Environmental Soil Chemistry
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Lecture – 31
Redox Chemistry of Soils

Welcome friends to this NPTEL online certification course of environmental soil chemistry and today we are going to start week 7 of lectures or module 7 of lectures and in this week 7, we are going to talk about the redox chemistry of soils which is very very important as far as the environmental soil chemistry is concerned. Now, we will be discussing different aspects of redox chemistry which is basically pertinent to the different soil processes.

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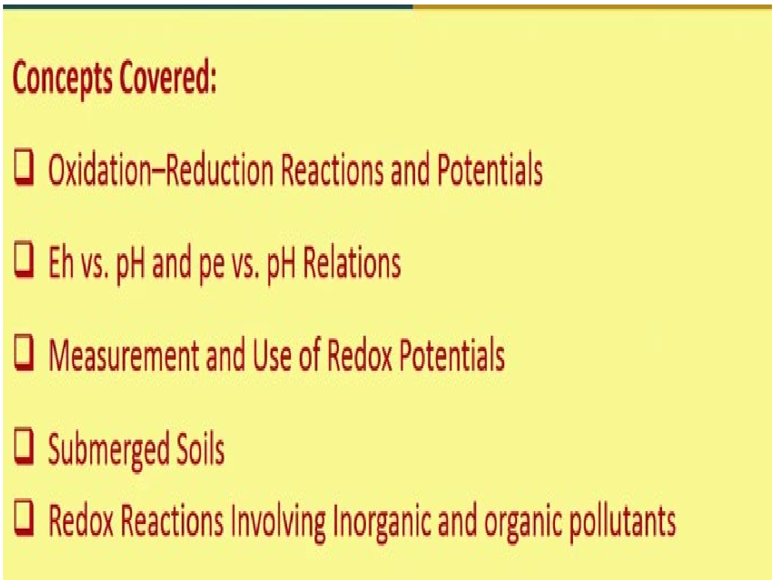

Concepts Covered:

- ☐ Oxidation–Reduction Reactions and Potentials
- ☐ Eh vs. pH and pe vs. pH Relations
- ☐ Measurement and Use of Redox Potentials
- ☐ Submerged Soils
- ☐ Redox Reactions Involving Inorganic and organic pollutants

So these concepts will be broadly covered. One is oxidation-reduction reactions and potentials and then we will be talking about Eh versus pH and pe versus pH relations, and then we will be talking about measurement and use of redox potentials and then we will be talking about submerged soils which is very important and then we will be talking about redox reactions involving inorganic and organic pollutants.

Now remember these redox reactions are, redox reactions are basically the short form of reduction-oxidation reactions. So these redox reactions are very much important for governing several process in the soil depending on aerobic and anaerobic systems, depending on the presence of water and also it can govern the movement and dynamics of several nutrients from the point of view of plant nutrition and also it can control the fate of different nutrients as well as other materials which are present in the soil.

So that is why it is very much important to discuss the redox chemistry of soil. Submerged soil is a very important aspect where we can apply this redox reaction more in a, more efficient way because in the submerged soil which is submerged under water, these redox reactions can govern the conversion of different forms of nutrients depending on the oxygen presence or absence of oxygen rather.

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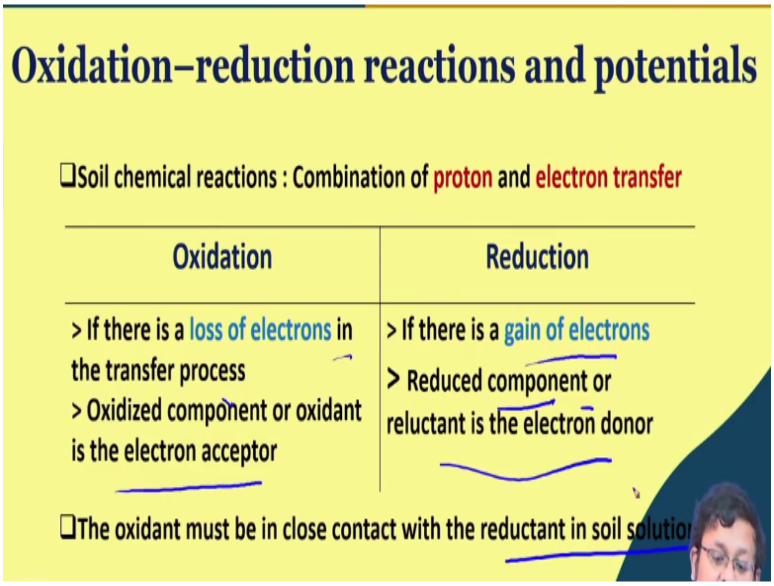

Oxidation–reduction reactions and potentials

❑Soil chemical reactions : Combination of proton and electron transfer

Oxidation	Reduction
> If there is a loss of electrons in the transfer process > Oxidized component or oxidant is the electron acceptor	> If there is a gain of electrons > Reduced component or reluctant is the electron donor

❑The oxidant must be in close contact with the reductant in soil solutio

So let us start with the first definition of ah you know oxidation and reduction. So what is oxidation and what is reduction? Now soil chemical reaction basically it shows the combination of proton and electron transfers and oxygen oxidation, we call it oxidation when there is a loss of electrons in the transfer processes. In contrast, in case of reduction there is a gain of electron, it is a common knowledge of chemistry.

Now oxidized component of our oxidant is the electron acceptor in case of oxidation and in case of reduction the reduced component or reductant is the electron donor. So in case of oxidation, there is a loss of electrons, in case of reduction there is a gain of electrons. In case of oxidation, the oxidized component or the oxidant is the electron acceptor whereas in case of reduction the reduced component or reductant is the electron donor.

So, the oxidant must be in close contact with the reductant in soil solution to govern these redox reactions. So obviously, we will see specifically when we will talk about different reactions and different conversion of different elements, specifically in submerged soil we will see that different oxidized form are in close contact with different reduced form so that there is dynamic changes of their, dynamic change of the, of the species occurs.

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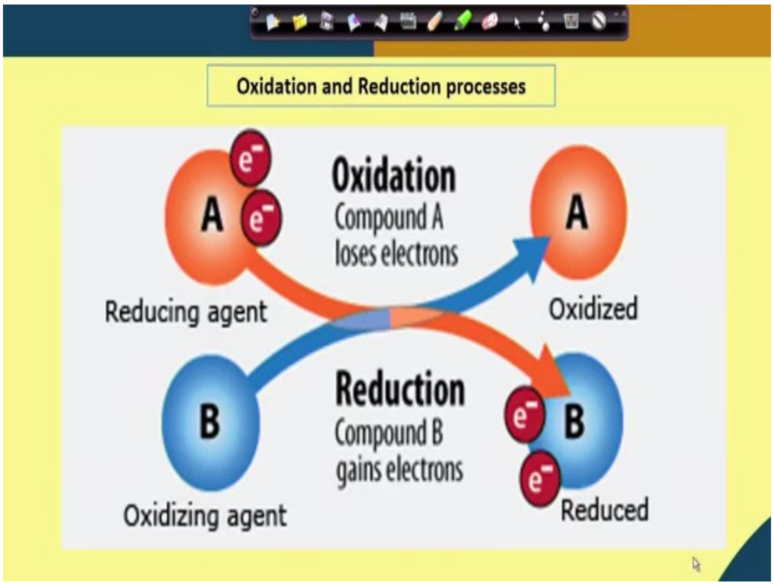

Oxidation and Reduction processes

So, this basically shows the gist of what is oxidation and reduction. So here you can see this is a reducing agent which is A and B is an oxidizing agent. So B basically oxidize the reducing agent and reducing agent basically reduce the oxidizing agent. So you can see here this reducing agent which has excess of electron, they can give this excess of electron to this oxidizing agent and by removing those excess of electrons it can be oxidized.

And in other way these oxidizing agents which are having less amount of electron they will gather or they will accept these electrons to be reduced to you know and then convert it into the reduced form, so that is B. So, reduction is basically denoted by this blue line which is component B where it is gaining electrons, however oxidation is denoted by these red lines where it is basically loses the electrons.

So, this is why we said that there has to be a close contact between the oxidized agent as well as the reduced agent for governing this redox reaction, specifically also in soils.

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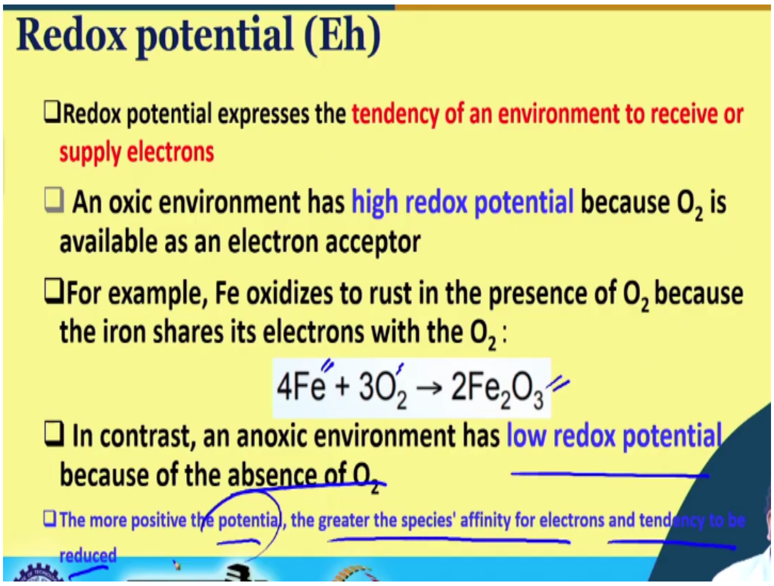

Redox potential (Eh)

- ❑ Redox potential expresses the tendency of an environment to receive or supply electrons
- ❑ An oxic environment has high redox potential because O_2 is available as an electron acceptor
- ❑ For example, Fe oxidizes to rust in the presence of O_2 because the iron shares its electrons with the O_2 :

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

- ❑ In contrast, an anoxic environment has low redox potential because of the absence of O_2
- ❑ The more positive the potential, the greater the species' affinity for electrons and tendency to be reduced

So what is redox potential? Now redox potential basically expresses the tendency of an environment to receive or supply electrons. Whether an environment where different types of reactions chemical reactions are going on will accept or supply electrons can be indicated by using the redox potential and redox potential basically is denoted by the, by Eh. So, Eh is basically called the redox potential.

Remember in an oxic environment the high redox potential, oxic environment has a high redox potential because oxygen is available as an electron acceptor obviously. In case of oxidized oxic environment, oxygen can you know accept the electrons. For example iron oxidizes to rust in the presence of oxygen because the iron shares its electrons with the oxygen. So you can see here, when 4 iron 4 atoms of iron reacts with 6 atoms of oxygen, so 4Fe + 3O2 basically gives rise to rust or Fe2O3, ferric oxide.

So in contrast an anoxic environment has a low redox potential because of the absence of oxygen oxygen. So redox potential basically gives you an indication whether this, a particular environment is oxic environment or anoxic environment. In case of oxic environment it has high redox potential, in case of anoxic environment it has low oxic, low redox potential because of the absence of oxygen.

So, the more positive the potential, the greater is the species' affinity for electrons and tendency to be reduced. So in other words, the more positive the potential that means more higher the redox potential, greater is the species' affinity for electrons and tendency to be reduced. So high redox potential means this environment is more you know has a more tendency to get reduced by accepting the electrons okay.

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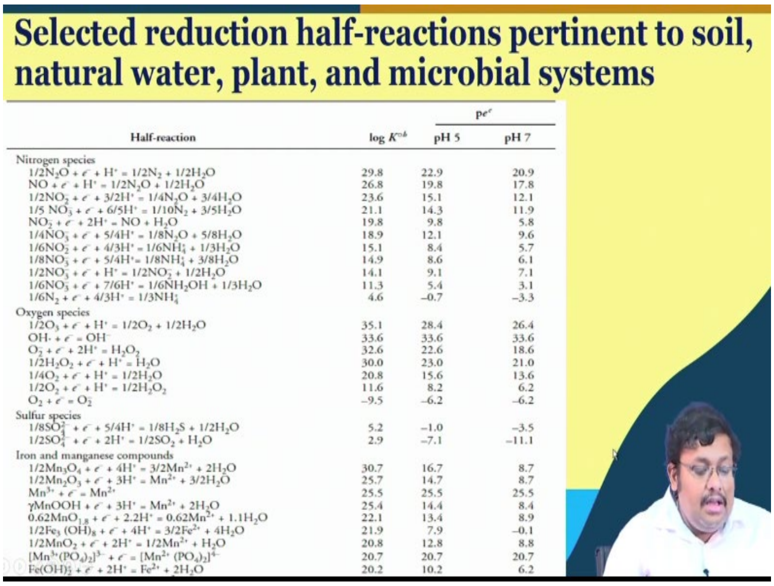

Selected reduction half-reactions pertinent to soil, natural water, plant, and microbial systems

Half-reaction	log $K^{\circ b}$	pe^c	
		pH 5	pH 7
Nitrogen species			
$1/2N_2O + e^- + H^+ = 1/2N_2 + 1/2H_2O$	29.8	22.9	20.9
$NO + e^- + H^+ = 1/2N_2O + 1/2H_2O$	26.8	19.8	17.8
$1/2NO_2^- + e^- + 3/2H^+ = 1/4N_2O + 3/4H_2O$	23.6	15.1	12.1
$1/5\ NO_3^- + e^- + 6/5H^+ = 1/10N_2 + 3/5H_2O$	21.1	14.3	11.9
$NO_2^- + e^- + 2H^+ = NO + H_2O$	19.8	9.8	5.8
$1/4NO_3^- + e^- + 5/4H^+ = 1/8N_2O + 5/8H_2O$	18.9	12.1	9.6
$1/6NO_2^- + e^- + 4/3H^+ = 1/6NH_4^+ + 1/3H_2O$	15.1	8.4	5.7
$1/8NO_3^- + e^- + 5/4H^+ = 1/8NH_4^+ + 3/8H_2O$	14.9	8.6	6.1
$1/2NO_3^- + e^- + H^+ = 1/2NO_2^- + 1/2H_2O$	14.1	9.1	7.1
$1/6NO_3^- + e^- + 7/6H^+ = 1/6NH_2OH + 1/3H_2O$	11.3	5.4	3.1
$1/6N_2 + e^- + 4/3H^+ = 1/3NH_4^+$	4.6	–0.7	–3.3
Oxygen species			
$1/2O_3 + e^- + H^+ = 1/2O_2 + 1/2H_2O$	35.1	28.4	26.4
$OH\cdot + e^- = OH^-$	33.6	33.6	33.6
$O_2^- + e^- + 2H^+ = H_2O_2$	32.6	22.6	18.6
$1/2H_2O_2 + e^- + H^+ = H_2O$	30.0	23.0	21.0
$1/4O_2 + e^- + H^+ = 1/2H_2O$	20.8	15.6	13.6
$1/2O_2 + e^- + H^+ = 1/2H_2O_2$	11.6	8.2	6.2
$O_2 + e^- = O_2^-$	–9.5	–6.2	–6.2
Sulfur species			
$1/8SO_4^{2-} + e^- + 5/4H^+ = 1/8H_2S + 1/2H_2O$	5.2	–1.0	–3.5
$1/2SO_4^{2-} + e^- + 2H^+ = 1/2SO_2 + H_2O$	2.9	–7.1	–11.1
Iron and manganese compounds			
$1/2Mn_3O_4 + e^- + 4H^+ = 3/2Mn^{2+} + 2H_2O$	30.7	16.7	8.7
$1/2Mn_2O_3 + e^- + 3H^+ = Mn^{2+} + 3/2H_2O$	25.7	14.7	8.7
$Mn^{3+} + e^- = Mn^{2+}$	25.5	25.5	25.5
$\gamma MnOOH + e^- + 3H^+ = Mn^{2+} + 2H_2O$	25.4	14.4	8.4
$0.62MnO_{1.8} + e^- + 2.2H^+ = 0.62Mn^{2+} + 1.1H_2O$	22.1	13.4	8.9
$1/2Fe_3\ (OH)_8 + e^- + 4H^+ = 3/2Fe^{2+} + 4H_2O$	21.9	7.9	–0.1
$1/2MnO_2 + e^- + 2H^+ = 1/2Mn^{2+} + H_2O$	20.8	12.8	8.8
$[Mn^{3+}(PO_4)_2]^{3-} + e^- = [Mn^{2+}\ (PO_4)_2]^{4-}$	20.7	20.7	20.7
$Fe(OH)_2^+ + e^- + 2H^+ = Fe^{2+} + 2H_2O$	20.2	10.2	6.2

Now, this table basically shows the selected reduction half-reaction pertinent to soil, natural water, plant and different microbial system. Now what is half-reaction? In case of redox reaction, the half-reaction basically says the either the reduction reaction or the oxidation reaction. So any one of these reaction if you denote, then you will use this term half-reaction.

So here basically we are using the reduction half-reaction to see what are the major reduction half-reaction which are pertinent to soil, natural water, plant, and microbial system. We will be discussing some of them in details while we discuss the submerged soil. Just for some examples you can see here the nitrogen dioxide when it accepts electrons, it produce the nitrogen gas. When the nitric oxide accepts electron, it produce the nitrous oxides.

So first nitrous oxide converted to nitrogen, then nitric oxide convert to nitrous oxides, then nitrogen dioxides converted to nitrous then the the nitrogen dioxides can be converted to nitrous oxide. So, you can see how different species of nitrogen are changing their form by accepting the electron or by getting reduced. So here one example is given for nitrous oxide to conversion to nitrogen, one is from nitric oxide to nitrous oxide, then nitrogen dioxide to nitrous oxide, nitrate to elemental nitrogen.

Then nitrogen dioxide to nitric oxide, then nitrate to nitrous oxide, nitrate to ammonium, nitrate to you know nitrogen dioxide, nitrate to NH2OH and then nitrate to NH4 ions. So you can see that by accepting electrons, the species of nitrogen or oxidized species of nitrogen can be converted into reduced form of nitrogen. In case of oxygen, you can see here this ozone when its accept electron converted to oxygen.

Then hydroxyl convert to, this OH group basically converts to hydroxyl ion, the O2 minus converts to H2O2 or hydrogen peroxide, H2O2 can be converted to H2O or water, then oxygen can be converted to water, reduced to water, oxygen can be also reduced to H2O2 and oxygen molecule can be reduced to you know O2 minus. So this is how you can see the oxygen species movement also in the, in the, you know by accepting the electrons.

Also corresponding pe values, we will be discussing pe values, and also equilibrium constants are given side by side. In case of sulfur, sulfur also undergoes you know different electron different oxidation reaction. You can see sulfate will be reduced to H2S or hydrogen sulfide and it can also reduce to sulfur dioxides. So you can see here the conversion of the sulfur species. Iron and manganese compound you can see Mn3O4 can be converted to Mn2+.

The Mn2O3 can be converted to Mn2+ and also different iron compounds also, oxidized iron forms also can be converted to reduce compound by accepting the electrons. So, these are some examples of selected reduction half-reactions, which are pertinent to soil, water, plant and microbial systems.

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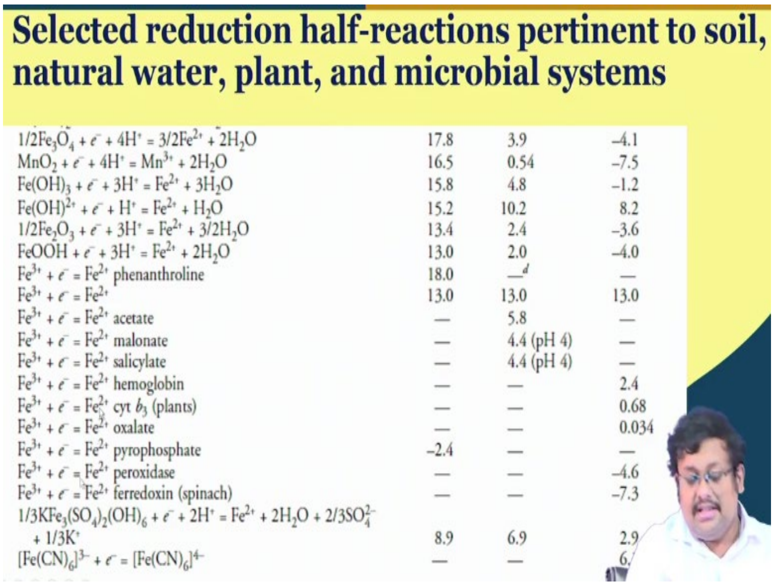

Selected reduction half-reactions pertinent to soil, natural water, plant, and microbial systems

$1/2Fe_3O_4 + e^- + 4H^+ = 3/2Fe^{2+} + 2H_2O$	17.8	3.9	–4.1
$MnO_2 + e^- + 4H^+ = Mn^{3+} + 2H_2O$	16.5	0.54	–7.5
$Fe(OH)_3 + e^- + 3H^+ = Fe^{2+} + 3H_2O$	15.8	4.8	–1.2
$Fe(OH)^{2+} + e^- + H^+ = Fe^{2+} + H_2O$	15.2	10.2	8.2
$1/2Fe_2O_3 + e^- + 3H^+ = Fe^{2+} + 3/2H_2O$	13.4	2.4	–3.6
$FeOOH + e^- + 3H^+ = Fe^{2+} + 2H_2O$	13.0	2.0	–4.0
$Fe^{3+} + e^- = Fe^{2+}$ phenanthroline	18.0	—[d]	—
$Fe^{3+} + e^- = Fe^{2+}$	13.0	13.0	13.0
$Fe^{3+} + e^- = Fe^{2+}$ acetate	—	5.8	—
$Fe^{3+} + e^- = Fe^{2+}$ malonate	—	4.4 (pH 4)	—
$Fe^{3+} + e^- = Fe^{2+}$ salicylate	—	4.4 (pH 4)	—
$Fe^{3+} + e^- = Fe^{2+}$ hemoglobin	—	—	2.4
$Fe^{3+} + e^- = Fe^{2+}$ cyt b_3 (plants)	—	—	0.68
$Fe^{3+} + e^- = Fe^{2+}$ oxalate	—	—	0.034
$Fe^{3+} + e^- = Fe^{2+}$ pyrophosphate	–2.4	—	—
$Fe^{3+} + e^- = Fe^{2+}$ peroxidase	—	—	–4.6
$Fe^{3+} + e^- = Fe^{2+}$ ferredoxin (spinach)	—	—	–7.3
$1/3KFe_3(SO_4)_2(OH)_6 + e^- + 2H^+ = Fe^{2+} + 2H_2O + 2/3SO_4^{2-} + 1/3K^+$	8.9	6.9	2.9
$[Fe(CN)_6]^{3-} + e^- = [Fe(CN)_6]^{4-}$	—	—	6.

And also, you know different you know Fe3 to Fe2 phenanthroline, Fe3 to you know Fe2+, Fe3 to acetate, Fe3 to Fe2 malonate. So you can see different different species of iron can be formed by reducing the oxidized form of iron that is Fe3+.

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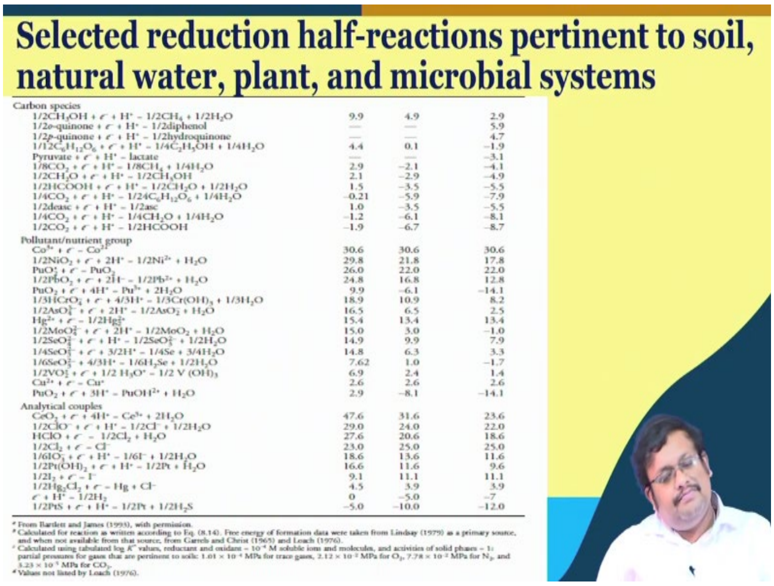

Selected reduction half-reactions pertinent to soil, natural water, plant, and microbial systems

Carbon species			
$1/2CH_3OH + e^- + H^+ = 1/2CH_4 + 1/2H_2O$	9.9	4.9	2.9
$1/2$o-quinone $+ e^- + H^+ = 1/2$diphenol	—	—	5.9
$1/2$p-quinone $+ e^- + H^+ = 1/2$hydroquinone	—	—	4.7
$1/12C_6H_{12}O_6 + e^- + H^+ = 1/4C_2H_5OH + 1/4H_2O$	4.4	0.1	−1.9
Pyruvate $+ e^- + H^+ =$ lactate	—	—	−3.1
$1/8CO_2 + e^- + H^+ = 1/8CH_4 + 1/4H_2O$	2.9	−2.1	−4.1
$1/2CH_2O + e^- + H^+ = 1/2CH_3OH$	2.1	−2.9	−4.9
$1/2HCOOH + e^- + H^+ = 1/2CH_2O + 1/2H_2O$	1.5	−3.5	−5.5
$1/4CO_2 + e^- + H^+ = 1/24C_6H_{12}O_6 + 1/4H_2O$	−0.21	−5.9	−7.9
$1/2$deasc $+ e^- + H^+ = 1/2$asc	1.0	−3.5	−5.5
$1/4CO_2 + e^- + H^+ = 1/4CH_2O + 1/4H_2O$	−1.2	−6.1	−8.1
$1/2CO_2 + e^- + H^+ = 1/2HCOOH$	−1.9	−6.7	−8.7
Pollutant/nutrient group			
$Co^{3+} + e^- = Co^{2+}$	30.6	30.6	30.6
$1/2NiO_2 + e^- + 2H^+ = 1/2Ni^{2+} + H_2O$	29.8	21.8	17.8
$PuO_2^+ + e^- = PuO_2$	26.0	22.0	22.0
$1/2PbO_2 + e^- + 2H^+ = 1/2Pb^{2+} + H_2O$	24.8	16.8	12.8
$PuO_2 + e^- + 4H^+ = Pu^{3+} + 2H_2O$	9.9	−6.1	−14.1
$1/3HCrO_4^- + e^- + 4/3H^+ = 1/3Cr(OH)_3 + 1/3H_2O$	18.9	10.9	8.2
$1/2AsO_4^{3-} + e^- + 2H^+ = 1/2AsO_2^- + H_2O$	16.5	6.5	2.5
$Hg^{2+} + e^- = 1/2Hg_2^{2+}$	15.4	13.4	13.4
$1/2MoO_4^{2-} + e^- + 2H^+ = 1/2MoO_2 + H_2O$	15.0	3.0	−1.0
$1/2SeO_4^{2-} + e^- + H^+ = 1/2SeO_3^{2-} + 1/2H_2O$	14.9	9.9	7.9
$1/4SeO_3^{2-} + e^- + 3/2H^+ = 1/4Se + 3/4H_2O$	14.8	6.3	3.3
$1/6SeO_3^{2-} + 4/3H^+ = 1/6H_2Se + 1/2H_2O$	7.62	1.0	−1.7
$1/2VO_2^+ + e^- + 1/2\ H_3O^+ = 1/2\ V(OH)_3$	6.9	2.4	1.4
$Cu^{2+} + e^- = Cu^+$	2.6	2.6	2.6
$PuO_2 + e^- + 3H^+ = PuOH^{2+} + H_2O$	2.9	−8.1	−14.1
Analytical couples			
$CeO_2 + e^- + 4H^+ = Ce^{3+} + 2H_2O$	47.6	31.6	23.6
$1/2ClO^- + e^- + H^+ = 1/2Cl^- + 1/2H_2O$	29.0	24.0	22.0
$HClO + e^- = 1/2Cl_2 + H_2O$	27.6	20.6	18.6
$1/2Cl_2 + e^- = Cl^-$	23.0	25.0	25.0
$1/6IO_3^- + e^- + H^+ = 1/6I^- + 1/2H_2O$	18.6	13.6	11.6
$1/2Pt(OH)_2 + e^- + H^+ = 1/2Pt + H_2O$	16.6	11.6	9.6
$1/2I_2 + e^- = I^-$	9.1	11.1	11.1
$1/2Hg_2Cl_2 + e^- = Hg + Cl^-$	4.5	3.9	3.9
$e^- + H^+ = 1/2H_2$	0	−5.0	−7
$1/2PtS + e^- + H^+ = 1/2Pt + 1/2H_2S$	−5.0	−10.0	−12.0

[a] From Bartlett and James (1993), with permission.

[b] Calculated for reaction as written according to Eq. (8.14). Free energy of formation data were taken from Lindsay (1979) as a primary source, and when not available from that source, from Garrels and Christ (1965) and Loach (1976).

[c] Calculated using tabulated log K° values, reductant and oxidant = 10^{-4} M soluble ions and molecules, and activities of solid phases = 1; partial pressures for gases that are pertinent to soils: 1.01×10^{-4} MPa for trace gases, 2.12×10^{-2} MPa for O_2, 7.78×10^{-2} MPa for N_2, and 3.23×10^{-5} MPa for CO_2.

[d] Values not listed by Loach (1976).

So similar for carbon also from pollutants or other nutrient group also, analytical couples also you can see the conversion of their oxidized form to reduced forms.

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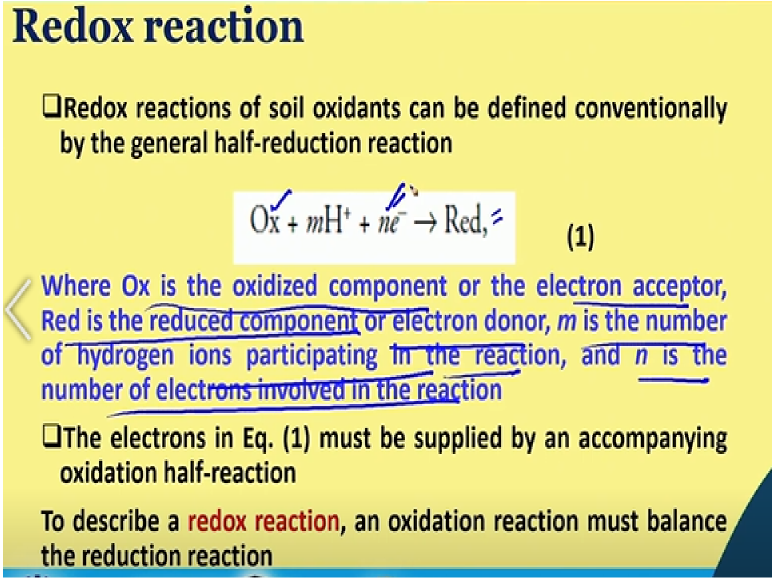

Redox reaction

❑Redox reactions of soil oxidants can be defined conventionally by the general half-reduction reaction

$$\mathrm{Ox} + m\mathrm{H}^+ + ne^- \rightarrow \mathrm{Red}, \quad (1)$$

Where Ox is the oxidized component or the electron acceptor, Red is the reduced component or electron donor, *m* is the number of hydrogen ions participating in the reaction, and *n* is the number of electrons involved in the reaction

❑The electrons in Eq. (1) must be supplied by an accompanying oxidation half-reaction

To describe a redox reaction, an oxidation reaction must balance the reduction reaction

Now redox reaction of soil oxidants can be defined conventionally by the general half-cell you know half reduction reaction which is basically denoted by oxidized form + mH plus + ne minus = reduced form. So you can see here in this Ox is the oxidized component or the electron acceptor, Red is the reduced component or electron donor, m is the number of hydrogen ion pertaining participating in the reaction and n is the number of electron involved in the reaction okay.

So the reduction half-reaction for any redox reaction can be expressed in terms of this equation 1. So the electrons in equation 1 must be supplied by an accompanying oxidation half-reaction. Remember we have talked about that oxidized species and the reduced species should coexist, so the electrons which are basically accepted by the oxidized species to get reduced should be donated by accompanying oxidation half-reaction.

Now to describe the redox reaction, an oxidation reaction must balance the reduction reaction. So it is a complete, it is not an individual reduction half-reaction, it should also involve the oxidation reaction to complete the total redox reaction.

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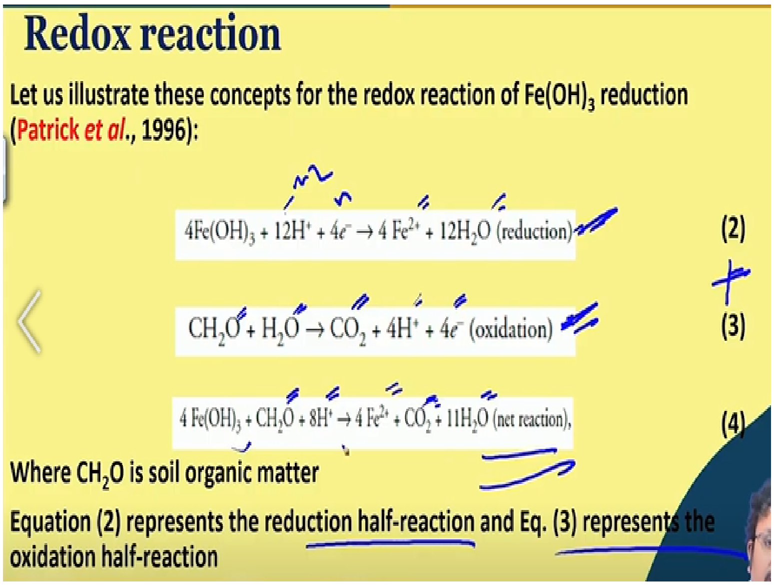

Redox reaction

Let us illustrate these concepts for the redox reaction of $Fe(OH)_3$ reduction (Patrick *et al.*, 1996):

$$4Fe(OH)_3 + 12H^+ + 4e^- \rightarrow 4Fe^{2+} + 12H_2O \text{ (reduction)} \quad (2)$$

+

$$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^- \text{ (oxidation)} \quad (3)$$

$$4Fe(OH)_3 + CH_2O + 8H^+ \rightarrow 4Fe^{2+} + CO_2 + 11H_2O \text{ (net reaction),} \quad (4)$$

Where CH_2O is soil organic matter

Equation (2) represents the reduction half-reaction and Eq. (3) represents the oxidation half-reaction

So let us see. So let us illustrate this concept for redox reaction of FeOH3 reduction and let us see this ferric hydroxide + 12 H+ so here m is 12, n is 4, ultimately we are getting reduced form of iron Fe2+ and or in other words ferrous and 12 molecules of water. So it is basically a reduction if we follow the equation 1 and also as we have seen we have talked about thus there will be a coexisting oxidation half-reaction also.

You can see this CH2O which is basically denoting a soil organic matter will be reacting with water to form the carbon dioxide, 4 protons and 4 electrons. So, basically it is getting rid of electrons, so this organic matter is getting rid of electrons ultimately oxidized. So this is an oxidation reaction and so finally if we combine these two reaction, oxidation reaction and reduction reaction together.

That is reaction 2 + reaction 3 we will get this final reaction where 4 molecules of ferric hydroxide and you know organic matter you know in the presence of 8 protons will produce 4 molecule you know 4 Fe ferrous ions, carbon dioxide and 11 molecules of water. So this is the net reaction. Here you can see one thing, here the FeOH3 is getting reduced to Fe2+ whereas this organic matter is getting oxidized to carbon dioxide.

So, it also supports our previous slide that the reductant will be oxidized and oxidant will be reduced. So equation 2 basically represents the reduction half-reaction and equation 3 we have already talked about this half oxidation half-reaction.

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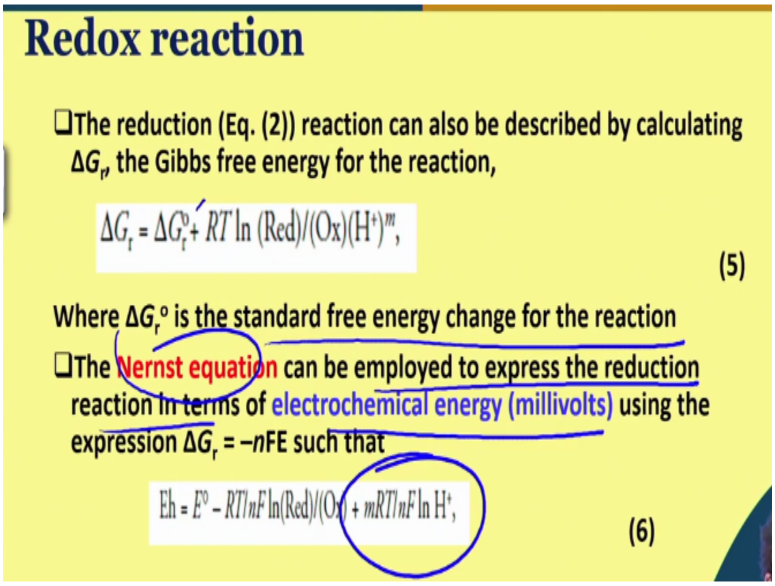

Redox reaction

- ❑The reduction (Eq. (2)) reaction can also be described by calculating ΔG_r, the Gibbs free energy for the reaction,

$$\Delta G_r = \Delta G_r^0 + RT \ln (\text{Red})/(\text{Ox})(\text{H}^+)^m, \qquad (5)$$

Where ΔG_r^o is the standard free energy change for the reaction

- ❑The Nernst equation can be employed to express the reduction reaction in terms of electrochemical energy (millivolts) using the expression $\Delta G_r = -n\text{FE}$ such that

$$\text{Eh} = E^0 - RT/nF \ln(\text{Red})/(\text{Ox}) + mRT/nF \ln \text{H}^+, \qquad (6)$$

So, the reduction reaction half-reaction that is equation 2, reaction can also be described by calculating the delta G which is known as the delta Gr which is Gibbs free energy for the reactions. The Gibbs free energy for the reaction can be expressed in terms of this delta G0 + RT ln natural logarithm of reduced by Ox that is oxidized and H+ m. So basically H+ to the power m where delta G0 is the standard free energy change of the reaction.

So from this equation we can have the Nernst equation which is very important equation. So, this Nernst equation can be employed to express the reduction reaction in terms of electrochemical energy or in terms of millivolts. So to express the reduction reaction in terms of electrochemical energy, we generally use the Nernst equation and using the expression of delta Gr = nFE such that we will get this value of Eh = E0 – RT by nF ln reduced by oxidized plus this expression. So let us see what are the meaning of these expressions and these.

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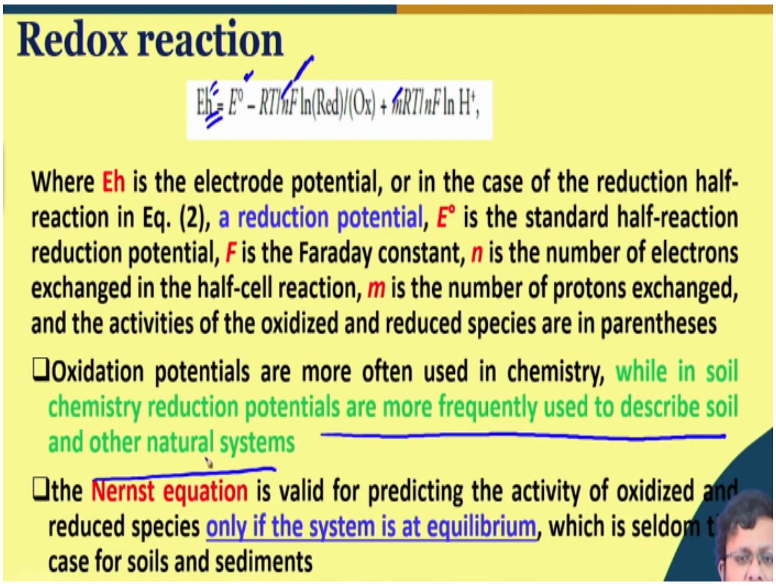

Redox reaction

$$Eh = E^{\circ} - RT/nF \ln(\mathrm{Red})/(\mathrm{Ox}) + mRT/nF \ln H^{+},$$

Where Eh is the electrode potential, or in the case of the reduction half-reaction in Eq. (2), a reduction potential, E° is the standard half-reaction reduction potential, F is the Faraday constant, n is the number of electrons exchanged in the half-cell reaction, m is the number of protons exchanged, and the activities of the oxidized and reduced species are in parentheses

- ☐Oxidation potentials are more often used in chemistry, while in soil chemistry reduction potentials are more frequently used to describe soil and other natural systems
- ☐the Nernst equation is valid for predicting the activity of oxidized and reduced species only if the system is at equilibrium, which is seldom t case for soils and sediments

So again, this is a Nernst equation. This Nernst equation says this Eh is the electrode potential or in the case of reduction half-reaction in equation 2, so this is an Eh, this is basically a reduction potential, E0 is basically the standard half you know half-reaction reduction potential and then F which we are using here is basically the Faraday constant, n is the number of electrons we know that, n is the number of electrons exchanged in the half-cell reaction, m is the number of protons exchanged.

So m is the number of protons exchanged we know that and the activities of the oxidized and reduced species are in parenthesis. So, oxidation potentials are more often, remember that these oxidation potentials are more often used in chemistry while the soil chemistry, you know, in case of soil chemistry reduction potentials are more frequently used to describe soil and other natural systems. So again, these oxidation potentials are more often used in chemistry while in soil chemistry reduction potential are more widely used.

So again, this Nernst equation basically comes when we express the reduction equation in terms of electrochemical energy, in terms of millivolts we can get this Nernst equation form. So the Nernst equation is valid for predicting the activity of oxidized and reduced species only if the system is at equilibrium, which is seldom found in case of soil and sediment. So this is one of the drawback of Nernst equation.

Nernst equation can be valid only at the equilibrium which is basically very hard to get, in case of very heterogeneous system like soil we have discussed that in details also.

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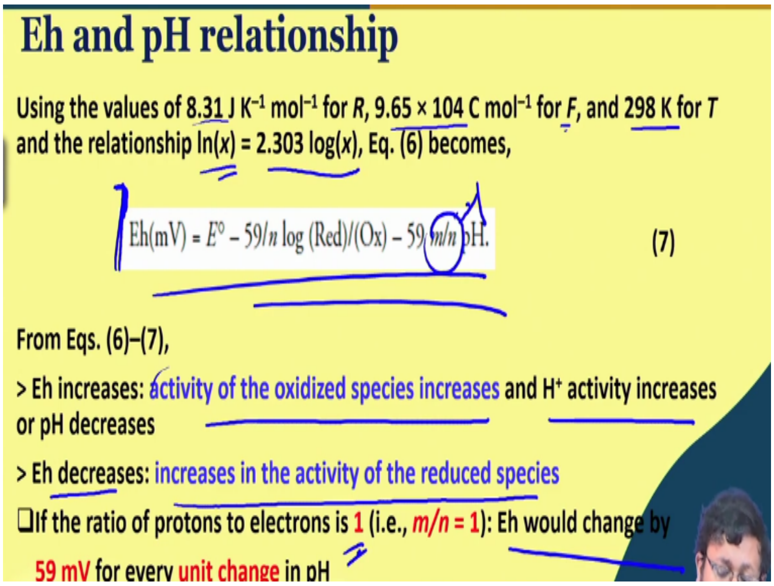

Eh and pH relationship

Using the values of 8.31 J K^{-1} mol^{-1} for *R*, 9.65 × 104 C mol^{-1} for *F*, and 298 K for *T* and the relationship ln(*x*) = 2.303 log(*x*), Eq. (6) becomes,

$$Eh(mV) = E^{o} - 59/n \log (Red)/(Ox) - 59\,m/n\,pH. \qquad (7)$$

From Eqs. (6)–(7),

> Eh increases: activity of the oxidized species increases and H^{+} activity increases or pH decreases

> Eh decreases: increases in the activity of the reduced species

☐If the ratio of protons to electrons is 1 (i.e., *m*/*n* = 1): Eh would change by 59 mV for every unit change in pH

Now what is the relationship between Eh and pH. Okay now using the values of, in the Nernst equation if we use the value of this R that is the you know molar gas constant that is 8.31 joule per kelvin per mole and then for Faraday constant we use a 9.65 into 10 to the power 4, it should be 10 to the power 4 indicated per mole and then 298 Kelvin for T and the relationship basically ln x equal to, we know that the ln x equal to basically 2.303 log of x.

Then equation 6 that Nernst equation basically you know converts to this simplified form okay. Now from this equation 6 and 7, we can see that as Eh increases, so if Eh increases, so if this term increases so activity of the oxidized species increases and the H+ activity increases and pH decreases. Obviously as the Eh increases pH will decrease okay and as the Eh increases activity of the oxidized species will increase to getting reduced okay.

Now as Eh decreases, obviously the vice versa, that means increases in the activity of the reduced species. So if the ratio of the protons to electrons is 1, so here the ratio of protons to electrons m by n = 1 Eh would change by 59 millivolt for every unit change in pH. So if we consider this fraction equal to 1, then pH, you know Eh would change by 59 millivolt per unit change in pH. So this is the relationship.

Basically there is an inverse relationship between Eh and pH. As Eh increases pH decreases, as Eh decreases pH increases.

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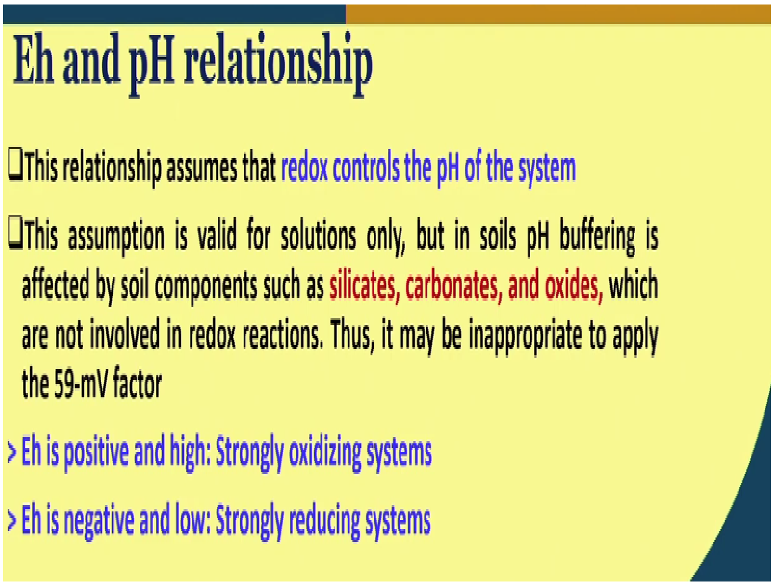

Eh and pH relationship

❑This relationship assumes that redox controls the pH of the system

❑This assumption is valid for solutions only, but in soils pH buffering is affected by soil components such as silicates, carbonates, and oxides, which are not involved in redox reactions. Thus, it may be inappropriate to apply the 59-mV factor

> Eh is positive and high: Strongly oxidizing systems

> Eh is negative and low: Strongly reducing systems

Now this relationship assumes that redox controls the pH of the system and this assumption is valid for solutions only, but in soils pH buffering is affected by soil components such as silicates, carbonates and oxides which are not involved in the redox reactions. Thus, it may be inappropriate to apply the 59 millivolts factor in case of soil. Now remember the thumb rule for using the redox potential in case of soil, Eh is positive and high.

When the Eh is positive and high then we use, then it is a strongly oxidizing system. When the Eh is negative and low, then it is basically a strongly negative reducing system. In case of submerged soil which is basically a strongly reducing system, you will see the Eh is basically negative and when we convert a soil from you know oxidized to you know reduced condition from aerobic to anaerobic condition, you will see the Eh will move from its positive value to more and more negative value.

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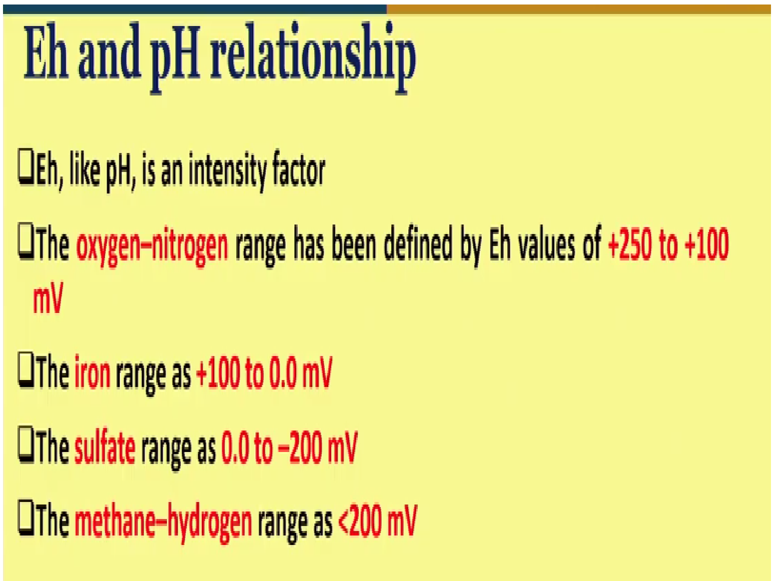

Eh and pH relationship

- Eh, like pH, is an intensity factor
- The oxygen–nitrogen range has been defined by Eh values of +250 to +100 mV
- The iron range as +100 to 0.0 mV
- The sulfate range as 0.0 to –200 mV
- The methane–hydrogen range as <200 mV

So Eh just like the pH is basically an intensity factor, you know the difference between intensity factor and capacity factor. So, Eh just like pH is an intensity factor and the oxygen-nitrogen range has been defined by you know and this different ranges of elements have been defined or conversion of different oxidized form to reduced form has been accompanied by a range of Eh values.

For example, in case of oxygen and nitrogen, this range has been defined by Eh values of +250 millivolt to +100 millivolt. However, in case of iron, this range of Eh changes from +100 to 0 millivolt. In case of sulfate, it varies from 0 to -200 millivolt. In case of methane-hydrogen it ranges from, it ranges as less than two 200 millivolts. So in extreme you know whenever these millivolts are you know, whenever this Eh is very low, then you will see the formation of more and more reduced of you know species than that of oxidized species.

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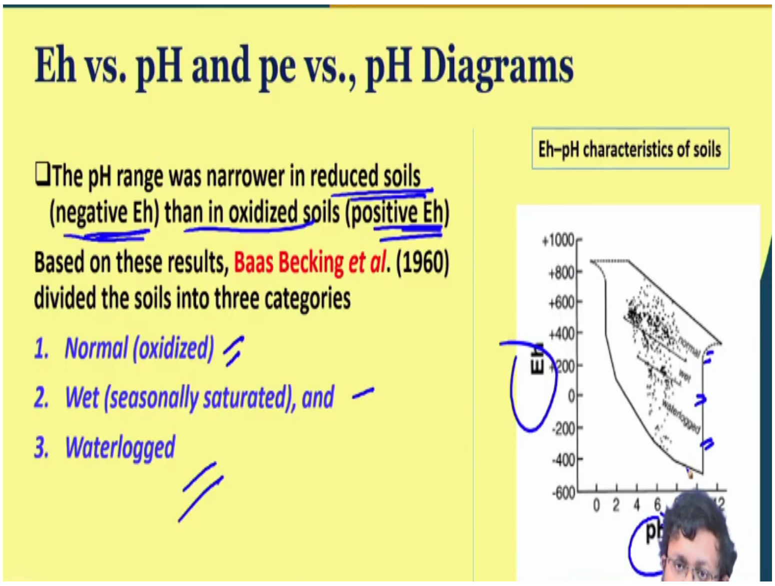

Eh vs. pH and pe vs., pH Diagrams

- The pH range was narrower in reduced soils (negative Eh) than in oxidized soils (positive Eh)

Based on these results, Baas Becking *et al.* (1960) divided the soils into three categories

1. *Normal (oxidized)*
2. *Wet (seasonally saturated), and*
3. *Waterlogged*

Eh–pH characteristics of soils

Now, let us see the relationship between Eh versus pH and pe versus pH diagrams. So the pH range was basically you know was narrower in reduced soils and because it is having the negative Eh, so negative Eh whatever you see is basically produced in reduced soil or submerged soils than in oxidized soils which is basically characterized by positive Eh, so again the oxidized soil is characterized by positive Eh, the reduced soil is characterized by negative pH.

So the pH range was narrower in reduced soils than in oxidized soil. Based on these results, the scientist Baas Becking et al in 1960 divided the soil into 3 categories. One is normal soil which is basically oxidized soil, wet soil which is seasonally saturated and waterlogged soil or submerged soil. So here you can see that based on the pH and Eh relationship, they have defined 3 different types of soil; waterlogged soils, wet soils and normal soils.

In case of normal soils, you can see the positive Eh values. In case of wet soils, you can see there is a fluctuation of Eh values. However, in case of waterlogged soil the Eh values are negative because they are reducing condition, they are they are residing in the reducing condition. So this shows the one of the graphical representation of Eh versus pH.

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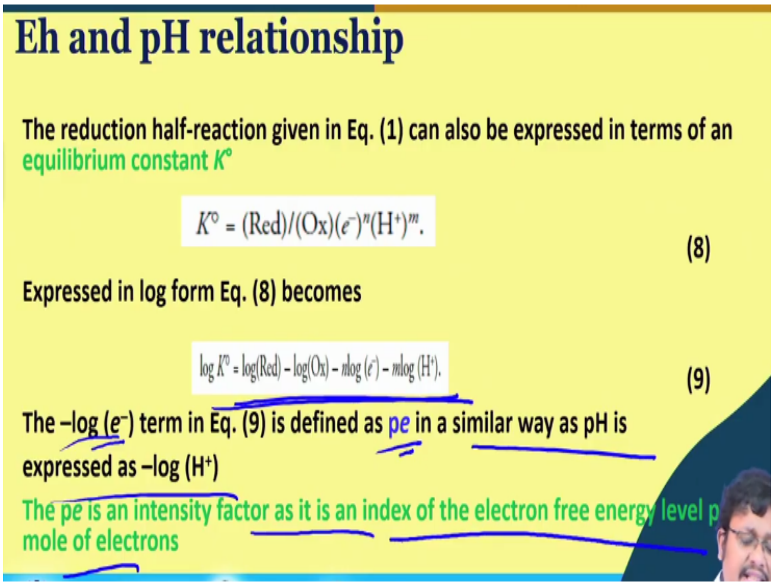

Eh and pH relationship

The reduction half-reaction given in Eq. (1) can also be expressed in terms of an equilibrium constant K°

$$K^{\circ} = (\mathrm{Red})/(\mathrm{Ox})(e^{-})^{n}(\mathrm{H}^{+})^{m}. \qquad (8)$$

Expressed in log form Eq. (8) becomes

$$\log K^{\circ} = \log(\mathrm{Red}) - \log(\mathrm{Ox}) - n\log(e^{-}) - m\log(\mathrm{H}^{+}). \qquad (9)$$

The $-\log(e^{-})$ term in Eq. (9) is defined as pe in a similar way as pH is expressed as $-\log(\mathrm{H}^{+})$

The pe is an intensity factor as it is an index of the electron free energy level p mole of electrons

Now the reduction half-reaction given in equation 1, remember the reaction which is, with which we started this lecture, given in equation 1 can also be expressed in terms of an equilibrium constant K0. This equilibrium constant K0 can be defined in terms of redox versus oxidized and then electron to the power n plus H+ of proton to the power m expressing in logarithmic form we will get this form and in this equation this minus log of electron concentration is known as pe.

In a similar way pH is known as the negative logarithm of hydrogen ion concentration. So pe is basically negative logarithm of electron concentration whereas pH is negative logarithm of hydrogen ion concentration. So pe basically an intensity factor and it is an index of the electron free energy level per moles of electrons. So in other words, it is the index of electron free energy level per mole of electrons.

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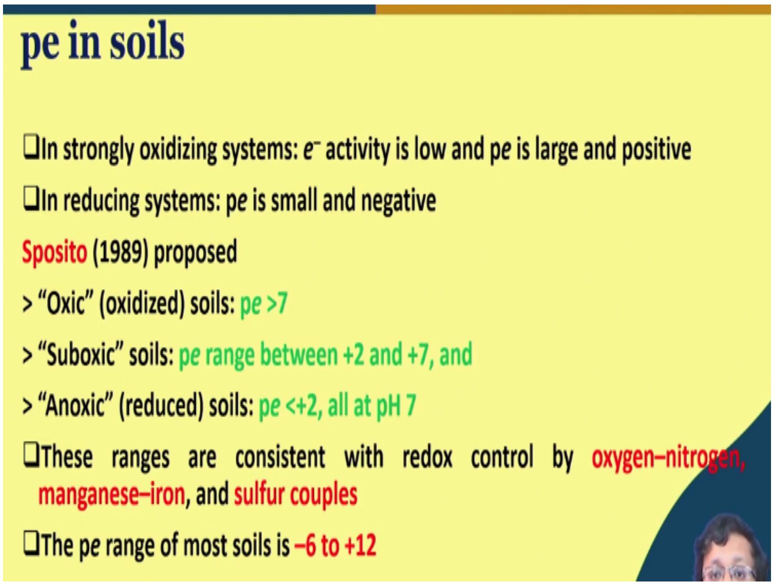

pe in soils

- ❑In strongly oxidizing systems: e^- activity is low and *pe* is large and positive
- ❑In reducing systems: *pe* is small and negative

Sposito (1989) proposed

- > "Oxic" (oxidized) soils: pe >7
- > "Suboxic" soils: pe range between +2 and +7, and
- > "Anoxic" (reduced) soils: pe <+2, all at pH 7

- ❑These ranges are consistent with redox control by oxygen–nitrogen, manganese–iron, and sulfur couples
- ❑The *pe* range of most soils is –6 to +12

So if we consider pe in soil in strongly oxidizing system, the electron activity is low and pe is large and positive since it is a negative logarithm of hydrogen ion, negative logarithm of electron concentration. However, in case of reducing system pe is small and negative. So according to Sposito in 1989 he proposed that in case of oxic soil oxidized soil, we known as oxic soils, they have a characteristic pe value of greater than 7.

In case of suboxic soils, the pe ranges between +2 to +7 and in case of anoxic soil or reduced soil the pe varies from less than +2 at all pH 7. So basically, the ranges are consistent with redox control, with redox control by oxygen-nitrogen, manganese-iron and sulfur couples. However, the pe range for most of the soil varies from -6 to 12. So, I hope guys you have learnt something new in this lecture.

We have defined first the reduction and oxidation and how this oxidized and reduced species basically coexist to govern this redox reaction, what is redox potential, how this, what are the values of the redox potential in different conditions and then we have talked about the Eh pH relationship and then we have talked about the pe. We have defined the pe and how the pe varies in soil.

So guys, let us wrap up this lecture. In the next lecture, we will be talking about more about pe and then we will be talking the other aspects of the redox reaction and redox chemistry of soils. Thank you very much. Let us meet in our next lecture.