygen and water
   
   • further oxidation of Fe(OH)$_2$
     
     \[
     6\text{Fe(OH)}_2(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Fe}_3\text{O}_4\cdot\text{H}_2\text{O}(\text{s}) + 4\text{H}_2\text{O}(\text{l})
     \]

   green hydrated magnetite
Corrosion of Iron

1. in the absence (little) of free oxygen and water
   - further reaction
     \[ \text{Fe}_3\text{O}_4\cdot\text{H}_2\text{O}(s) \rightarrow \text{Fe}_3\text{O}_4(s) + \text{H}_2\text{O}(l) \]
     black magnetite
   - \( \text{Fe}_3\text{O}_4(s) \) is rusted nail in moist soil
Corrosion of Iron

2. in the presence of oxygen and $\text{H}_2\text{O}$

- rate of corrosion 100 x faster than those without oxygen and water
Corrosion of Iron

2. in the presence of oxygen and $H_2O$

- Reactions
  - anode:
    \[ 2Fe(s) \rightarrow 2Fe^{2+}(aq) + 4e^- \]
  - cathode:
    \[ O_2(g) + 4H_3O^+(aq) + 4e^- \rightarrow 6H_2O(\ell) \]
  - net reaction:
    \[ 2Fe(s) + O_2(g) + 4H_3O^+(aq) \rightarrow 2Fe^{2+}(aq) + 6H_2O(\ell) \]
Corrosion of Iron

2. in the presence of oxygen and H₂O

- further oxidation of Fe²⁺ by O₂ → Fe³⁺

  \[ 2\text{Fe}^{2+}(\text{aq}) + \frac{1}{2} \text{O}_2(\text{g}) + (6 + x) \text{H}_2\text{O}(\ell) \rightarrow 2\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}(s) + 4\text{H}_3\text{O}^+(\text{aq}) \]

  red brown

- Fe₂O₃·xH₂O: rust on car
- H₃O⁺: allow the corrosion cycle continue
Corrosion of Iron

3. in the presence of chloride
   e.g. rapid rusting of car in salted water area
Corrosion of Iron

3. in the presence of chloride

- relative small amount
  - diffuse & through metal oxide coating
  - form metal chloride
    - leach back through metal oxide coating
      - patch is opened
        - more soluble than metal oxide & metal hydroxide
        - further attack by $\text{H}_2\text{O}$ & $\text{O}_2$
        - small pit on corroded metal
Corrosion of Iron

4. in the presence of sulfur dioxide
   – formed in the combustion of oil and coal
   – 1300 times more soluble in water than \( \text{O}_2 \)
   – oxidized to form sulfuric acid solution
      \( \rightarrow \) acid rain
Corrosion of Iron

4. in the presence of sulfur dioxide

• redox reaction

\[
\text{Fe(s)} + \text{SO}_2(g) + \text{O}_2(g) \rightarrow \text{FeSO}_4(s) \\
\text{FeSO}_4(s) + \text{O}_2(g) + 6\text{H}_2\text{O}(\ell) \rightarrow 2\text{Fe}_2\text{O}_3.\text{H}_2\text{O}(s) + 4\text{H}_2\text{SO}_4(\text{aq}) \\
4\text{H}_2\text{SO}_4(\text{aq}) + 4\text{Fe(s)} + 2\text{O}_2(g) \rightarrow 4\text{FeSO}_4(s) + 4 \text{H}_2\text{O}(\ell)
\]
Corrosion of Iron

4. in the presence of sulfur dioxide
   - $\text{H}_2\text{SO}_4$:
     - Once it produce, difficult to be removed
     - Allow corrosion continue
Corrosion of Iron

- Cathodic protection
- Painting

Usual method:
- Inhibit anodic process
- Inhibit cathodic process

To do both:
- Preventing of corrosion
Painting

- formation of thin film of oxide
- prevent the oxidation half reaction of metal
- iron oxidized by Cr(II) salt to form Cr(VI) and Fe(III) oxides.

\[ 2 \text{Fe(s)} + 2\text{Na}_2\text{CrO}_4(\text{aq}) + 2\text{H}_2\text{O}(\ell) \rightarrow \text{Fe}_2\text{O}_3(s) + \text{Cr}_2\text{O}_3(s) + 4\text{NaOH(aq)} \]

- \( \text{Cr}_2\text{O}_3 \) protect iron for further oxidation by \( \text{O}_2 \) & water
Passivation

• to force the metal to become passive

• thin oxide layer formed on the surface

• prevent further electrochemical reaction
Passivation

• aluminum
  – with oxygen form aluminum oxides
• stainless steel
  – alloy of iron & chromium
• special design of paint
  – \( \text{K}_2\text{Cr}_2\text{O}_7 \) & \( \text{Pb}_3\text{O}_4 \)
  – superficial oxidation & passivation of iron
Cathodic protection

- to force the metal to become the cathode in electrochemical cell
- attaching more readily oxidized metal
- e.g. galvanized iron (iron coated by zinc)
  → sacrificial anode

Zink prevent corrosion of iron
Cathodic protection

• $E^{\circ}_{\text{red}} \text{ Zn} < \text{ Fe} \text{ or } E^{\circ}_{\text{ox}} \text{ Zn} > \text{ Fe}$
• Zn more readily oxidized than Fe
• Anodic :
  \[ -2\text{Zn}(s) \rightarrow 2\text{Zn}^{2+} + 4\text{e}^- \]
• Cathodic :
  \[ -\text{O}_2 + 2\text{H}_2\text{O}(l) + 4\text{e}^- \rightarrow 4\text{OH}^- (aq) \]
• Redox :
  \[ -2\text{Zn}(s) + \text{O}_2 + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Zn(OH)}_2(s) \]
Cathodic protection

- $\text{Zn(OH)}_2(s)$:
  - less soluble than $\text{Fe(OH)}_2$
  - slows the corrosion of iron

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \]

\[ \text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \quad \text{Fe (cathode)} \rightarrow 2\text{e}^- + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O} \]
Mg used to prevent corrosion of iron in:

- buried pipe
- ship hulls
- bridges