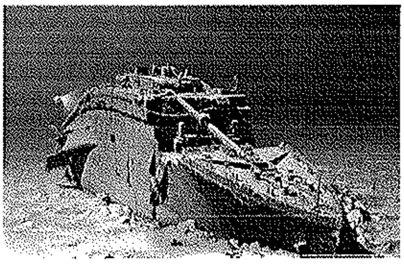
Corrosion at great depths



Corrosion at great depths

- The wreck of the Titanic was found in 4000m deep waters
- Ship wrecks at great depths are corroded by **electrochemical reactions** and by **anaerobic bacteria**

Corrosion at great depths

- Sufficient light for plant growth does not occur below 200m
- Dead organisms provide nutrients for deep-dwelling animals and micro-organisms
- Thermal vents from ocean floor release sulphur rich water
- Ocean floor 4°C
- Intense pressure reduces O_2 concentration (0.2ppb)
- Anaerobic condition prevail at this depth

Corrosion at great depths

- Some parts of the Titanic had long red hanging rusticles (rust-like / icicle-like)
- Other parts had black iron (II) sulfide
- Sulfate reducing bacteria (SRB) were important in forming the red rusticles and black FeS

Corrosion at great depths

- Bacteria associated with the rusticles are called "iron-eating bacteria"
- Two types of bacteria are found with the rusticles:
  -Anaerobic SRB which do not need oxygen are found on the inside
  -Oxygen dependent aerobic bacteria are found on the outside of the rusticles
- Chemical reactions carried out by this combination of bacteria increased the rate of corrosion of the iron in the Titanic

Corrosion at great depths

- Sea water normally has a pH 8 (almost all seawater cations are from strong bases (Na, K, Mg)
- But the increased solubility of CO_2 with depth makes deep ocean water slightly acidic

- **Carbon dioxide as bicarbonate**
  Carbon dioxide binds loosely with water to form bicarbonate: $CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow H^+ + H^+ + CO_3^{2-}$

Corrosion at great depths

- As the pH drops with depth in ocean water the presence of more hydrogen ions favours corrosion of metals
- Corrosion of metals with acid produces metal ions:
  $Fe + 2H^+ \text{-->} Fe^{2+} + H_2$
- Some metal ions produced can undergo hydrolysis (reaction with water) to produce even more hydrogen ions

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Corrosion at great depths

Describe the action of sulfate reducing bacteria (SRB) around deep wrecks

- Corrosion of metals with acid produces metal ions:
  $Fe + 2H^+ \text{-->} Fe^{2+} + H_2$
- The SRB are able to change the H_2 to $2H^+$ which they then use to reduce sulfate ions to hydrogen sulfide (H_2S)
- SRB produce hydrogen sulfide from the sulfate ions that are plentiful in sea water:
  $SO_4^{2-} + 10H^+ + 8e^- \text{-->} H_2S + 4H_2O$

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Corrosion at great depths

- Note that the oxidation state of sulfur has been reduced from:
  +6 in SO_4^{2-}
  to
  −2 in H_2S
- This is why the anaerobic bacteria that cause this change are called sulfate reducing bacteria (SRB)

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Corrosion at great depths

- Hydrogen ions can produce small acidic environments as low as pH 4 in some locations around a shipwreck
- H_2S produced by the action of SRB is a weak acid that releases hydrogen ions and sulfide ions:
  $H_2S \rightleftharpoons 2H^+ + S^{2-}$
- H_2S produced by sulfate reducing bacteria can react with just about any metal except gold and silver

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Corrosion at great depths

- The sulfide ions from the H_2S can precipitate Fe^{2+} ions to form insoluble black iron (II) sulfide FeS:
  $Fe^{2+} + S^{2-} \text{-->} FeS(s)$
- The presence of black FeS indicates that SRB are present
- The precipitation of FeS removes sulfide ions and encourages further ionisation of H_2S releasing more H^+

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Corrosion at great depths

- Metal near wood on the Titanic was badly corroded
- As the wood cellulose $(C_6H_{10}O_5)_n$ decayed it released oxygen which stimulated the growth of aerobic bacteria
- Waste from these aerobic bacteria provided nourishment to the anaerobic SRB
- Hence the SRB flourished and increased corrosion of metal near wood

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Corrosion at great depths

Acidic environments accelerate corrosion in non-passivating metals

- Acidic conditions lead to an acceleration of the corrosion process compared with basic or neutral conditions
- Hydrogen ions can react with non-passivating metals, such as iron.
  $Fe(s) + 2H^+ \text{-->} Fe^{2+} + H_2(g)$

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Corrosion at great depths

Account for the differences in corrosion of active and passivating metals

- Corrosion is the oxidation of metal in the presence of oxygen, water, and an electrolyte
- Non-passivating (active) metals such as iron continues to corrode because rust is a porous compound that allows oxygen and water to reach the fresh layers of iron below

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Corrosion at great depths

- **Passivation** is the spontanious process of making a material "passive" by the deposition of an oxide layer a few nanometers thick that adheres to the metals surface and inhibits further corrosion
- Metals with protective passivation layers include aluminium, chromium, titanium, and tin
- Non-passivating metals such as iron do not have a protective oxide layer that would prevent hydrogen ions reacting with metal atoms

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Corrosion at great depths

- **Rust** is formed when iron compounds corrode in the presence of water and oxygen to form a mixture of iron oxides and hydroxides
- Iron is found naturally as iron oxide and purified iron quickly returns to a similar state when exposed to air and water

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Corrosion at great depths

- This corrosion is due to the oxidation of a metal being an energetically favourable process: rust formation is exothermic
- The process of rusting can be summarised as three basic stages:
  -The formation of iron (II) ions from the metal
  -The formation of hydroxide ions
  -Their reaction together with the addition of oxygen to create rust

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Corrosion at great depths

The formation of iron (II) ions from the metal

- When an iron compound comes in to contact with a drop of water an electrochemical process starts
- On the surface of the metal iron is oxidised to iron (II):
  $Fe \text{->} Fe^{2+} + 2e^-$

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Corrosion at great depths

The formation of hydroxide ions

- The electrons released travel to the edges of the water droplet where there is plenty of dissolved oxygen. They reduce the oxygen and water to hydroxide ions:

  $2e^- + 1/2O_2 + H_2O \text{ -> } OH^-$

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Questions

1. How is a passivating metal protected from corrosion
2. Using equations explain how corrosion in a non-passivating metal such as iron is accelerated in an acidic medium
3. Identify if seawater is acidic or basic
4. Account for the presence of anaerobic bacteria at great depths in the ocean

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Corrosion at great depths

Their reaction together with the addition of oxygen to create rust

- The hydroxide ions react with the iron (II) ions and more dissolved oxygen to form iron oxide. The hydration is variable (with *x* water molecules surrounding each iron oxide molecule):

  $Fe^{2+} + 2OH^- \text{ -> } Fe_2O_3.xH_2O$

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Questions

5. Compare the role of electrochemical cells and anaerobic bacteria at great depths in the ocean
6. By using oxidation numbers demonstrate the reduction of sulfate ions to sulfide ions as utilised by anaerobic bacteria
7. Construct an equation to show the reduction of sulfate ions to form hydrogen sulfide and water by anaerobic bacteria

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Corrosion at great depths

Conclusion

- Rusting tends to happen faster in deep sea
- Ship wrecks at great depths are corroded due to factors such as: **pH, temperature, sulfur compounds, anaerobic bacteria, electrochemical reactions**

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Questions

8. By using equations describe how the iron in shipwrecks can react with hydrogen sulfide produced by anaerobic bacteria and water to produce an acid environment and iron hydroxide
9. Write an equation representing the effect of the acid microenvironment on corrosion
10. Outline how the above equation can account for the observation of corrosion found at the site of shipwrecks at depth

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