Lectures 9-10
More Aqueous Geochemistry of Natural Waters – OXIDATION/REDUCTION (aka Redox)

please read these bits in White
For the first two lectures of the week
- *Ch3 (100-110), Ch13 <u>digital</u> (555-563)*
  - *(note, there is no Ch 13 in the hardcopy text)*

for Friday
- *Ch12 (12.1-12.6) -or- White digital Ch14 (589-626)*

"Master variables" in aquatic chemistry:

<u>Redox state</u> is one of two fundamental chemical controls on the compositional make up of natural and non-natural waters.

<u>pH</u> is the other.

1. Oxidation- Reduction:

Review of "oxidation state" concept.

Oxidation state is a measure of the charge on an atom in any chemical form. It is the atomic number minus the number or orbital electrons a chemical species contains.

For monatomic species, it is equal to the ionic charge (e.g., Fe^{+3} ox. state = +3, Cl^- ox. state = -1).

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1. Oxidation- Reduction: *Review of "oxidation state" concept.*

For atoms in molecules or compound ions...

oxidation state is calculated using these 6 simple rules:

a. the algebraic sum of the oxidation states of individual atoms in a compound equals the charge on that compound

(e.g., for SO_4^{2-}: ox state O= -2, ox state S= +6)

b. any atom bonded only to itself (i.e., in a pure covalent bond) is given an oxidation state of 0

(e.g., N, O and H in O_2, N_2 and H_2, respectively).

c. the oxidation state of O is -2 in all compounds except peroxides

(H_2O_2, Na_2O_2)

1. Oxidation- Reduction: *Review of "oxidation state" concept.*

some more simple rules:

d. The oxidation state of H is +1 in all compounds

Exceptions:

1. when bound to itself (e.g., H_2, as per rule "b")

2. where a metal-hydrogen bond exists, where H is -1 ("hydride").

e. halogens are assigned an oxidation state of -1 in compounds lacking H and O

Exceptions:

1. when bound to itself (e.g., Cl_2, as per rule "b")

2. When bound to O

f. Generally assume that alkali metals (e.g., Ba) and alkaline earths (e.g., Ca) have ox. states of +1 and +2, respectively.

Remember:

Oxidation state is an approximation of charge distribution in molecules.

With strongly ionic bonds, the oxidation state we assign with these rules are probably pretty close to reality.

Example:

in the molecule **NaCl**

Cl is given a charge of -1

Na is given a charge of +1, to allow the molecule's charge to be zero.

The bond is highly ionic so oxidation states are realistic measures of electron distribution.

But, in covalent molecules, electrons are "shared" rather than transferred. Assigned oxidation states are not close to reality.

Example:

the molecule **N-O**

The oxidation state rules and calculation tells us that:

O is -2 (an assigned value)

N is given a charge of +2

O = -2 and N = +2 implies that N has donated two of its valence electrons to O.

But, we know that bonds between direct neighbors in the periodic chart are mostly covalent (close to true electron sharing), so that this "donation" is not really taking place.

Nevertheless, the oxidation-state convention is still very useful – we use it to balance the net flow of electrons in redox reactions.

Redox in chemical reactions
Our rules help us understand for instance that

$NO + ClO^- \leftrightarrow NO_2 + Cl^-$
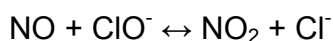
is a redox reaction where 2 electrons are transferred per reactant molecule going to product.

compound:	element:	Ox. State
reactants		
NO	O	-2
NO	N	+2
ClO$^-$	O	-2
ClO$^-$	Cl	+1
products		
NO$_2$	O	-2
NO$_2$	N	+4
Cl$^-$	Cl	-1

2. Half Reactions:

Any Redox reaction can be broken down into two "half reactions":

One half reaction will be an oxidation and one will be a reduction.
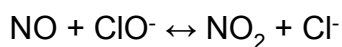A simple rule is......

LEO the lion goes "GER"

Lose an <u>E</u>lectron is <u>O</u>xidation,

<u>G</u>ain an <u>E</u>lectron is <u>R</u>eduction

Half Reactions

Let's decompose the reaction I mentioned 2 slides ago:

$NO + ClO^- \leftrightarrow NO_2 + Cl^-$

is really the sum of these two 1/2 rxns:

$NO \leftrightarrow NO_2 + 2e^-$ and $ClO^- + 2e^- \leftrightarrow + Cl^-$.
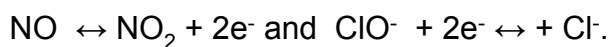
As written, both 1/2 rxns are balanced for electrons but not for material (1 atom of O is missing from each). If we were looking in a table of 1/2 rxns, we would actually find these:

$NO + H_2O \leftrightarrow NO_2 + 2e^- + 2H^+$ "L E O"

$ClO^- + 2H^+ + 2e^- \leftrightarrow + Cl^- + H_2O$ "G E R"
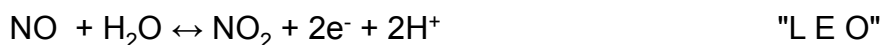
when added back together, the H_2O and $2H^+$ cancel out.

3. The Nernst Equation:
$\Delta E = \Delta E^o + (0.059/n)\log Q$ at 298° K

We describe this system at equilibrium (when Q =K) using $\Delta E = 0$
$\Delta E^o = -(0.059/n)\log K$, where $K = \dfrac{[NO_2][Cl^-]}{[NO][ClO^-]}$

ΔE^o_{rxn} is calculated by adding the applicable 2 $E^o_{1/2rxn}$, which we get out of a table ("rxn"= reaction). $E^o_{1/2rxn}$ are tabulated for 1/2 rxns written as reductions or oxidations.

(Note: $E^o_{1/2rxn}$ is often abbreviated as E^o; ΔE^o_{rxn} is often abbreviated as ΔE^o).

E^o are given relative to the Standard Hydrogen Electrode

upon which the 1/2 rxn $2H^+ + 2e^- \rightarrow H_2$ occurs

and for which E^o is given a value of 0.000 volts.

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4. Redox poising and The concept of pE:

In natural systems, it is common for the extent to which Redox reactions will occur to be limited by the availability of electrons being controlled by one dominant half-reaction. We then say that the system is *poised* at or near a certain value.

Poising is exactly analogous to **buffering** of pH by weak acids and bases.

In **Redox poising**, the availability of electrons is close to fixed by a predominant redox reaction

in **acid-base buffering**, the availability of H^+ ions is close to fixed by a predominant acid-base reaction.

4. The concept of pE:
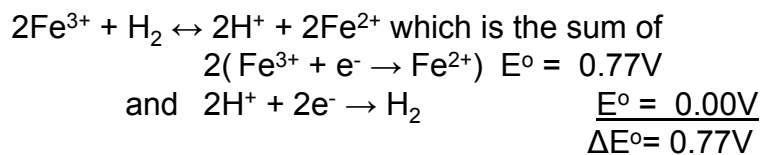
pE is defined analogously to pH :

pH = -log[H$^+$] (H$^+$ = hydrogen ion concentration)

pE = -log[e$^-$]   (e$^-$ = electron concentration)

How can you define the activity of an electron in a solution when none actually exist as free entities?

pE is a concept not a reality.

$2Fe^{3+} + H_2 \leftrightarrow 2H^+ + 2Fe^{2+}$ which is the sum of
$\qquad 2(Fe^{3+} + e^- \rightarrow Fe^{2+})$ $E^o = 0.77V$
$\qquad$ and $\quad 2H^+ + 2e^- \rightarrow H_2$ $\qquad \underline{E^o = 0.00V}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Delta E^o = 0.77V$

the equilibrium expression for the top ½ reaction is:
$K = [Fe^{2+}]/[Fe^{3+}][e^-]$

Rearranging....$\qquad [e^-] = [1/K] \bullet [Fe^{2+}]/[Fe^{3+}]$
and $\qquad\qquad\qquad$ -log $[e^-]$ = -log[1/K] -log($[Fe^{2+}]/[Fe^{3+}]$)
$\qquad\qquad\qquad\qquad \downarrow \qquad\qquad\quad \downarrow$
$\qquad\qquad\qquad$ pE $\quad = \quad$ pE^o $\quad$ -log($[Fe^{2+}]/[Fe^{3+}]$)

In a more general form: pE = pE^o - (1/n)log(red/ox)
-or-$\qquad\qquad\qquad$ **pE = pE^o + (1/n)log(ox /red)**
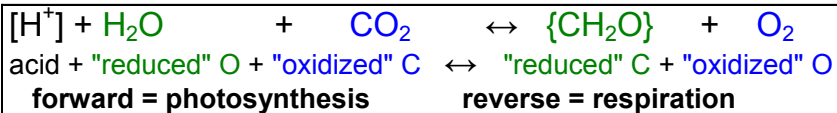
7

Other relationships:

$\Delta G_{rxn} = n f \, \Delta E$ (f is the Faraday constant, 23.06 kcal/V·g)
$pE^o = \dfrac{\log[K]}{n}$ *and* $\log[K] = \dfrac{-\Delta G^o}{2.3RT}$
$pE = \dfrac{-\Delta G^o}{n\,2.3RT} + \dfrac{\log(ox/red)}{n}$
$pE = E\left(\dfrac{f}{2.3RT}\right)$ *and* $pE^o = E^o\left(\dfrac{f}{2.3RT}\right)$
$pE = \dfrac{E}{0.059}$ *and* $pE^o = \dfrac{E^o}{0.059}$ at 25°C

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5. Biological control on pE and pH:

The cycle of photosynthesis and respiration is one process that governs the "availability" of electrons (and pH) in natural waters.

This can be schematically represented as a "redox" reaction:

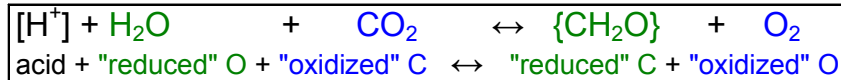| |
|---|
| $[H^+] + H_2O$ + CO_2 ↔ $\{CH_2O\}$ + O_2 |
| acid + "reduced" O + "oxidized" C ↔   "reduced" C + "oxidized" O |
| **forward = photosynthesis**   **reverse = respiration** |
| |
| *this reaction is not balanced as written for H; in fact the only about 0.17 mole H^+ is consumed per mole of CO_2 converted to organic matter.* |
| |
| *For simplicity we write generic organic matter as carbohydrate: "$\{CH_2O\}$"* |
| |
| *We discuss the details of this reaction later this week.* |

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5. Biological control on pE and pH:

$$[H^+] + H_2O \quad + \quad CO_2 \quad \leftrightarrow \quad \{CH_2O\} \quad + \quad O_2$$

acid + "reduced" O + "oxidized" C $\leftrightarrow$ "reduced" C + "oxidized" O

✓ For waters with excess photosynthesis, O_2 builds up and pE increases (gets more oxidizing).

✓ The opposite is true in respiration-dominant waters.

In essence, plants are the major "**reducing**" agents of carbon on Earth

and respiring organisms are the "**oxidizers**".

Aerobic respiration uses O_2 to Oxidize $\{CH_2O\}$.

As we discuss next lecture…

some microbial organisms use other oxidizing agents to oxidize $\{CH_2O\}$ in environments where O_2 is absent or rare.

These microorganisms specialize in using one or another electron receptor to release energy from "fixed" (reduced) C in the form of organic matter.

This oxidant gets reduced as it is used by the microbe to break down $\{CH_2O\}$.

The 1/2 rxn for this microbial process poises pE at a value that is lower then the one set by photosynthesis and respiration.
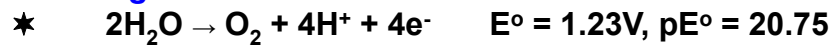
6. The limits of pE and pH in natural waters.
The limits on natural pE and pH in waters are the limits of stabilitly of water itself.

Water is stable if the availability of electrons is such that it is not all oxidized or reduced by these 1/2 rxns:

oxidizing limit
✶ $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $E^o = 1.23V, pE^o = 20.75$

reducing limit
✶ $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

only the oxidation state of H changes in this reaction, so this is equivalent to:
✶ $4H^+ + 4e^- \rightarrow 2H_2$ $E^o = 0V, pE^o = 0$

✶ The oxidizing limit for the stability of water can be described as a function of E^o (or pE) and pH:

$$E = E^o + 0.059/n \cdot \log (P_{O2}[H^+]^4/[H_2O])$$
which reduces to this following, using n=4 and P_{O2} =1 atm
$$E = E^o + 0.059/4 \cdot 4\log (P_{O2}[H^+]/[H_2O])$$
or $E = E^o + 0.059\log [H^+]$
or $E = E^o - 0.059pH$

$E = -0.059pH + 1.23V$
or $pE = -pH + 20.75$ *in terms of pE*

Solving instead using P_{O2}=0.2 atm (the value in the modern atmosphere instead of P_{O2}=1 atm), the equation becomes:

$$E = -0.059pH + 1.22V \text{ (small shift).}$$
The corresponding pE/pH equation is also slightly shifted.

✹ And the reducing limit for the stability of water @ H_2=1 atm is:

$$E = E^o + 0.059/n \cdot \log ([H^+]^4/P_{H2}^2)$$

which reduces to this following, using n=4 and P_{H2} =1 atm

$$E = E^o + 0.059/4 \cdot 4\log ([H^+]^4/P_{H2}^2)$$

or $\qquad E = E^o + 0.059\log [H^+]$

or $\qquad E = E^o - 0.059pH$

$E = - 0.059pH + 0V$
or $pE = - pH$ $\qquad$ *in terms of pE*

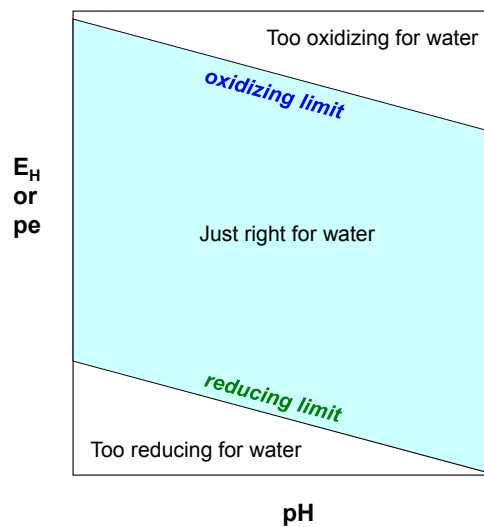### 7. pE/ pH and E_H/pH diagrams.

These stability limits of water are linear equations of the form
$y = mx + b$, where "x" is pH

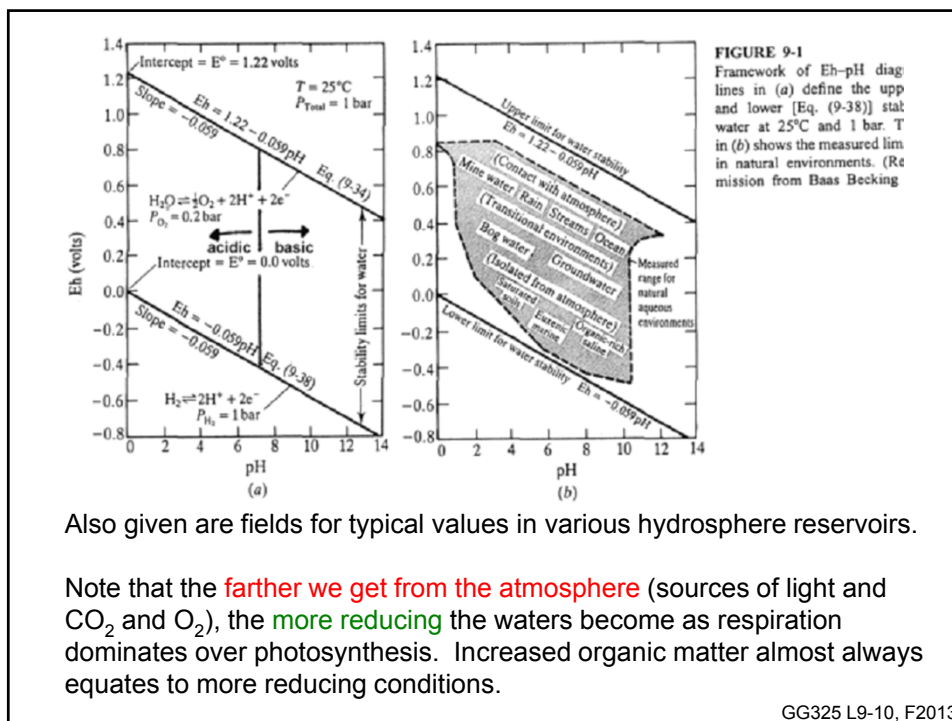$y = E_H$ $\qquad$ m = - 0.059 $\qquad$ b = E^o $\qquad$ -or-

$y = pE$ $\qquad$ m = 1 $\qquad$ b = pE^o

These are parallel lines on EH vs pH or pE vs pH plots (see below)
The parallelogram defines the stability of water on Earth's surface in terms of E_H and pH

FIGURE 9-1
Framework of Eh–pH diag[ram]
lines in (a) define the upp[er]
and lower [Eq. (9-38)] stab[ility of]
water at 25°C and 1 bar. T[he diagram]
in (b) shows the measured lim[its]
in natural environments. (R[eprinted with per-]
mission from Baas Becking[...])

Also given are fields for typical values in various hydrosphere reservoirs.

Note that the farther we get from the atmosphere (sources of light and CO_2 and O_2), the more reducing the waters become as respiration dominates over photosynthesis. Increased organic matter almost always equates to more reducing conditions.

8. Other ions in the water stability field.

For any solute ion, or combination of solute ions, we can create "phase" diagrams that will tell the *speciation* (form) of that ion in E_H vs. pH or pE vs. pH space for a given solute concentration in solution.
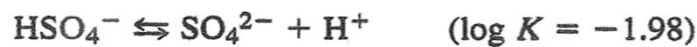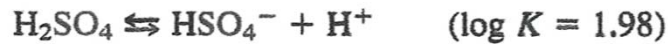
Mixed ion diagrams are quite complex to construct but single ion diagrams are not.

Each speciation field in an E_H/pH or pE/pH diagram is governed by a chemical reaction and each boundary is the location where the activity products = activity reactants.

Vertical lines have are dependent on pH only (no electron transfer)

Let's look at the Sulfate-sulfide system:

Using the equilibrium expressions and K values it is easy to show that at $[HS^-] = [H_2S]$ at pH = 7, which is the basis of a line on a pH-pe plot. This line happens to not be dependent on pe since no electrons are transferred in this chemical reaction.

$$H_2SO_4 \leftrightarrows HSO_4^- + H^+ \qquad (\log K = 1.98)$$

$$HSO_4^- \leftrightarrows SO_4^{2-} + H^+ \qquad (\log K = -1.98)$$

$$H_2S \leftrightarrows HS^- + H^+ \qquad (\log K = -7)$$

$$HS^- \leftrightarrows S^{2-} + H^+ \qquad (\log K = -12.9)$$

and the redox half reaction that couples sulfate to sulfide:

$$SO_4^{2-} + 8H^+ + 8e^- \leftrightarrows S^{2-} + 4H_2O \qquad (\log K = 20.74)$$

redox changes are non vertical lines.

Diagram for water

acid-base equilibria

Full pe-Ph diagram for sulfur

non-Vertical lines are dependent pE (electron transfer) and sometimes pH.

Each line is governed by an equilibrium expression

This boundary marks equal activities of SO_4^- and S^{-2} as in the rxn below.

This eqn. corresponds to a pE-pH line: $pE = 2.6 - pH$

$$SO_4^{2-} + 8H^+ + 8e^- \leftrightarrows S^{2-} + 4H_2O \qquad (\log K = 20.74)$$

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These diagrams are for Fe oxides and hydroxides in water.

FIGURE 9-2 Eh-pH diagram for the simple ions of iron at 25°C and 1 bar. The dashed lines denote Eh and pH conditions for equal activities of the aqueous species. Lines marked A, B, and C represent equal activities of iron species determined from Eq. (9-11), (2-27), and (9-42), respectively. Redox potential is expressed as volts (Eh) on the left side and as pe on the right side. (Reprinted by permission from Nordstrom and Munoz, 1985.)

Figure 6.16 Stability fields for hematite, magnetite, and aqueous ions in water at 25°C and 1 atm total pressure. Boundaries involving aqueous species are calculated by assuming that the total activity of dissolved species is 10^{-6}. Lighter-weight lines indicate the field boundaries when the sum of dissolved species activities is 10^{-4}.

Note that such diagrams depend on the total concentration of the element in the system.

The bold solid line is marked with stars is for $[Fe] = 1 \times 10^{-6}$. A lighter line to its left is shown for $[Fe] = 1 \times 10^{-4}$.

Dissolved ions: only exist in fairly acidic media (to the left of the line marked with stars).

Insoluble forms: Except for low pE situations, Fe is not particularly soluble in basic media.

Diagram like the one on the right concern themselves only with the dissolved forms.

Boundaries A, B and C are examined on the next slide.

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A. $Fe^{3+} + e^- \rightarrow Fe^{2+}$. There is no pH dependence, so the slope of the line is 0

A horizontal line

$E_H = E^o + \log [Fe^{3+}]/[Fe^{2+}]$, so $E_H = E^o$, since $[Fe^{3+}]=[Fe^{2+}]$

B. $Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$. There is no transfer of electrons. This is simply a speciation change for Fe(III).

$\log K = \log[Fe(OH)^{2+}][H^+]/[Fe^{3+}] = \log[Fe(OH)^{2+}]/[Fe^{3+}] + pH$
$\log K = 2.2$ at $298°K$ and $P= 1$ atm (from a thermodynamic data table).

Thus,
solving at $[Fe(OH)^{2+}] = [Fe^{3+}]$

$2.2 = \log [Fe(OH)^{2+}]/[Fe^{3+}] + pH$
$\rightarrow\rightarrow \quad 2.2 = pH$
a vertical line at pH = 2.2

C. $Fe^{2+} + H_2O \ ^o \ Fe(OH)^{2+} + H^+ + e^-$ $\qquad E^o = 0.900$

$E_H = 0.900 + 0.059 \ C \log [Fe(OH)^{2+}]/[Fe^{2+}] - 0.059 \ C \ pH$

at $[Fe(OH)^{2+}] = [Fe^{2+}] \ \rightarrow\rightarrow E_H = 0.900 - 0.059 \ C \ pH$
this line is parallel to those bounding the stability field of water.

9. Multiple species in the water stability field.

We can also construct more complicated (mixed species) diagrams for the case of one cation and many anions, many cations and one anion or many cations and many anions.

Here's an example for the Fe, O_2, H_2O, S and CO_2 system showing ions and solids.

The orange and yellow fields are affected by the presence of other biologically important elements.
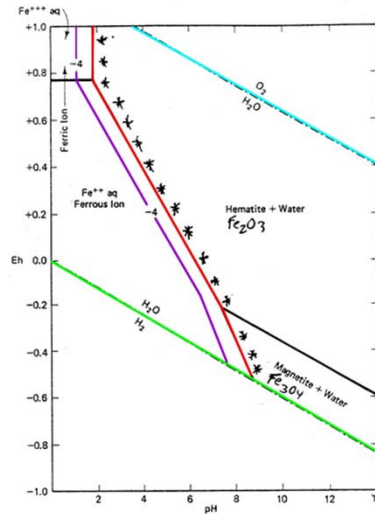
Figure 6.16 Stability fields for hematite, magnetite, and aqueous ions in water at 25°C and 1 atm total pressure. Boundaries involving aqueous species are calculated by assuming that the total activity of dissolved species is 10^{-6}. Lighter-weight lines indicate the field boundaries when the sum of dissolved species activities is 10^{-4}.
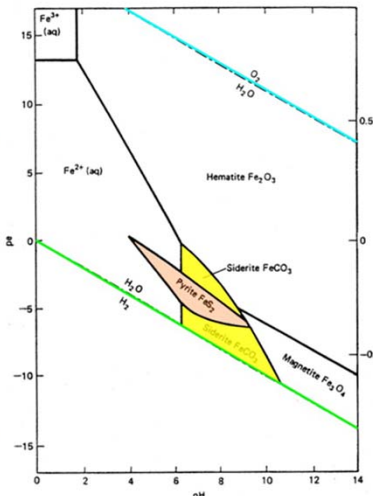
Figure 13-12 Stability relations in the system Fe–O–H₂O–S–CO₂ at 25°C, assuming $\Sigma S = 10^{-6}$, $\Sigma CO_2 = 10^0$ (after Garrels and Christ, 1965).

The orange and yellow fields on the mixed ion pE diagram of the previous page are affected by the presence of the biologically important elements shown below, which are also redox sensitive.
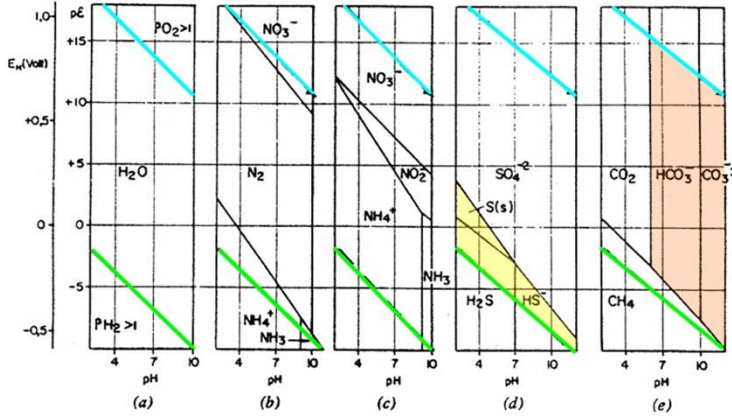

Figure 7.8 pε–pH diagrams for biologically important elements (25°C). (a) The upper and lower lines represent equations 44 and 43, respectively, the oxygen and hydrogen equilibria with water. (b) The nitrogen system, considering only stable equilibria. The only oxidation states involved are (-III), the elemental state, and (V). (c) NH_4^+, NH_3, NO_3^- and NO_2^- are treated as species metastable with regard to N_2; that is, N_2 is treated as a redox inert component (cf. Figure 9.10c and text). (d) Sulfur species stable for assumed conditions are SO_4^{2-}, elemental sulfur, and sulfides (cf. Figure 7.5 and Example 7.7). (e) The thermodynamically possible existence of elemental C (graphite) is ignored.

The "Redox Ladder"

In suboxic (limited O_2) or anoxic waters (no O_2) we find a predictable pattern of redox poise values that arise from bacterial usage of different half reactions that microbes use to digest organic matter.
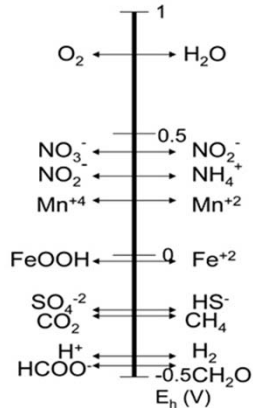
In this sequence the most energetically favorable reactions occur first and reactions that release less energy follow.

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The general order of microbially-mediated reactions after O_2 consumption is:

$NO_3^- \rightleftarrows N_2$ or NO_2^- (soluble species $\rightleftarrows$ soluble species)
$MnO_2 \rightleftarrows Mn^{2+}$ (insoluble species $\rightleftarrows$ soluble species)
$Fe_2O_3 \rightleftarrows Fe^{2+}$ (insoluble species $\rightleftarrows$ soluble species)
$SO_4^{2-} \rightleftarrows H_2S$ (soluble species $\rightleftarrows$ soluble species)
$CH_2O \rightleftarrows CH_3OH$ (fermentation)
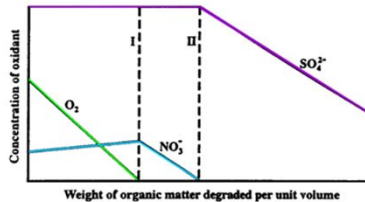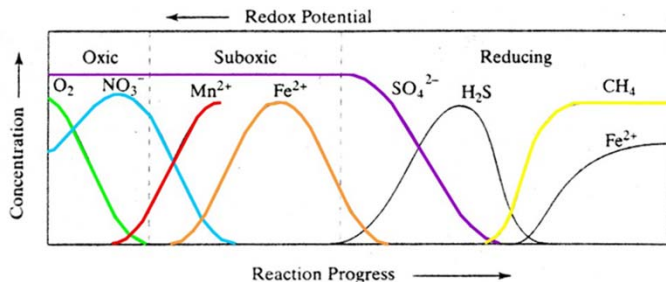CO_2 or $CH_2O \rightleftarrows CH_4$ (methanogenesis)

Figure 6.11. Oxidation of organic matter by O_2, NO_3^-, and SO_4^{2-}.

From Manahan, "Environmental Chemistry"

Aspects of some of these reactions are shown in these two figures.

FIGURE 5–15 Conceptual changes in concentrations of redox parameters with time or distance along a flow path when organic carbon and appropriate electron acceptors are present (reprinted from: *Geochemistry, Ground Water, and Pollution*, revised edition, Appelo, C. A. J. and D. Postma, 1996, A. A. Balkema, Rotterdam). *from Kehew, "Applied Chemical Hydrology"*
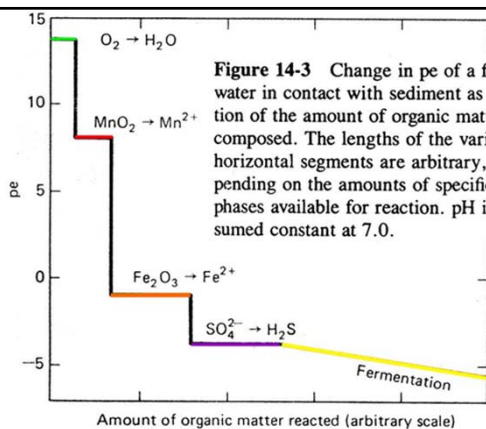

Figure 14-3 Change in pe of a fresh water in contact with sediment as a function of the amount of organic matter decomposed. The lengths of the various horizontal segments are arbitrary, depending on the amounts of specific solid phases available for reaction. pH is assumed constant at 7.0.

In a system where the **"Redox Ladder"** reactions are posing the water, a stepwise pE profile is formed wherein at a particular place or time, pE is fixed until a particular oxidant is consumed

This example, which may represent depth in a sediment or horizontal distance along and isolated fluid flow path, shows poise values for most of the common natural oxidants.

More general redox categories:

	oxidant
Oxic:	O_2 or NO_3^-
Suboxic:	MnO_2 or Fe^{+3}
Reducing:	SO_4^{2-} or CO_2

Remember, oxidants oxidize something else, meaning they get reduced in the process (e$^-$ acceptor = "GER")

During **"Redox Ladder"** reactions , organic carbon (DOC or POC) is getting oxidized meaning that C is the reductant (e$^-$ donor = "LEO").

Environments that progress beyond oxic usually do so because of:

✶ low O_2 Oxygen-limited environments may include sediment pore waters or fresh groundwaters.

✶ high DOC/POC   Most high organic matter ("OM") environments are associated with high biological activity (e.g., over fertilized rivers and lakes) or waste streams (e.g., urban sewage)

BOD - "biological oxygen demand"
High OM content is referred to as high BOD because oxygen is consumed rapidly by heterotrophs that digest the organic matter.

Because the various chemical species in the **"Redox Ladder"** have different solubilities, we see various chemical changes occurring at the different pE-poising boundaries.

Sediment pore water profiles nicely illustrate the "Redox Ladder".

Rain of organic matter provides reducing power that fuels a series of microbially mediated redox reactions.

water

sediment

These chemncal reactions are reflected in the changing composition of pore fluids with depth in the sediment column → often leading to different color, smell, etc.

Figure 9.19 The sediment-water interface. (a) Direction of fluxes expected for dissolved constituents between sediment pore waters and the overlying waters (oceans and lakes). (b) For sediments and pore water, the one-dimensional distribution of concentrations is time- and depth- dependent. Arrows indicate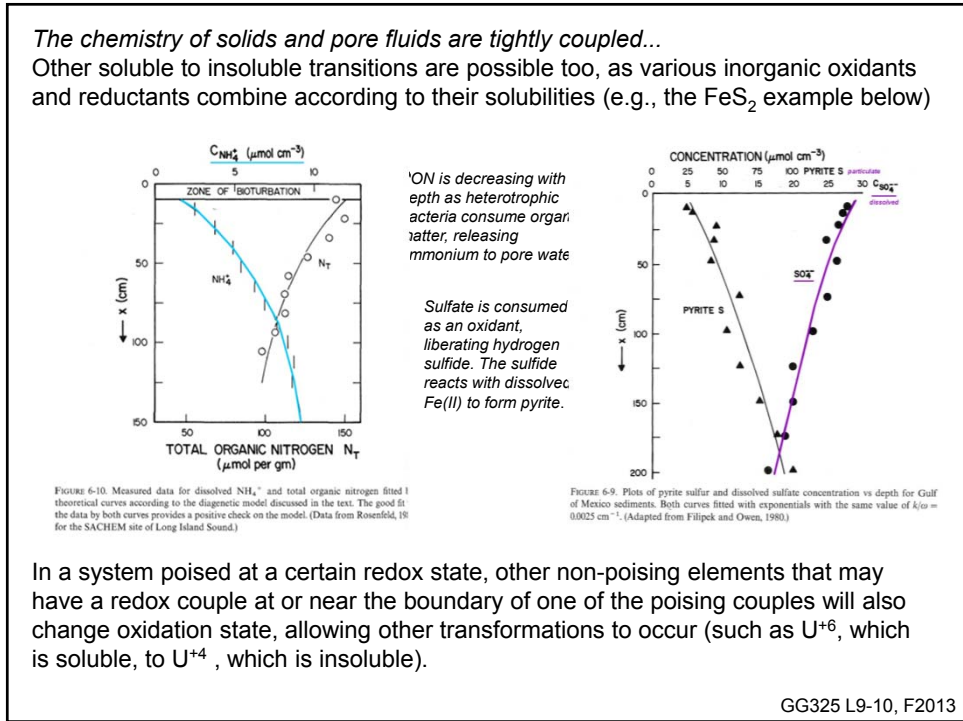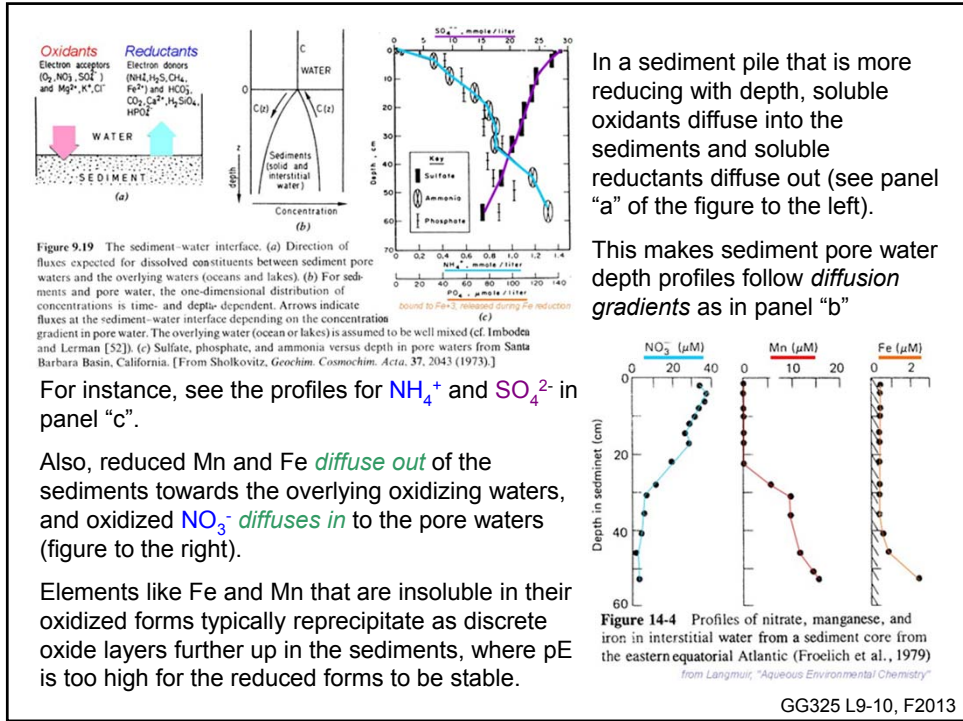 fluxes at the sediment-water interface depending on the concentration gradient in pore water. The overlying water (ocean or lakes) is assumed to be well mixed (cf. Imboden and Lerman [52]). (c) Sulfate, phosphate, and ammonia versus depth in pore waters from Santa Barbara Basin, California. [From Sholkovitz, *Geochim. Cosmochim. Acta*, 37, 2043 (1973).]

In a sediment pile that is more reducing with depth, soluble oxidants diffuse into the sediments and soluble reductants diffuse out (see panel "a" of the figure to the left).

This makes sediment pore water depth profiles follow *diffusion gradients* as in panel "b"

For instance, see the profiles for NH_4^+ and SO_4^{2-} in panel "c".

Also, reduced Mn and Fe *diffuse out* of the sediments towards the overlying oxidizing waters, and oxidized NO_3^- *diffuses in* to the pore waters (figure to the right).

Elements like Fe and Mn that are insoluble in their oxidized forms typically reprecipitate as discrete oxide layers further up in the sediments, where pE is too high for the reduced forms to be stable.

Figure 14-4 Profiles of nitrate, manganese, and iron in interstitial water from a sediment core from the eastern equatorial Atlantic (Froelich et al., 1979)
from Langmuir, "Aqueous Environmental Chemistry"

The chemistry of solids and pore fluids are tightly coupled...
Other soluble to insoluble transitions are possible too, as various inorganic oxidants and reductants combine according to their solubilities (e.g., the FeS_2 example below)

'ON is decreasing with depth as heterotrophic bacteria consume organic matter, releasing ammonium to pore water

Sulfate is consumed as an oxidant, liberating hydrogen sulfide. The sulfide reacts with dissolved Fe(II) to form pyrite.

FIGURE 6-10. Measured data for dissolved NH_4^+ and total organic nitrogen fitted to theoretical curves according to the diagenetic model discussed in the text. The good fit to the data by both curves provides a positive check on the model. (Data from Rosenfeld, 1979 for the SACHEM site of Long Island Sound.)

FIGURE 6-9. Plots of pyrite sulfur and dissolved sulfate concentration vs depth for Gulf of Mexico sediments. Both curves fitted with exponentials with the same value of $k/\omega = 0.0025$ cm^{-1}. (Adapted from Filipek and Owen, 1980).

In a system poised at a certain redox state, other non-poising elements that may have a redox couple at or near the boundary of one of the poising couples will also change oxidation state, allowing other transformations to occur (such as U^{+6}, which is soluble, to U^{+4}, which is insoluble).
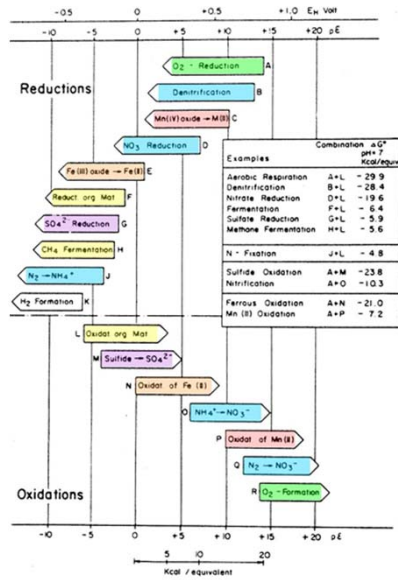
Environmental Poising

Figure 7.11 Sequence of microbially mediated redox processes.
from Strumm and Morgan, "Aquatic Chemistry"

Redox poising involves microbial consortia that collectively exploit various oxidizing and reducing agents to obtain metabolic energy by decomposing organic carbon molecules.

In a more general sense, microbes can cause a diversity of redox transformations as part of their overall metabolic pathways. Various reactions (see also Table 6.1 in Manahan) can be combined (one oxidation and one reduction) to poise the pE value of the environment

Note: $pE°(w) = pE°$ for UNIT ACTIVITY of reactant and oxidant and at pH=7, T=298° K. The half reactions are written for 1 electron mole transfer.

Other Examples of where the **"Redox Ladder"** occurs:
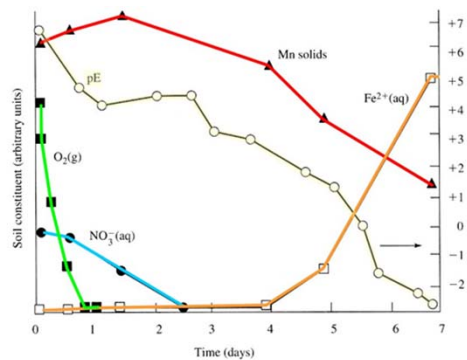
Figure 11.13 Relative changes in O_2, NO_3^-, Mn(IV) solids, Fe^{2+}(aq), and pE of a soil with time after flooding. From G. Sposito, *The chemistry of soils.* Copyright 1989 by Oxford University Press. Used by permission. *from Langmuir, "Aqueous Environmental Geochemistry"*

This case shows a soil that has gone anoxic after a flooding event.

The flood filled the pore spaces and limited the oxygen content, allowing the microbes and the high BOD soil particles to force the soil water down the "redox ladder"

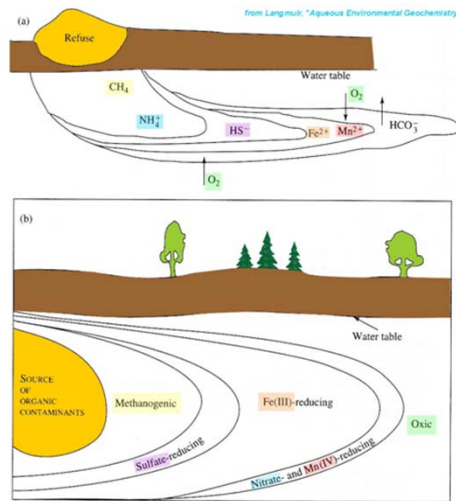Other Examples of where the **"Redox Ladder"** occurs:

Figure 11.16 Schematic cross-sections of groundwater systems contaminated by organic-rich wastes. (a) Development of redox zones down gradient from a landfill in the ground-water flow direction (Baedecker and Back 1979). (b) Possible sequence of redox zones encountered in the groundwater flow direction from a source of organic contamination. After D. R. Lovley, F. H. Chapelle, and J. C. Woodward, Use of dissolved H₂ concentrations to determine distribution of microbially catalyzed redox reactions in anoxic groundwater. *Envir. Sci. & Technol.* 28(7):1205–10. Copyright 1994 by American Chemical Society.

Groundwater near a source of high BOD waste (such as beneath a municipal landfill or where labile (reactive) organic contaminants have been spilled can reach very low pE.

Right in the vicinity of the high BOD waste, pE is the lowest and the effect of diminished pE are "felt" for some distance downstream in the flow direction until mixing with more oxygenated/lower DOC waters takes place and restores a more "normal" condition.

"Redox Ladder" effects on pH

Like pE, pH is important system parameter that determines the condition of a natural or polluted water.
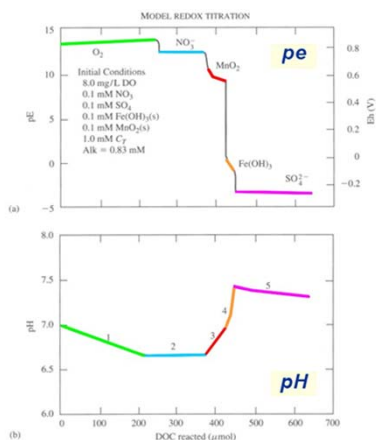

Figure 11.12 Redox titration curve of a model groundwater system of initial composition shown in (a), which also describes the computed response in pE and Eh as specific species are reduced during the titration. The computed pH change during the titration is shown in (b). Numbered segments correspond to sequential reduction: (1) O₂(aq), (2) NO₃⁻, (3) MnO₂(s), (4) Fe(OH)₃(s), and (5) SO₄²⁻. From Scott and Morgan (1990). Reprinted with permission from M. J. Scott and J. J. Morgan. Energetics and conservative properties of redox systems. In *Chemical modeling of aqueous systems II*, ed. D. C. Melchior and R. L. Bassett. Am. Chem. Soc. Symp. Ser. 416, pp. 368–78. Copyright 1990 by the American Chemical Society. *from Langmuir, "Aqueous Environmental Geochemistry"*

Recall that oxic respiration liberates H⁺, thereby changing the pH of the environment.

Other microbial forms of organic matter oxidation also liberate H⁺, although not necessarily in the same proportion to "CH₂O" decomposed in Redfield Reaction proportions.

The net effect on pH of each step in the idealized scheme of redox reactions acting on a water initially at pH=7 is shown to the left. Note that the net effect of Mn and Fe reduction is to raise the pH.

"Redox Ladder" transformations of Fe by Chemoautotrophs in polluted Environments: **Examples from acid mine drainage**

Ground or surface waters issuing from metal ore mines are often acidic because of the oxidation of pyrite associated with the ore body.

$$4FeS_{2(s)} + 14O_{2(g)} + 4H_2O_{(l)} \rightarrow 4Fe^{2+}_{(aq)} + 8SO_4^{2-}_{(aq)} + 8H^+_{(aq)}$$
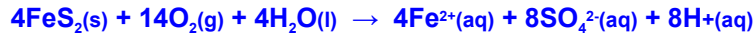
Abiotic pyrite oxidation to produce ferric ions and hydrogen ions is slow.

30,000X magnification
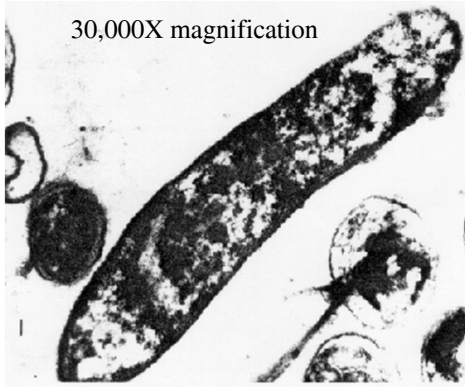
But *Thiobacillus ferrooxidans* (left) catalyzes the oxidation of FeS_2, producing ferric ions and hydrogen ions.
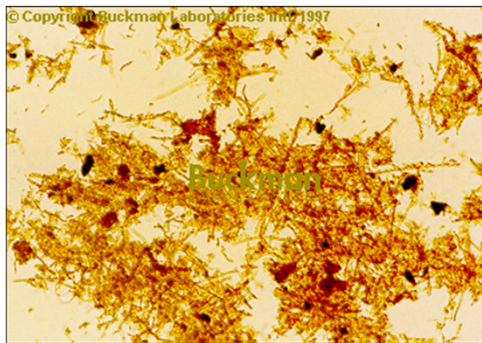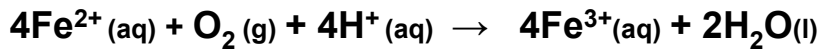
It is responsible for iron and inorganic sulfur oxidation of in mine tailings and coal deposits where these compounds are abundant.

Subsequent **Fe^{2+}** oxidation by organisms like *Gallionella* produces **Fe^{3+}** in these environments (next 2 slides)

http://www.mines.edu/fs_home/jhoran/ch126/index.htm

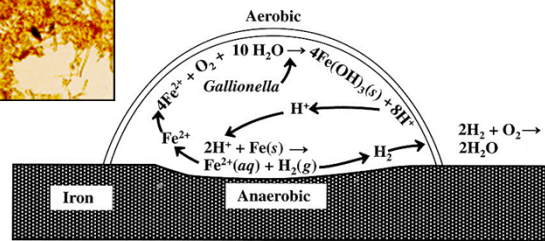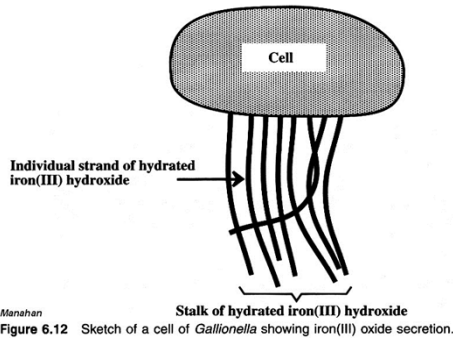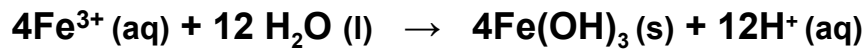*Gallionella* is a microbe that catalyzes Fe oxidation to get energy.

$$4Fe^{2+}_{(aq)} + O_{2\ (g)} + 4H^+_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)}$$

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http://www.buckman.com/eng/micro101/2266.htm

Aerobic

$4Fe^{2+} + O_2 + 10\ H_2O \rightarrow 4Fe(OH)_{3(s)} + 8H^+$

Gallionella

H^+

Fe^{2+}

$2H^+ + Fe(s) \rightarrow$
$Fe^{2+}(aq) + H_2(g)$

H_2

$2H_2 + O_2 \rightarrow 2H_2O$

Iron

Anaerobic

Figure 6.13 Tubercle in which the bacterially mediated corrosion of iron occurs through the action of *Gallionella*. *Manahan*

This organism probably produces Fe-hydroxide strands as a means of eliminating waste Fe(III)

$$4Fe^{3+} \text{ (aq)} + 12\ H_2O \text{ (l)} \quad \rightarrow \quad 4Fe(OH)_3 \text{ (s)} + 12H^+ \text{ (aq)}$$

Cell

Individual strand of hydrated iron(III) hydroxide

Stalk of hydrated iron(III) hydroxide

Manahan
Figure 6.12 Sketch of a cell of *Gallionella* showing iron(III) oxide secretion.

Acc.V Spot Magn Det WD Exp   2 µm
20.0 kV 3.0 12800x GSE 12.2 1 Gallion2

http://www.buckman.com/eng/micro101/2266.htm

Figure 1: Hematite crystallites in and on stalks by Gallionella

---

$Fe(OH)_3$ precipitates cause a rusty color in acid mine drainage waters. Low pH makes these waters quite corrosive in the environment, an attribute that remediation needs to eliminate.

http://www.science.uwaterloo.ca/research/ggr/MineWasteGeochemistry/AcidMineDrainage.html

see also a related site for a great description of Cr(VI) remediation:

http://www.science.uwaterloo.ca/research/ggr/PermeableReactiveBarriers/Cr-TCE_Treatment/Cr-TCE_Treatment.html