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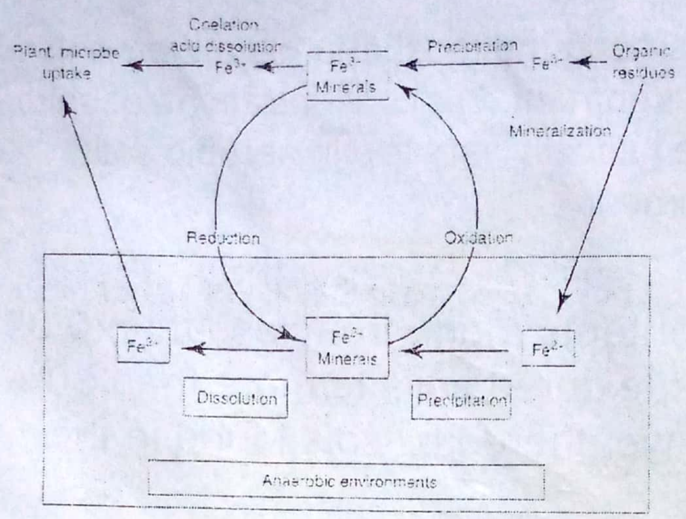
IRON

- Iron is among the most abundant elements in the soil environment, but concentrations of soluble iron are typically very low in aerobic soil environment.

- Iron contents range from less than 0.05% in coarse textured soils to more than 10% in highly weathered oxisols found in the tropics.

- The iron cycle is characterized by the oxidation and reduction of iron compounds in soils and sediments.

- However, mineralization from organically bound iron and solubilization of iron from inorganic compounds by microorganisms are also important processes.



- Chemical oxidation of Fe^{2+} occurs very rapidly under aerobic conditions at pH >3 and is the major pathway of iron oxidation in most soil environments.

- Under acidic conditions ferrus (Fe^{+2}) can be oxidized to ferric (Fe^{3+}) by chemotrophic bacteria such as *Thiobacillus ferroxidans*.

- Currently it is recognized that at pH values near neutrality, abiotic oxidation of ferrus iron commonly occurs.

- *Leptothrix* is a sheath-forming filamentous, chemorganotrophic bacterium that accumulates ferric iron. Its accumulation of $Fe(OH)_3$ in the sheath is believed to protect the bacterium from high levels of soluble iron in the environment.

- *Sphaerotilus* and *Crenothrix* are two other genera of sheathed bacteria that accumulate the iron compounds.
- The sheated bacteria may also produce large gelatinous masses that can clog iron pipes.

- When these bacteria die, their decomposition may cause a disagreeable odor. The $Fe(OH)_3$ remain as a red precipitate.

- Iron –precipitating bacteria in wells and pipes can usually be killed by agents such as chlorine bleach.

- Apart from *Thiobacillus ferroxidans, diverse other bacteria are now known to accomplish* Fe^{2+} *oxidation enzymatically*. These include, *Leptospirillum ferroxidans, sulfolobus* spp., *Acidianus* spp. *and Gallionella* spp.

- Just as iron can be oxidized enzymatically and nonenzymatically, iron reductions can occur by a number of processes.
  - Ferric iron iron can act as a respiratory electron acceptor.
  - It can also be reduced by reactions with microbial end products such as fromate or H_2S.
  - Bacteria, in genera such as *Bacillus*, *Pseudomonas*, *Desulfovibrio*, and *Thiobacillus*, and fungi such as *Alternaria*, and *Fusarium* are capable of Fe^{3+} reduction.

- The enzyme nitrate reductase may be involved in the reaction; NO_3^- if present usually inhibits iron reduction.

Transformations of Iron in Nature

- In nature, the oxidation-reduction processes over geologic time continue through sediments to sedimentary rocks and result in the formation of minerals such as goethite and pyrite.

- In the presence of sulphate and sulphate reducing bacteria, the reduced iron reacts with H_2S to form pyrite (FeS_2).
- As sulphates are in excess in oceanic waters so iron content of the ocean water is maintained at a very low concentration.

- Iron oxidations and reductions play a major role in the soil formation process known as **gleization**.

- Under waterlogged conditions, a light gray to greenish color attributable to the presence of reduced Fe is produced.

- Gleyed soils usually have mottled spots of Fe_2O_3, where root channels or cracking have permitted localized oxidation.

- The gleying reaction is useful for sealing the soil under ponds.

- If a layer of straw approximately 15 cm is buried at the bottom of a pond and covered with 15 cm of soil, the decay of the straw causes reduction of Fe^{3+} to Fe^{2+} and of SO_4^{2-} to S^{2-}. FeS_2 is precipitated and the soil colloids are dispersed resulting in an effective seal.

- In well-aerated soils, Fe^{3+} is the dominant form of iron.
- The activity of Fe^{3+} in soil solution under aerobic conditions is low.
- The low solubility of Fe^{3+} in alkaline soils results in iron-deficient conditions for plants and microorganisms.

- Many microorganism produce Fe^{3+}- complexing, low molecular weight, organic compounds having strong affinity for iron through the process of chelation.
- These compounds are called ferrichromes or **siderophores**.
- Siderophore producing microorganisms act in the control of root pathogens.

- Translocation of Fe is involved in the soil **podzolization** process in which Fe- and organic-rich subsurface horizons of spodosols are formed.

- Organic acids and chelating agents produced by microorganisms in upper horizons solubilize Fe; this is leached downward by percolating rainwater.

- Precipitation of Fe in the soil B horizon results in the formation of spodosols, consisting of a leached upper layer and an organic and Fe-rich B horizon.

- A soil-forming process in which Fe is left on the surface while silica is translocated downward by leaching results in the **laterization** process that occurs in tropical soils.

Anaerobic Corrosion of Iron Pipes

- Microorganisms participate in aerobic and anaerobic corrosion processes.

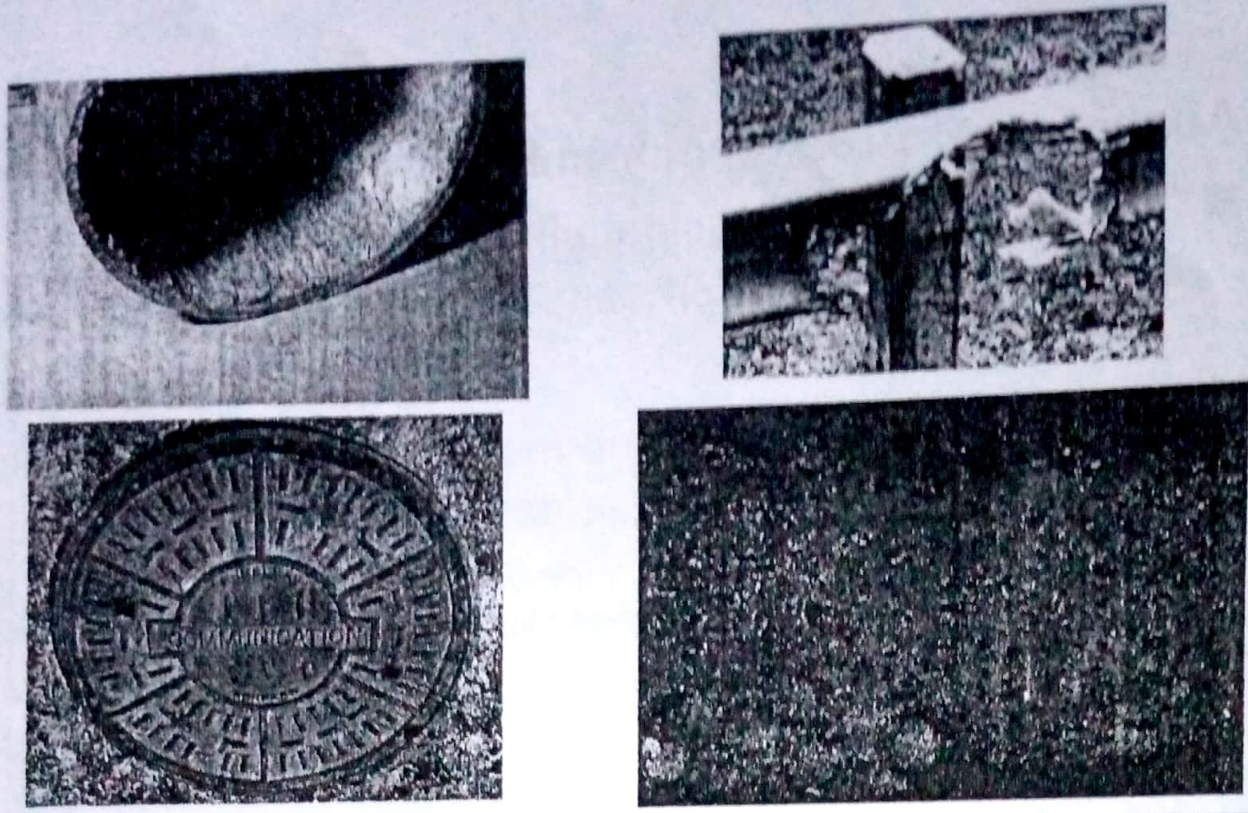
- In anaerobic corrosion, the metal surface acts as an anode in an electrochemical reaction and is transformed to Fe^{2+}.

- An equivalent number of H^+ ions are produced at the cathode site.

- The anaerobic, sulfate-rcducing bacterium *Desulfovibrio* produces S_2^- , which reacts with Fe^{2+} to produce FeS.
- At the same time, hydroxyls from water react with H^+ ions. The overall reaction is:

$$4Fe + SO_4^{2-} + 4H_2O \longrightarrow FeS + 3FeOH^{2-} + 5OH^-$$

- The conditions required for the reaction include anaerobic sites at redox potentials less than - 400 mV, a pH greater than 5.5, low free O_2 content, and the presence of SO_4^{2-} .



- Under these conditions, an Fe pipe of 3-mm wall thickness can be corroded through in 5 to 7 years.
- This is one of the most costly microbial reactions in nature. It means that buried Fe pipes must be continually replaced or else protected by wrapping with asphalt or plastic.

- Additional protection is obtained by maintaining a small electrical current along the pipe (cathodic protection) to prevent the formation of an electrode half-cell.

- Other corrosion processes are accomplished by miscellaneous aerobic and facultative bacteria.
- The corrosion by these organisms, although appreciable, is not as economically important as the anaerobic process.

Microbial Participation in Ore Leaching

- Microbial leaching of ore bodies *in situ*, in stockpiles, or in mine tailings makes metal recovery feasible from low-grade ores in which the metal is not economically recoverable by smelting.

- Leaching is commonly used for recovery of copper (Cu) and uranium.

- Ferric sulfides usually accompany the Cu sulfides in ore and hence Fe transformations are components of the reaction chain.

- Ferrous iron is formed in the ore body by reaction of ferric iron with CuS

$$2Fe^{3+} + CuS \longrightarrow Cu + 2Fe^{2+} + S^0$$

- The mobilized Cu is recovered from the leachate by sedimentation, solvent action, or electrolysis.

- The Fe^{2+} remaining after Cu removal is reoxidized.

- Sulfur-oxidizing bacteria convert S° to sulfuric acid. This acid fortifies the leaching solution, which is recirculated following the metal harvest.

- Inoculation of the ore body with microorganisms is usually unnecessary.

- Normally occurring Fe and S oxidizers and acidophilic heterotrophs establish themselves unaided.

- Among important species in ore leaching are the following: *Thiobacillus ferrooxidans*, *T.thioxidans*, and *Leptospirillum ferrooxidans*.