

# Iron and Manganese Cycle

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# Reduction and Solubilisation reactions

- In an anaerobic or anoxic medium, the oxidised forms Fe(III) and Mn(IV) can act as electron acceptors thus enabling the different biodegradable organic matter (glucids, organic acids ...) to be oxidised via the bacterial method, the final stage being CO<sub>2</sub>.
- This process, termed **dissimilatory reduction**, causes **iron and manganese to become soluble**, as a result of a simultaneous reduction in Eh and **pH** and the appearance of reduced Fe<sup>2+</sup> and Mn<sup>2+</sup> ions in the water.

# Reduction and Solubilisation reactions

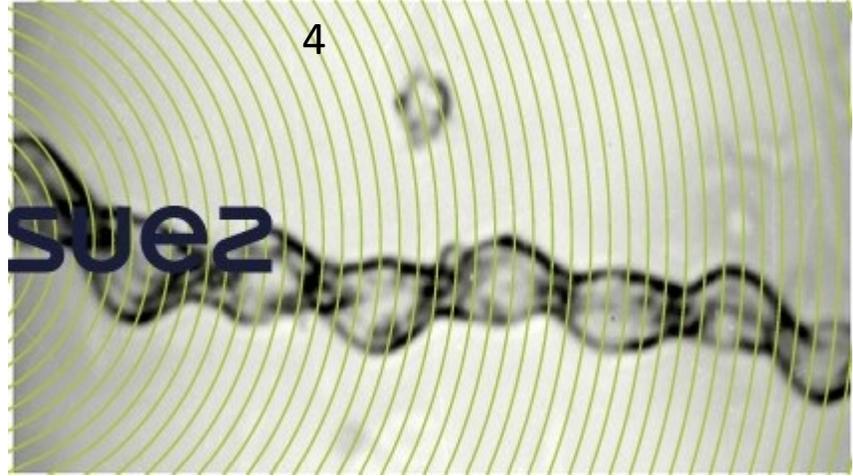
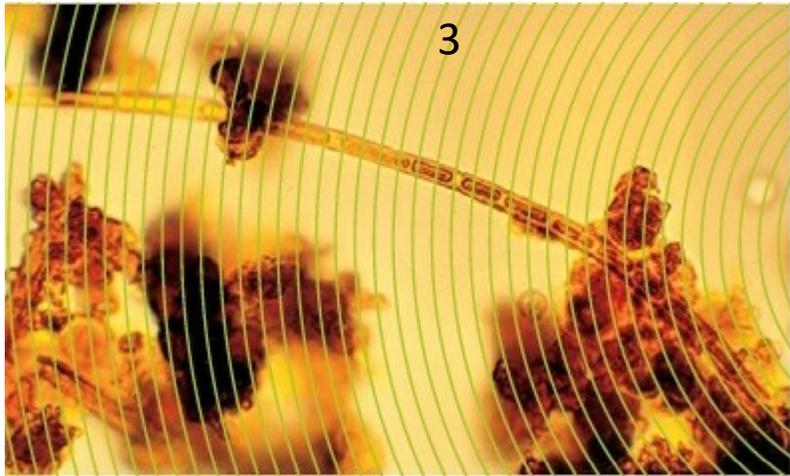
- These reactions are caused by many heterotrophic bacteria where the *Acinetobacter*, *Bacillus*, *Pseudomonas* are present in significant numbers.
- In the natural environment, these bacteria occur frequently in ground water and sediments where they constitute one of the most important biogeochemical phenomena (which is why iron and manganese have to be removed from groundwater and lake bed water).
- These bacteria can also be found in fouled filters when they go into a state of anoxia during a shutdown period.

# Oxidation reactions

- In an aerobic or micro-aerobic medium, depending on its **pH**, some specific bacteria may encounter conditions that encourage their development by promoting them to oxidise Fe(II) and Mn(II).

# Iron Oxidation

- Iron oxidation is an **exothermic reaction** that can be catalysed by some bacteria because of the oxidation-reduction enzymes they excrete (**flavins**): trivalent iron, rendered insoluble as the **hydroxide**  $\text{Fe}(\text{OH})_3$  or **oxyhydroxide**  $\text{FeOOH}$ , then accumulates over mucilaginous secretions (sheaths, stalks, capsules) produced by these bacteria. The organisms responsible for these phenomena are primarily the Siderobacteria and specifically :
  - **Chlamydobacteriaceae**: *Leptothrix* (*L. ochracea*, *L. crassa*, *L. discophora*);
  - **Crenothricaceae**: *Crenothrix* (*Cr. polyspora*), *Clonothrix* (*Cl. ferruginea*, *Cl. fusca*);
  - **Siderocapsaceae**: *Siderocapsa*, *Ferrobacillus*, *Sideromonas*;
  - **Gallionellaceae**: *Gallionella* (*G. ferruginea*, *G. major*);
  - or **Protobacteriaceae** (*Thiobacillus ferro-oxidans*).



**Photo 3 & 4. *Leptothrix ochracea* & *Gallionella ferruginea***

- This oxidation process has two purposes :
  - providing the energy required for the development of autotrophic species
  - detoxifying the medium by removing dissolved iron which is deleterious to this type of bacteria.
- Of these different bacteria, three main types can easily be recognised under a microscope:
- ***Leptothrix***: Filament (or trichome) containing a single line of cylindrical cells enclosed in a sheath; this sheath starts off as thin and colourless before thickening and becoming increasingly brown in colour as it is impregnated with oxidised iron (photo 3).
- ***Crenothrix***: Trichomes flare out at one end. It is through this end that the sporulated cells (conidia) escape in several rows to form new trichomes. Their sheath changes in the same way as that of the *Leptothrix*.
- ***Gallionella***: isolated cells, in principle attached to a spiral stalk (which may or may not be ramified) that these cells have secreted. In fact, this is a fragile connection and it is not unusual to find just the stalk (photo 4).

# Manganese oxidation

- Most of these organisms (except *Gallionella*) are also capable of converting manganese into  $MnO_2$  through oxidation providing the iron oxidation has been completed when these two elements were present together at the outset; in addition, other bacteria have a specific action in this respect, e.g:
- true bacteria: *Pseudomonas* (*Ps. manganoxydans*), *Metallogenium* (*M. personatum*, *M. symbioticum*);
- Siderobacteria: *Leptothrix* (*L. echinata*, *L. lopholes*);
- Hyphomicrobia: *Hyphomicrobium* (*H. vulgare*).

# Practical consequences

- The action exercised by these micro-organisms constitutes the basis of **biological treatment** used to remove iron and manganese from groundwater (please refer to **eliminating iron and manganese removal**). However, this action can be harmful in raw water catchment basins by causing **clogging inwells**, and inside cast iron or steel pipes by causing **bacterial corrosion** (please refer to **microbiological corrosion**).