Chapter 10

OXIDATION-REDUCTION REACTIONS

Oxidation – reduction reactions are those involving the transfer of electrons from one substance to another (no bonding formed or broken).

Example: $Fe^{3+} + e^{-}$ ç è Fe^{2+}

Protons (H^+) are often involved in these reactions also.

Another example of redox reactions is:

$$H_2O_2 + 2e^{-} + 2H^{+} \rightleftharpoons 2H_2O$$

Rules for the assigning of oxidation numbers

1. All species in their elemental form are given the oxidation number of zero.
2. All monoatomic ions have the same oxidation number as the charge on the ion. e.g. Mg^{2+} has the oxidation number of +2.
3. All combined hydrogen has an oxidation number of +1 (except metal hydrides where its oxidation number is -1).
4. All combined oxygen has an oxidation number of -2 (except peroxides where the oxidation number is -1).
5. In polyatomic species, the sum of the oxidation numbers of the element in the ion equals the charge on that species (we can use this to find the oxidation number of elements in polyatomic species).

A. <u>Source of electrons in soils.</u>

Electrons do not flow around by themselves but they must be provided by some sources . In soils, the main source of electrons is carbon atoms of organic matter because carbon has a wide range of oxidation states.

Example:

$$\underset{\text{Ox. \# (-4)}}{\underset{\downarrow}{CH_4}} + 2O_2 \longrightarrow 2H_2O + \underset{\text{Ox. \# (+4)}}{\underset{\downarrow}{CO_2}}$$

The reaction ($CH_4 \rightarrow CO_2$) releases $8e^-$

Other common sources of e^- are nitrogen and sulfur atoms because they can also have several oxidation states.

The availability of electrons usually controls the oxidation/reduction reactions and this availability is expressed as <u>redox</u> potentials.

Soil microbes often serve as catalysis for the release of electrons from a substance.

B. <u>Source of H^+ (water).</u>

In soils, the main source of protons is water. H_2O ç è $H^+ + OH^-$

C. <u>Definition</u>

1. Oxidizing agents (oxidizers) accept electrons from other substances.
2. Reducing agents (reducers) donate electrons to other substances.
3. Oxidation is the donation of electrons to other substances.
4. Reduction is the acceptance of electrons from another substance.

Example:

Half cell (reaction): $\underset{\text{Oxidizer}}{\underset{\downarrow}{Fe^{3+}}} + e^- \rightarrow \underset{\text{reducer}}{\underset{\downarrow}{Fe^{2+}}}$ This reaction is called REDUCTION process

2nd half cell: $\underset{\text{reducer}}{\underset{\downarrow}{1/2H_2}} \rightarrow \underset{\text{oxidizer}}{\underset{\downarrow}{H^+}} + e^-$ OXIDATION process

II. **ELECTRON ACCEPTORS (OXIDIZERS) IN SOILS.**

A. **Oxygen.** Oxygen is the strongest common electron acceptor and therefore yields the most energy from its reaction (reduction process). Oxygen is also the only electrons acceptor that plant roots can utilize. When oxygen is available (aerobic conditions), it accepts electrons by the half reaction:

$O_2 + 4e^- + 4H^+ = 2H_2O$ (here, oxygen is being reduced to water or water is being oxidized to oxygen).

Source and electrons in this reaction, again, is organic matter.

B. **Fe and Mn.** When oxygen is unavailable (anaerobic conditions), the prominent electron acceptors in soils and their half reactions may include.

$$FeOOH + e^- + 3H^+ \rightleftarrows Fe^{2+} + 2H_2O$$

And Fe_2O_3 (hematite) $+ 2e^- + 6H^+ \rightleftarrows 2Fe^{2+} + 3H_2O$

Or $MnO_2 + 2e^- + 4H^+ \leftrightarrows Mn^{2+} + 2H_2O$

Remember: In theory, these reactions will not occur until all oxygen is consumed from the system. That is, the system must be anaerobic such as in flooded soils.
On the other hand, when soils are subjected to seasonal flooding, minerals such as FeOOH and MnO_2 become more soluble and some $Fe2^+$ and Mn^{2+} may be removed by leaching.

C. **SO_4^{2-} and NO_3^-**

In the absence of Oxygen, SO_4^{2-} and NO_3^- can serve as electrons acceptors:

$$SO_4^{2-} + 8e^- + 8H^+ \leftrightarrows S^{2-} + 4H_2O$$

This reaction occurs in swampy areas and H_2S is the main cause for the stinky odor often associated with swamps.

$$NO_3^- + 2e^- + 2H^+ \rightleftharpoons NO_2^- + H_2O$$

$$N_2O + 2e^- + 2H^+ \leftrightharpoons N_2 \uparrow + H_2O$$

These reactions yield products that are unfavorable to agriculture and aquaculture. Their reduced species are often more toxic than the oxidized species: For example nitrite NO_2^- is more toxic than NO_3^-, (H_2S) is more than SO_4^{2-} and Fe^{2+}, Mn^{2+} can cause phytotoxicity in rice paddy.

Of all other electron acceptors are exhausted, then H^+ (protons) can serve as the final electron acceptor in the aqueous system.

$$H^+ + e- \leftrightharpoons \frac{1}{2} H_2$$

D. **Soil oxygen supply**.

The supply of oxygen to soils is dependent upon the diffusion rate of oxygen and pore size of soil aggregates.

1. oxygen diffusion rate through a gas filled pore is about 10^4 times faster than the rate through a water filled pore .
2. solubility of oxygen in water is only about 8-10 mg/L.

The supply of oxygen in a water –logged soil can be exhausted in less than 24 hours.

III. ELECTRONS DONORS (REDUCERS) IN SOILS.

A. **Organic matter.** The major electron donors in soils are freshly fallen plant matter and soil organic matter. If we represent organic matter and plant material in the most simple way as $(CH_2O)_n$ which is the general formula of carbohydrate, then the half reaction of oxidation is:

$$CH_2O \rightleftarrows C^{4+} + H_2O + 4e^- \qquad (1)$$

The other half-reaction that completes reaction (1) is the electron acceptance by O_2

$$O_2 + 4e^- \longrightarrow 2O^{2-} \qquad (2)$$

The overall reaction is:

$$CH_2O + O_2 \leftrightarrows CO_2 + H_2O + \text{energy}$$

B. **Inorganic matter.** Other electrons donors in soils besides organic matter are :

$$\underset{(-3)}{NH_3} = \underset{(NO_2^-)}{N^{3+}} + 3H^+ + 6e^- \quad (NH_4^+ + 2H_2O = NO_2^- + 8H^+ + 6e^-)$$

$$\underset{(-2)}{H_2S} = \underset{(SO_4^{2-})}{S^{6+}} + 2H^+ + 8e^- \quad (H_2S + 4H_2O = SO_4^{2-} + 10H^+ + 8e^-)$$

$$Fe^{2+} = Fe^{3+} + e^-$$

IV. Oxidation-Reduction in Soils.

A. Electrode Potential: is the tendency of a substance to accept electrons. For example,

$$\begin{array}{lcll} & & & Eh^o(v) \\ O_2 + 4H^+ + 4e^- & = & 2H_2O & 1.23 \\ Fe^{3+} + e^- & = & Fe^{2+} & 0.77 \\ 2H^+ + 2e^- & = & H_2 & 0 \text{ (reference)} \\ Na^+ + e^- & = & Na & -2.71 \end{array}$$

High electrode potentials mean that the elements or ions on the left side of the equations in Table (4.2) would readily accept electrons.

For example, halogen gases, fluorine or chlorine, have very high electrode potentials and are strong oxidizes agents.

Low electrode potentials mean that the elements or ions on the right side of the equations in Table (4.2) readily donate electrons.

Table 4.2. Electrode potentials (reduction potentials) of selected half-reactions at 25° C. (The dashed lines show the limits of electrode potential in aqueous systems).

Reaction	Eh^0 (V)
$F_2 + 2e^- = 2F^-$	+2.87
$Cl_2 + 2e^- = 2Cl^-$	1.36
$NO_3^- + 6H^+ + 5e^- = \frac{1}{2}N_2 + 3H_2O$	1.26
$O_2 + H^+ + 4e^- = 2H_2O$	1.23
$NO_3^- + 2H^+ + 4e^- = NO_2^- + H_2O$	0.85
$Fe^{3+} + e^- = Fe^{2+}$	0.77
$SO_4 + 10H^+ + 8e^- = H_2S + 4H_2O$	0.31
$CO_2 + 4H^+ + 4e^- = C + 2H_2O$	0.21
$N_2 + 6H^+ + 6e^- = 2NH_3$	0.09
$2H^+ + 2e^- = H_2$	0
$Fe^{2+} + 2e^- = Fe$	−0.44
$Zn^{2+} + 2e^- = Zn$	−0.76
$Al^{3+} + 3e^- = Al$	−1.66
$Mg^{2+} + 2e^- = Mg$	−2.37
$Na^+ + e^- = Na$	−2.71
$Ca^{2+} + 2e^- = Ca$	−2.87
$K^+ + e^- = K$	−2.92

The Nernst equation:

Considering a generalized redox reaction:

$$\text{OX. (oxidizer)} + ne^- + mH^+ = \text{Red. (reducer)} + m/n\ H_2O$$

The Nernst equation is expressed as:

$$Eh = Eh^0 - RT/nF\ \ln (\text{Red})/(O_x)(H^+)^m$$

Where Eh^0 = the standard electrode potential.

R = gas constant.

T = absolute temp (Kelvin).

F = Faraday constant

At 25°C ([RT/F]*2.303 = 0.059 volt)

$$\boxed{Eh = Eh^0 - 0.059/n \log (\text{Red})/(O_x) - 0.059\ m/n\ pH}$$

Electrode potential is also often repressed in term of ***pe*** which is $-\log(e^-)$.

Relationship between *pe* and *Eh* is as follows:

$$\boxed{pe = Eh\ (\text{in volt})/\ 0.059 \quad \text{at } 25^oC}$$

Example: $O_2 + 4e^- + 4H^+ = 2H_2O$

$$Eh = Eh^o - 0.059/4 \log 1/P_{O2} - 0.059pH$$

$$\downarrow$$

$$Eh = 1.23 - 0.059/4 \log 1/P_{O2} - 0.059pH$$

B. Electrode potential range in water (aqueous limits)

Only a narrow portion of the total range of electrode potentials is available in soils. If you look at Table 4.2, this portion is the region between the two dashed lines.

The upper limit is the reduction of O_2 to H_2O:

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad Eh^o = 1.23 \text{ v}$$

And the lower limit is the reduction of proton (H^+) to H_2

$$2H^+ + 2e^- = H_2 \qquad Eh^o = 0 \text{ v}$$

These stability of water with respect to the oxidation of H_2O to O_2, and the reduction of H_2O to H_2, limits the range of electrode potentials and the oxidation states possible in soils and living systems because these systems contain water.

1. Unstability of chlorine in water.

If a solution contains an oxidizing agent, much as aqueous chlorine, with an electrode potential greater them that of the $O_2 – H_2O$ couple, then the oxidizing agent will tend to oxidize water to O_2. Such strong oxidizing agents as ClO^- (hypochlorite) and aqueous chlorine will decompose by oxidizing H_2O until the supply of the oxidizing agent is exhausted.

2. Unstability aqueous alkali metals in water.

If a solution contains reducing agents, such as alkali metals (Na, K) with an electrode potential lower than that of the H^+ - H_2 couple, then the reducing agent will tend to reduce H^+ (or H_2O) to H_2 and become unstable. For example, Na, K, Ca, Al metals are unstable in water, and will transform quickly to their cationic species such as Na^+, K^+, Ca^{2+} or Al^{3+}. Na in water will explode due to the decomposition of H_2O.

$Fe + H_2O \longrightarrow Fe^{2+}$ (corrosion process), Aluminum is special, it is meta-stable in water. Because it can form a protective oxide layer on its surface and stop further oxidation.

<u>Remember</u>: redox potential only indicates the direction of a reaction; it says nothing about the rate. For example, the most stable oxidation state of nitrogen is NO_3^- under the presence of O_2 (or aerobic condition), it means that theoretically N_2 gas would be converted to NO_3^- eventually according to:

$$N_2 + 5/2O_2 + H_2O = 2HNO_3$$

However, this reaction does not take place, or if it does, it takes several million years to complete. That's why nitrogen is still the most abundant gas on the earth, and oxygen is still floating around, otherwise we would have had nitric acid atmosphere instead.

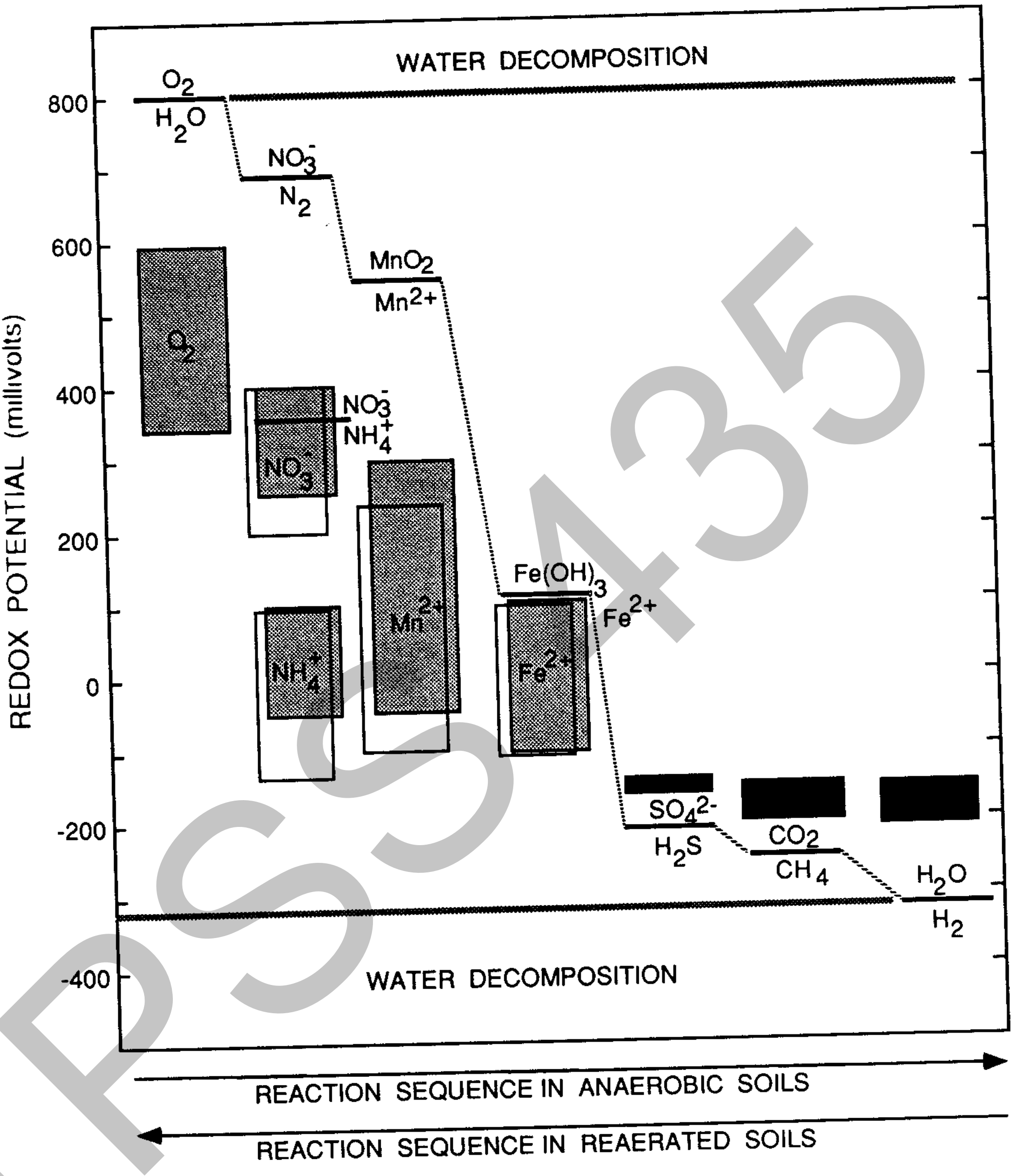
V. **FLOODED SOILS.**

A. <u>Idealized steps in utilization of principal electrons acceptors.</u>

If the oxygen supply is insufficient, soil microorganisms are forced to utilize progressively weaker electron acceptors (See Fig.).

After oxygen disappearance, NO_3^- will be the next to be reduced to NO_2^-, amino acids, N_2, or N_2O.

$$NO_3^- + 2e^- + 2H^+ = NO_2^- + H_2O$$



After oxygen and NO_3^- have been exhausted, Fe(3+) and Mn (4+) hydroxides are reduced into Fe^{2+} an Mn^{2+}.

$$FeOOH + e^- + 3H^+ = Fe^{2+} + 2H_2O$$

$$MnO_2 + 2e^- + 4H^+ = Mn^{2+} + 2H_2O$$

Finally, SO_4^{2-} will be reduced to sulfur or sulfide.

$$SO_4^{2-} + 9H^+ + 8e^- = HS^- + 4H_2O$$

B. Rice fields.

Under submerged conditions, soil pH is usually about 1 unit higher than under aerobic condition, and Fe^{3+} is reduced to Fe^{2+}. Ferrous phosphate is much more soluble than ferric phosphate (See Fig. below). However, NO_3^- would be reduced and lost as gaseous NOx species. Therefore, you should use urea or NH_4^+ instead of NO_3^- fertilizers as N source in rice paddy.

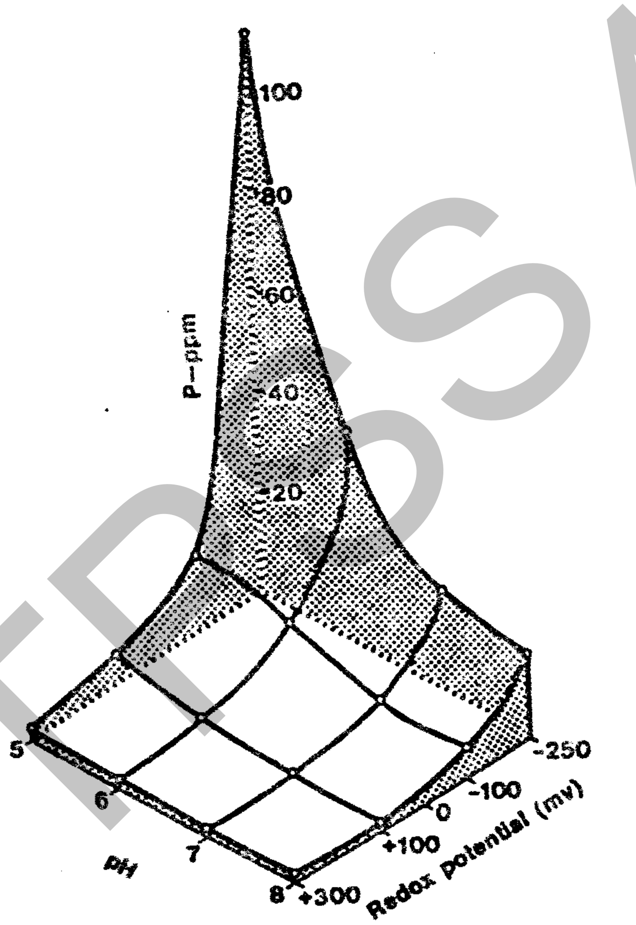


Fig. 6. Solubility of P as influenced by pH and redox potential.