Environmental Soil Chemistry
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Lecture – 32
Redox Chemistry of Soils – Continued

Welcome friends to this second lecture of week 7 of this online NPTEL online certification course of environmental soil chemistry, and in this week we are talking about redox chemistry of soils. So, in the first lecture we have briefly talked about different concepts of what is redox potential and what is the relationship between the redox potential as well as the pH and pe.

So, before going to the new topic in this week, in this lecture, I want to give you a quick recap of whatever we have discussed, so that it will be easy for you guys to relate the new things.

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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, in the previous lecture we started, these are the concepts which we are going to discuss in this week. Oxidation-reduction reactions and oxidation-reduction potentials or redox potential, then Eh versus pH and pe versus pH relationship and measurement and use of redox potential, submerged soils and redox reactions involving inorganic and organic pollutants.

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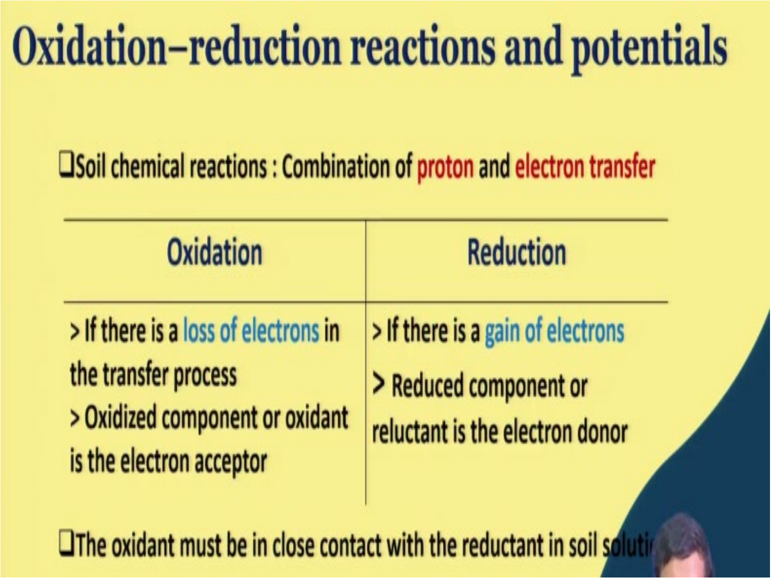

Oxidation–reduction reactions and potentials

❑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 soluti

So, in the first lecture we have talked about the difference between the oxidation and reduction. You all know that oxidation means the loss of electrons in the transfer process whereas reduction means there is a gain of electrons. In case of oxidation, oxidized components or oxidant is electron acceptor, whereas in case of reduction the reduced component or reductant is the electron donor and the oxidant must be in close contact with the reductant in soil solution.

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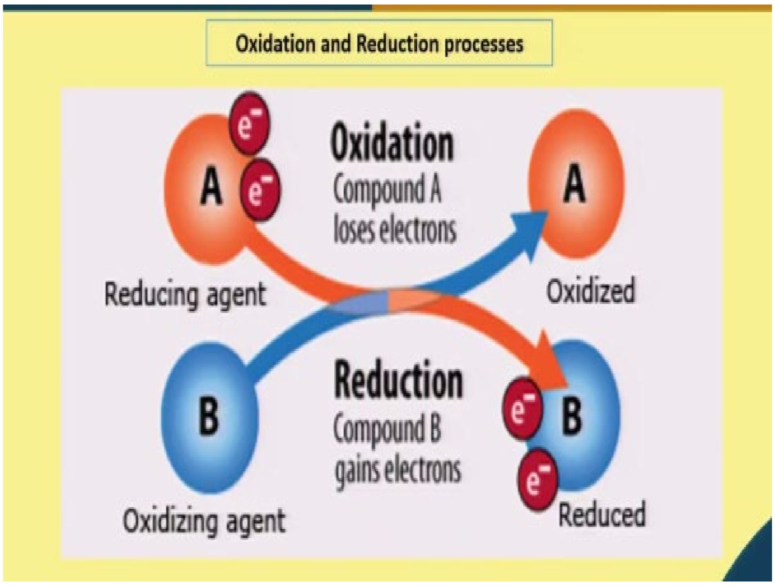

Oxidation and Reduction processes

As we have seen in this picture, the reducing agent and oxidizing agent has to be, they have to be you know in close proximity to be oxidized and reduced.

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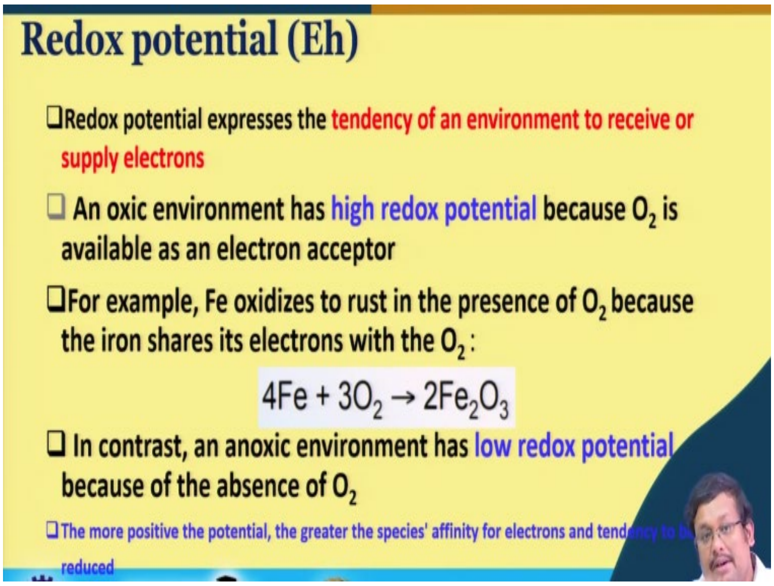

Redox potential (Eh)

- ☐ 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

Now, regarding the redox potential we can, in short we can denote this as Eh and redox potential express the tendency of environment to receive or supply the electrons and we have discussed the redox potential on the light of this iron oxygen reactions to produce the ferric oxides. You know, remember that an oxic environment has a high redox potential because oxygen is available as an electron acceptor, in contrast an anoxic environment has low redox potential because of the absence of oxygen.

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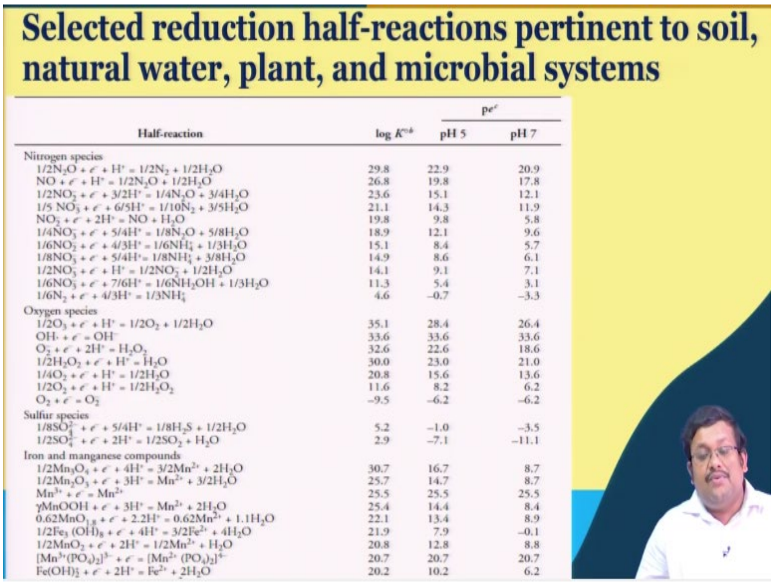

Selected reduction half-reactions pertinent to soil, natural water, plant, and microbial systems

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
$1/6NO_3^- + e^- + 7/6H^+ = 1/6NH_3OH + 1/3H_2O$	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

And then I showed you the, you know selected reduction half-reaction which are very important for soil, natural water, plant and microbial system. We have seen the nitrogenous species, we have seen oxygen species, we have seen sulfur species, iron, manganese compound, their logarithmic of equilibrium constant as well as their pe value at different 2 different pH, pH 5 and pH 7.

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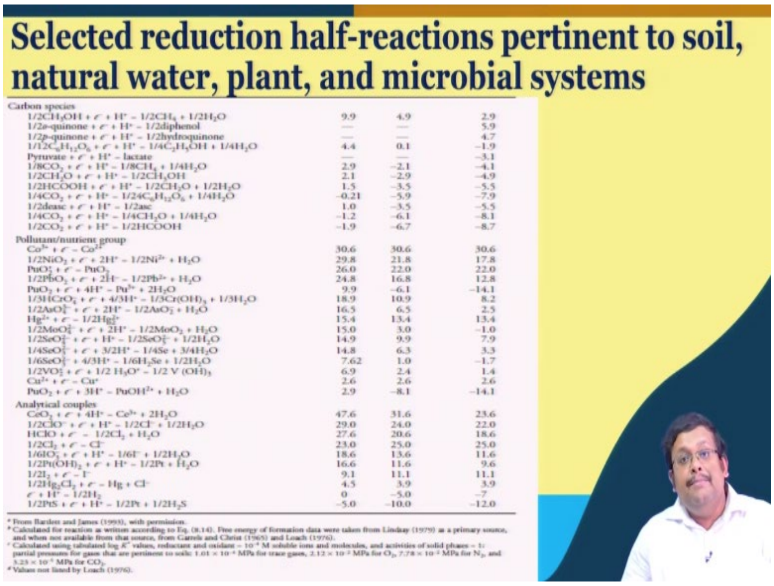

Selected reduction half-reactions pertinent to soil, natural water, plant, and microbial systems

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

And, so, we have we have seen these, you know, half reactions reduction half-reactions for carbon species, pollutant and nutrient groups as well as analytical couples also.

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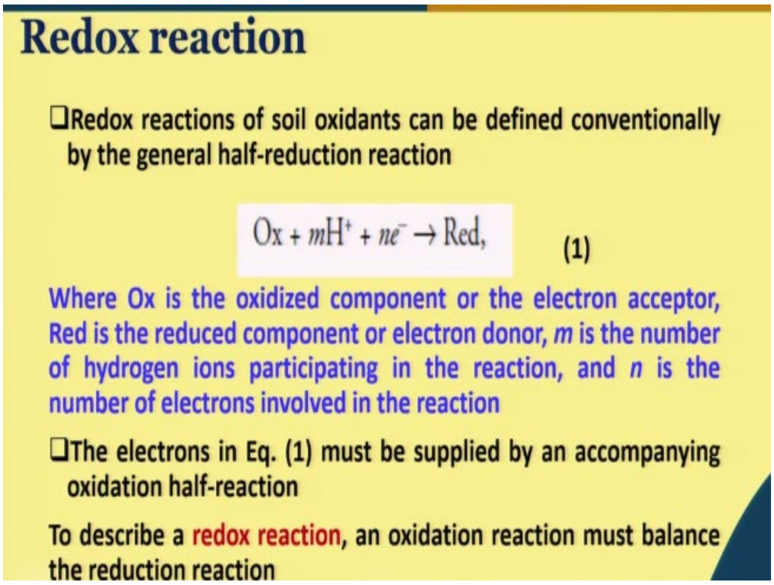

Redox reaction

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

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

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

Then we have seen the redox reaction, I mean the generalized form of the redox reaction in the soil.

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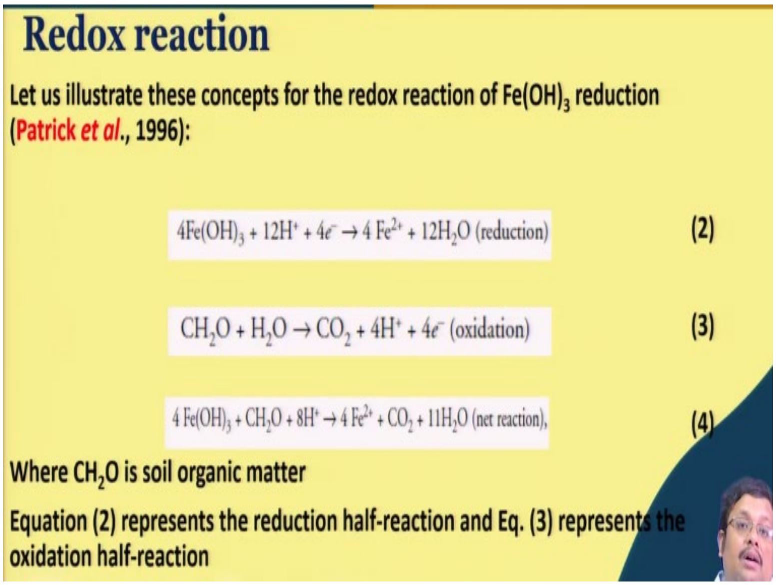

Redox reaction

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

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

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

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

Where CH_2O is soil organic matter

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

And then based on that we have you know illustrated the redox reaction of FeOH whole 3 according to the Patrick et al and then we have seen how this FeOH whole 3 first reduced to ferrous and then how this organic matter act as a, you know, acts as a reducing agent.

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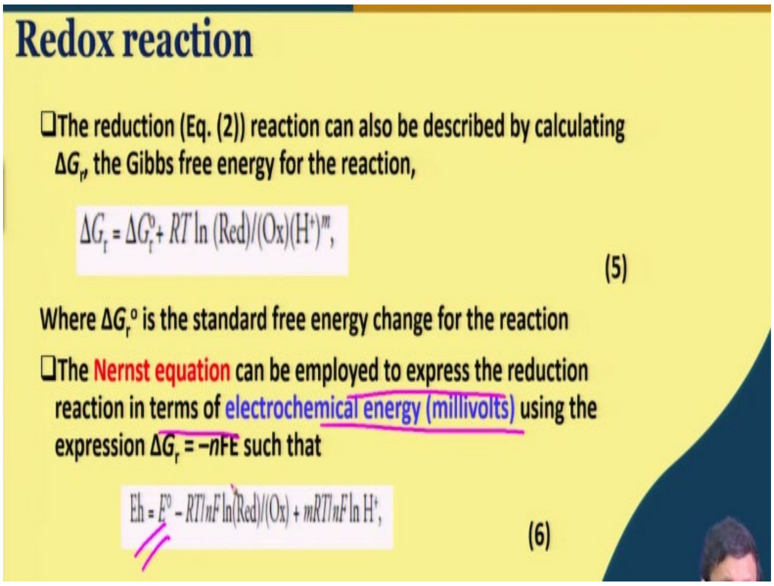

Redox reaction

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

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

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 $\Delta G_r = -nFE$ such that

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

Then we have discussed these reductions in terms of Nernst equation. This is the Nernst equation which can be employed to express the reduction reaction in terms of electrochemical energy or millivolt and this is the Nernst equation. We have expressed this Nernst equation where the Gibbs free energy is basically -nFE. So, we have discussed all these things or standard free energy.

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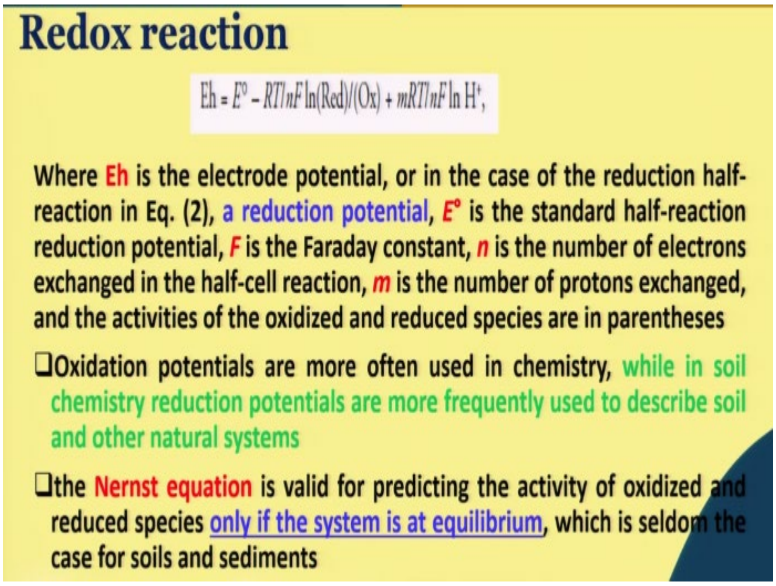

Redox reaction

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

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 the case for soils and sediments

So, we have expressed this redox reaction or redox potential in terms of this Nernst equation and also the standard half-cell reduction reaction. Remember that the oxidation potential are more often used in chemistry, whereas in soil we more generally use the reduction potential. Remember, the Nernst equation is valid for predicting the activity of the oxidized and reduced species only in case of a system which is in equilibrium. However, in soil we seldom see the equilibrium between different reactions.

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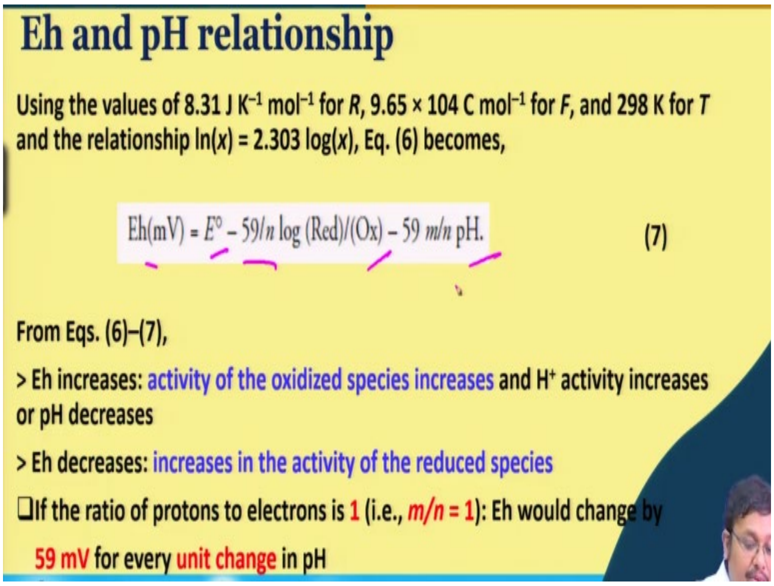

Eh and pH relationship

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,

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

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

So, then we have discussed about the Eh and pH relationship using the values of the molar gas constant as well as Faraday constant and then absolute temperature in Kelvin and so we have expressed the you know Eh and pH relationship which is basically we can express that Eh mV = basically E0 - 59 minus by n log reduced over oxidized - 59 m by n pH and basically when the, m and n basically shows the protons and electrons.

When this m by n ratio become 1, then we can say that the Eh would change by 59 millivolt per every unit you know change in pH. So, we can simplify this relationship between Eh and pH relationship.

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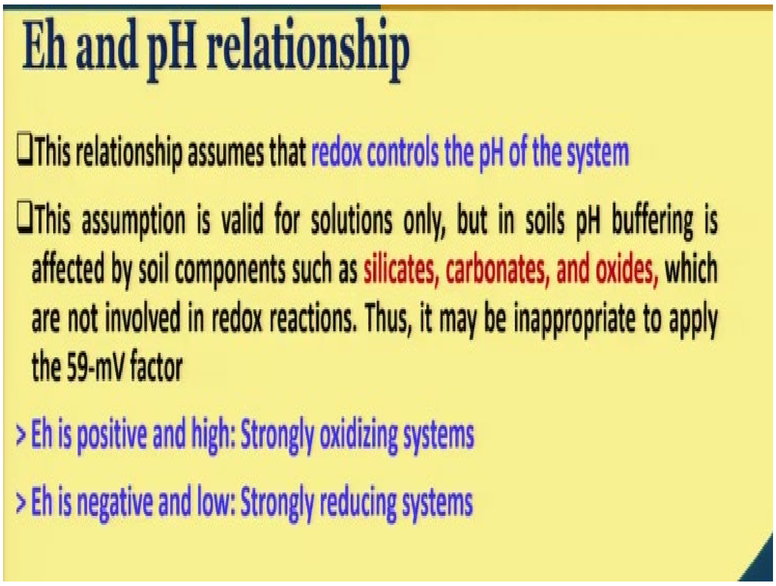

Eh and pH relationship

☐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

So, also we have discussed the implication of Eh and pH relationship, remember that when Eh is positive and high then it is basically showing the strongly oxidizing system. Whereas in case of even the Eh is negative and low that basically shows the strongly reducing systems.

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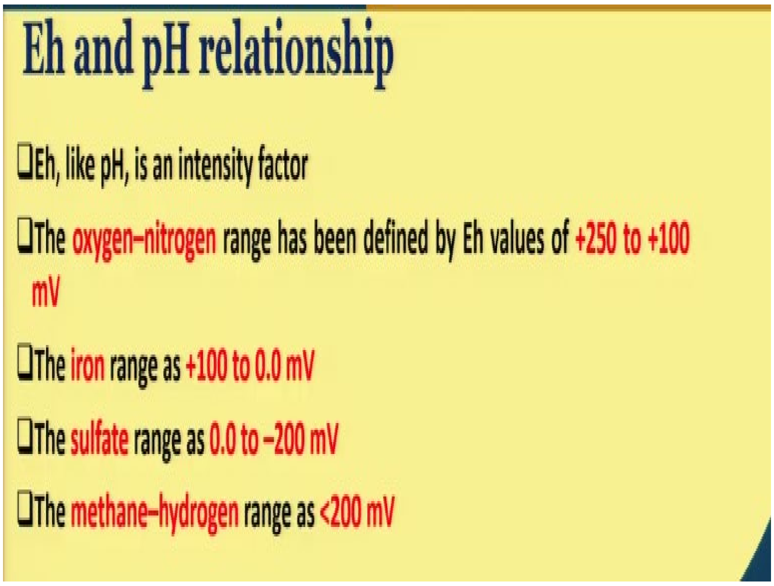

Eh and pH relationship

☐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

And then we have talked about the, you know, more about the Eh pH relationship. Remember Eh just like a pH is an intensity factor and the oxygen-nitrogen range has been defined by Eh values from +250 millivolt to 100 millivolt and the iron basically you know, the redox potential of iron or the major reaction of conversion of iron basically ranges between 100 to 0 millivolt and the sulfate ranges from 0 to -200 millivolt, whereas the methane-hydrogen ranges between, methane-hydrogen range with a value of less than 200 millivolt.

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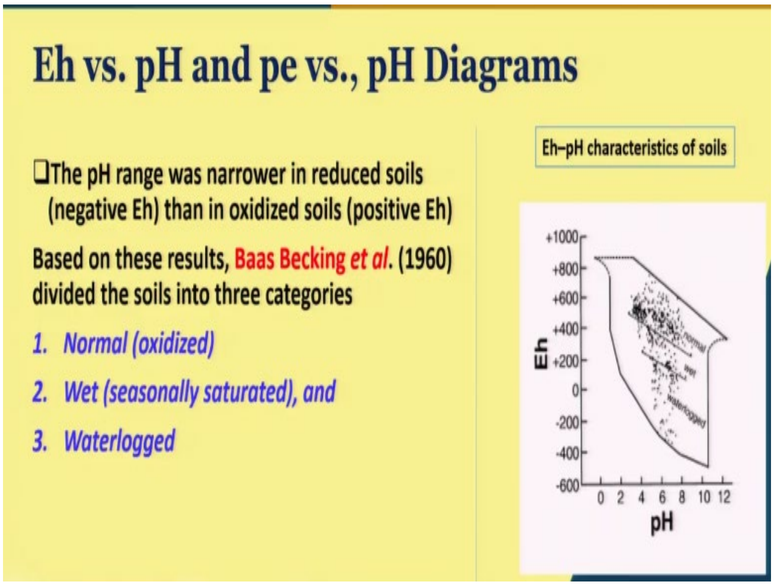

Eh vs. pH and pe vs., pH Diagrams

❑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

And then, we have divide the, you know, we have discussed the Eh and pH graph and then we divide the zone as you can see here in the three zone that is one is oxidized or normal zone and then seasonally saturated or wet zone and waterlogged zone or anoxic zone. So, based on that we can calculate, we can see the relationship between the Eh and pH.

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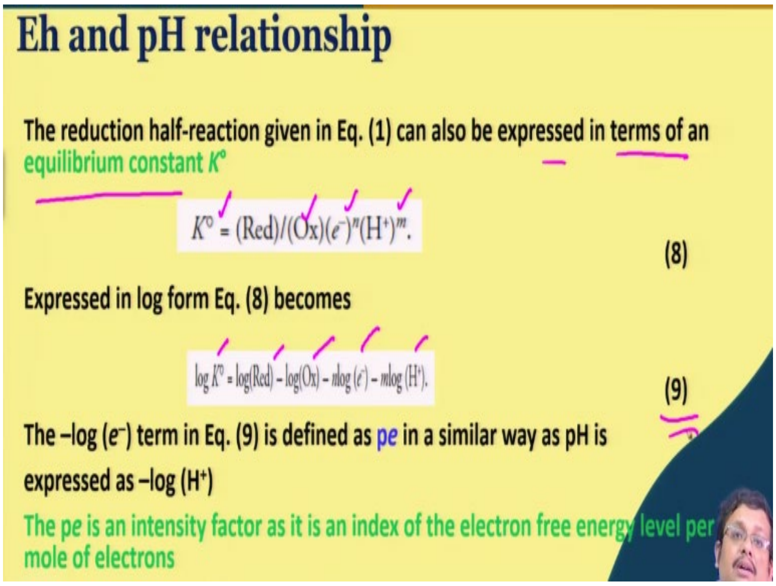

Eh and pH relationship

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

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

Expressed in log form Eq. (8) becomes

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

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 per mole of electrons

Now, today we are going to discuss from this slide. So, basically Eh and pH relationship you can see the reduction half potential, this reduction half-reaction which is given in our previous equation 1 can also be expressed in terms of an equilibrium constant K0 value. So, K0 basically, is basically can be expressed by a reduced species concentration of reduced species by concentration of oxidized species and electron to the power n and proton to the power m.

So, expressed we can if we can take the logarithmic form from this equation 8, let us consider this as an equation 8. So, if you convert it to the logarithmic form, then we will get the log of K0, then log of reduced species concentration log of oxidized species concentration minus n log of electron concentration and m log of H+ ion concentration. Now here, these negative logarithm of electron concentration term in this equation is known as the pe.

And it is just like the similar way as pH is basically the negative logarithm of proton concentration or hydrogen ion concentration. Remember that the pe is an intensity factor as it is an index of electron free energy level per mole of electron. Just like pH and Eh, the pe is also an intensity factor because it shows the negative logarithm of electron concentration.

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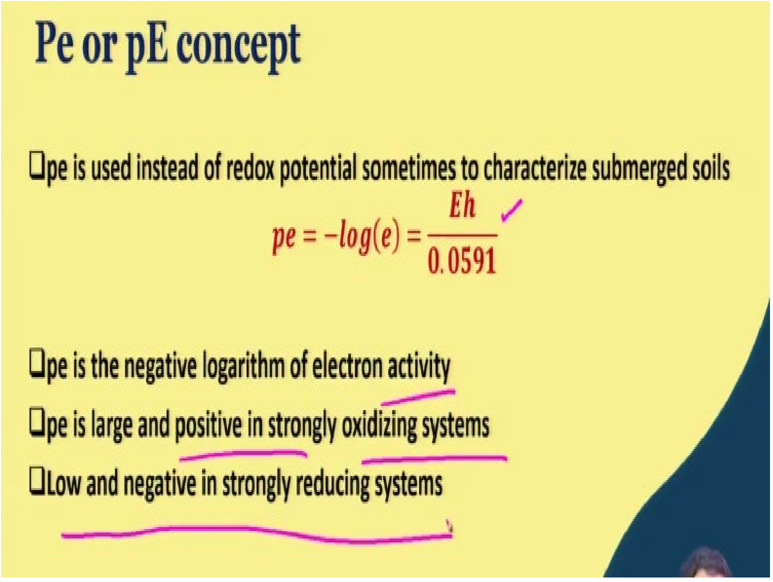

Pe or pE concept

☐pe is used instead of redox potential sometimes to characterize submerged soils

$$pe = -log(e) = \frac{Eh}{0.0591} \checkmark$$

☐pe is the negative logarithm of electron activity

☐pe is large and positive in strongly oxidizing systems

☐Low and negative in strongly reducing systems

So, again the pe and pE, pe sometime we can express in terms of p capital E. So, basically the concept is the, basically used instead of redox potential. So, these pe and Eh can be used interchangeably to denote the, you know, oxidation reduction state of a system. So, pe is used instead of redox potential sometimes to characterize the submerged soil. Now, submerged soil is a very important phenomena in case of soil, in case of soil oxidation reduction chemistry.

Now, this reduction potential is more applicable for different transformation which are going, which are which are happening in the submerged soils. So, in this submerged soil instead of Eh, we sometimes use the pe concept also. Now, we know that pe is basically negative logarithm of electron ion concentration, electron concentration we can and pe is basically equal to Eh by 0.0591. Now, pe is a negative logarithm of electron activity we know that.

Now pe is large and positive in strongly oxidizing system, just like in case of you know, in case of Eh it is basically positive, in case of oxidizing system, strongly oxidizing system. However, pe is also low and negative in strongly reducing system just like as Eh. So, the implication of pe and Eh are basically same generally, we generally use the term pe in terms of defining when we are trying to define the chemical dynamics in submerged soil. So, what is submerged soil? We will see in a moment.

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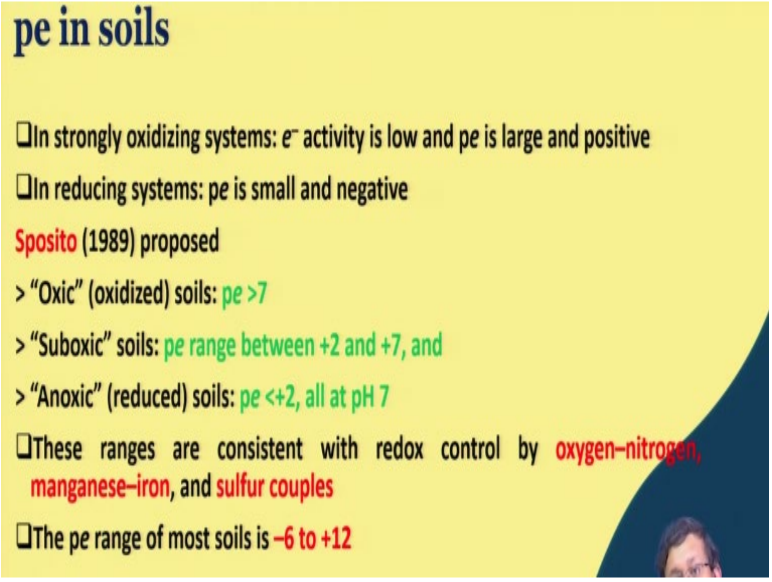

pe in soils

❑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

Now, what are the other implications of pe in soils? Now in strongly oxidizing system, the electron activity is low and pe is large and positive, I have already told you just like as the Eh. In terms of Eh you know in the oxidized system and you know aerobic soil you will see that it is positive in terms of millivolts unit. So, so similarly, in case of strongly oxidizing system also electron activity is low and that is why the pe is large and positive.

Now in reducing system pe is small and negative. So the scientist Sposito in 1989, he proposed that some range of pe which we can see generally in oxic soil, suboxic soil and anoxic soils. Now in the oxic soil, we can see a pe value of greater than 7, whereas in case of suboxic soil pe basically ranges between +2 to +7. However, in case anoxic soil, the pe generally you know is less than + 2, all at pH 7.

So, these ranges are consistent with redox control by oxygen-nitrogen, manganese-iron and sulfur couples. So, basically these oxygen-nitrogen, manganese-iron, sulfur couples are very important reactions as far as the redox reactions in the submerged soil is concerned. So, these ranges, they can be, you know, these ranges are true when you compare these oxygen-nitrogen, manganese-iron and sulfur couples in the submerged soils and the pe range for most of the soil generally it varies from -6 to +12.

So, this is basically the implication of the pe. Again pe is basically negative logarithm of electron concentration and in, in in case of oxic soil, strongly oxidized soil the value of electron activity is low, as a result, the pe is large and positive, vice versa in case of anoxic soil. Now, that is why in case of, you know in defining the redox reaction in submerged soils or anoxic soil we generally use pe sometime instead of Eh, it varies from -6 to +12.

However, in oxic soil it is, the range is greater than 7, in case of suboxic soil or periodically saturated soil it is, it varies from + 2 to +7, however in case of anoxic soil it is less than + 2.

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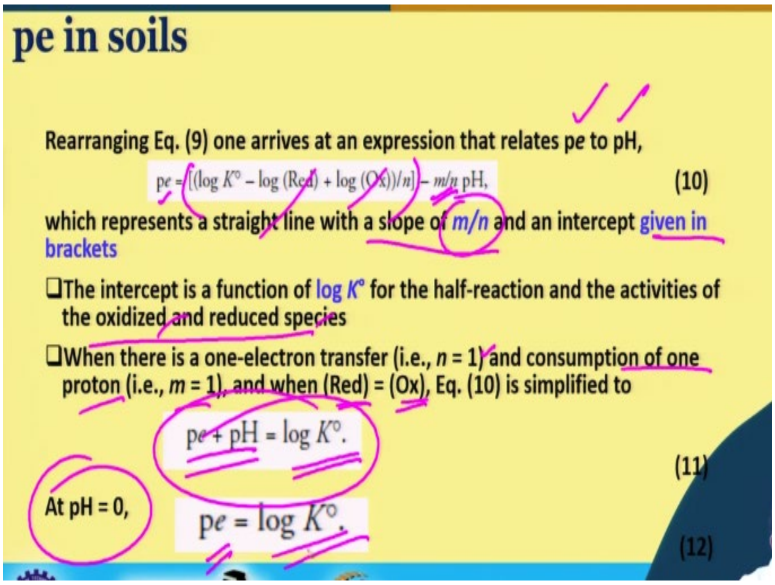

pe in soils

Rearranging Eq. (9) one arrives at an expression that relates pe to pH,

$$pe = [(\log K^{\circ} - \log (\mathrm{Red}) + \log (\mathrm{Ox}))/n] - m/n \ \mathrm{pH}, \quad (10)$$

which represents a straight line with a slope of *m/n* and an intercept given in brackets

- The intercept is a function of log *K*° for the half-reaction and the activities of the oxidized and reduced species
- When there is a one-electron transfer (i.e., *n* = 1) and consumption of one proton (i.e., *m* = 1), and when (Red) = (Ox), Eq. (10) is simplified to

$$pe + \mathrm{pH} = \log K^{\circ}. \quad (11)$$

At pH = 0,

$$pe = \log K^{\circ}. \quad (12)$$

So, so if we just rearrange the equation 9, so, what was the equation 9? So, if we go back and see this is the equation 9 we have talked about log K= logarithmic of reduced you know, reduced species concentration minus logarithm of oxidized species concentration minus n log e electron - m log H+. So, basically if we take this equation and if we rearrange this equation, we can arrive at an expression that relates pe to pH.

So, you can see here if we rearrange that then it becomes pe = -log K0 - logarithm of reduced species concentration to logarithmic of oxidized species concentration by n - m by n pH, now which represent a straight line with a slope of m slash n. So if we relate the pe to pH in a graph, we will see that there is a straight line, where the slope is m by n, we can see here just like here, an intercept given in this bracket.

So, this bracketed portion is basically the intercept. Now, this intercept as you can see from this formula is a function of log of equilibrium constant or K0 for the half-reaction and the activities of the oxidized and the reduced species. Now, for calculating this log K0, we have already calculated this log K0 in our previous modules. So, you can see that the intercept which is basically a combination of these terms.

It basically depends on log K0 for the half-reaction and also the activities of oxidized and reduced species as you can see in the bracket, in the parenthesis, concentration of reduced species as well as concentration of oxidized species. So, when there is only one electron transfer that means when there is n = 1 and the consumption of 1 proton that is m equal to also 1 and when the concentration of the reduced species is equal to the concentration of the oxidized species.

So, basically this and this are same, concentration of oxidized species and concentration of reduced species n = 1. So, basically these two nullify each other and then m - n is also 1 because we are considering that m =1 and n = 1, that is one proton, consumption of 1 proton and 1 electron transfer, then this equation can be simplified equal to pe and this pH will come to this side So, pe + pH = log K0 okay.

Now at pH 0, when the pH is 0, so obviously pe = log K0. So, basically this is the general relationship between this negative logarithm of hydrogen ion concentration and negative logarithm of electron concentration as well as log of equilibrium constant. So, this can be simplified for pH 0 when pe = logarithm of K0. So, when the pH nullifies, the pH becomes 0, then we can see you know here pe equals to logarithm of equilibrium ion concentration equilibrium concentration.

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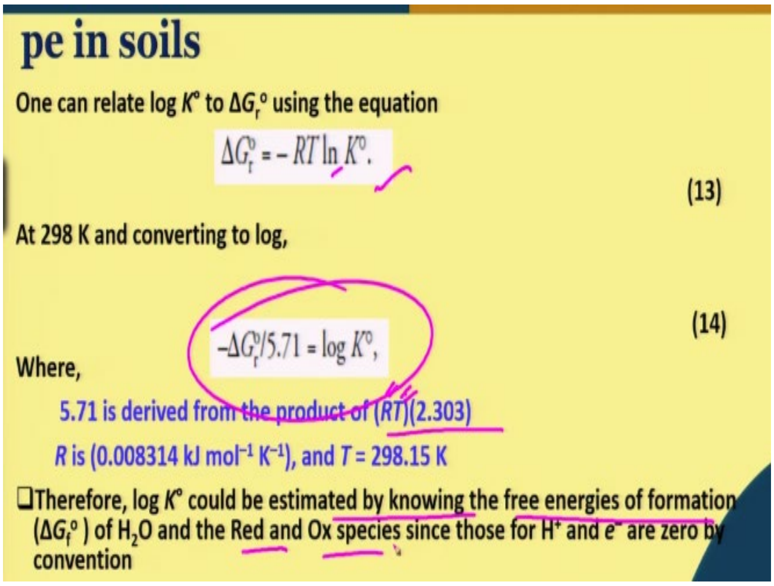

pe in soils

One can relate log K° to ΔG_r° using the equation

$$\Delta G_r^\circ = -RT \ln K^\circ. \quad (13)$$

At 298 K and converting to log,

$$-\Delta G_r^\circ/5.71 = \log K^\circ, \quad (14)$$

Where,

5.71 is derived from the product of $(RT)(2.303)$

R is (0.008314 kJ mol^{-1} K^{-1}), and $T = 298.15$ K

- Therefore, log K° could be estimated by knowing the free energies of formation (ΔG_f°) of H_2O and the Red and Ox species since those for H^+ and e^- are zero by convention

Now, the pe in soils also one can relate this logarithmic of equilibrium constant equilibrium constant to this delta Gr also using this equation just like this. Delta Gr = -RT ln K0. Now at 298 Kelvin and converting it to logarithmic, then we can see when we are converting these natural logarithms to log then we can get this 5.71 and then from there we can have this relationship. Now, this 5.71 is derived from the product of RT into 2.303.

We know that when you convert this natural logarithm to log, then we have to use this factor 2.303 and RT you know R is basically molar gas constant and T is the temperature in Kelvin. So, when you multiply all these things, then we can get a value of 5.71. So basically, we simplify these in terms of this free energy Gibbs free energy with the log of equilibrium constant.

So, therefore, this logarithmic of K0 or log of equilibrium constant could be estimated by knowing the free energies formation, that is delta 0 f of water and the reduced and oxidized species since those for H + and electron are zero by convention. So, we can see that we can simplify the whole reaction in terms of this, you know, free energies of formation as well as the logarithm of the equilibrium constant equilibrium constant.

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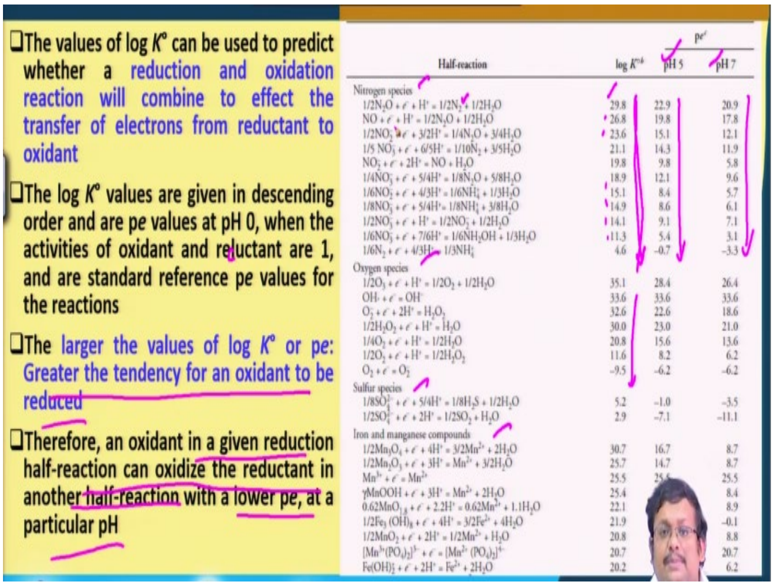

- The values of log K° can be used to predict whether a reduction and oxidation reaction will combine to effect the transfer of electrons from reductant to oxidant
- The log K° values are given in descending order and are pe values at pH 0, when the activities of oxidant and reductant are 1, and are standard reference pe values for the reactions
- The larger the values of log K° or pe: Greater the tendency for an oxidant to be reduced
- Therefore, an oxidant in a given reduction half-reaction can oxidize the reductant in another half-reaction with a lower pe, at a particular pH

Half-reaction	log K°	pe′ pH 5	pe′ 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	[illegible]	25.5
$\gamma MnOOH + e^- + 3H^+ = Mn^{2+} + 2H_2O$	25.4		8.4
$0.62MnO_{1.8} + e^- + 2.2H^+ = 0.62Mn^{2+} + 1.1H_2O$	22.1		8.9
$1/2Fe_3(OH)_8 + e^- + 4H^+ = 3/2Fe^{2+} + 4H_2O$	21.9		−0.1
$1/2MnO_2 + e^- + 2H^+ = 1/2Mn^{2+} + H_2O$	20.8		8.8
$[Mn^{3+}(PO_4)_2]^{3-} + e^- = [Mn^{2+}(PO_4)_2]^{4-}$	20.7		20.7
$Fe(OH)_2^+ + e^- + 2H^+ = Fe^{2+} + 2H_2O$	20.2		6.2

So, we can see here these values are basically, you know we have seen this table previously. So, this is the half-reaction of reduction for different species starting from nitrogen species, oxygen species, sulfur species, iron and manganese compounds. So, some of the observation which we can see from here, the values of logarithm of K0 can be used to predict whether a reduction and oxidation reaction will combine to effect the transfer of electron from reductant to oxidant.

So, by seeing these values, we can conclude whether a reduction oxidation reaction will occur, and if the reduction oxidation will occur, whether, you know, how the electron transfer will you know how these electron will transfer from the reductant to oxidant. So, you can see here the log K0 values here are given in descending order, so we can get the highest log K0 value here and then we are getting it in descending order and our pH value is at pH = 0.

So, when the activities of oxidant and reductant are basically 1 and are standard, so it is reductant. So, oxidant and reductant are 1 and the standard reference pe values for the reaction. So, we can see standard reference pe values for 2 different pH, one is pH 7 and another is pH 5. So, we can see for each of these species, nitrogen species, oxygen species, sulfur species and iron inorganic compound, all these reactions are arranged in terms of basically descending order of their log of equilibrium constant.

Now, remember one thing one thumb rule that the larger the value of this K0 or pe, so similarly, you can see here one more thing, you know here not only the ascending order of the K0 the logarithm of K0, but you can see, I am sorry, that the descending order of log of

K0 and also you can see descending order of pe also in both these cases more or less. So, the larger the value of K0 or pe, greater the tendency of an oxidant to be reduced.

Obviously, higher pe basically indicates higher, higher pe basically indicates oxidized system. So, a species which is highly oxidized will be, you know, will have more tendency to be reduced. So, it is quite natural that a species which has a higher pe value such as in case of oxidized system as well as it has high logarithm of K0 value, then that species will be more, will have more tendency to get reduced. So, therefore an oxidant in a given reaction reduction half-reaction can oxidize the reductant in another half-reaction with a lower pe at a particular pH.

So, obviously, you can see here one example that this N2O that is the nitrous oxide, nitrous oxide when it is reacting with one electron that means it is getting reduced. So, we are here getting you know after reduction of this nitrous oxide we are getting elemental nitrogen. This elemental nitrogen is more amenable to reduce than the other nitrogenous compound which are presented below.

So, this nitrogen will further reduce into other species. So, this is how this reaction basically goes on. So, this basically denotes in terms of this logarithm of K0 values as well as pe values. So, let us see some other examples also.

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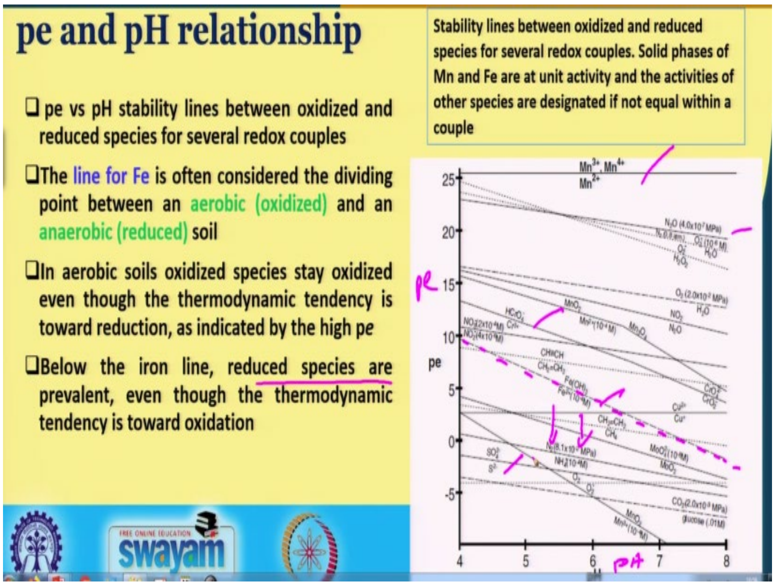

pe and pH relationship

- ☐ pe vs pH stability lines between oxidized and reduced species for several redox couples
- ☐ The line for Fe is often considered the dividing point between an aerobic (oxidized) and an anaerobic (reduced) soil
- ☐ In aerobic soils oxidized species stay oxidized even though the thermodynamic tendency is toward reduction, as indicated by the high pe
- ☐ Below the iron line, reduced species are prevalent, even though the thermodynamic tendency is toward oxidation

Stability lines between oxidized and reduced species for several redox couples. Solid phases of Mn and Fe are at unit activity and the activities of other species are designated if not equal within a couple

Now, pe and pH stability lines between the oxidized and reduced species for we can see here this is basically a pe, we are we are we are plotting pH and pe here in x and y axis and basically shows the pe and pH stability lines. These lines are basically showing pe and pH stability lines between the oxidized and reduced species for several redox couples. So, we can see here for example Mn3+, Mn4+ and Mn2+.

Similarly, we can see here Fe3+, Fe2+, Cu2+, Cu+. So, we can see several redox couples and these lines are showing the stability between the oxidized and the reduced species for this different you know redox couples. So, the line for Fe you can see here, this is the line for Fe okay. So, this is basically the, this dotted line is for the EC which I am drawing right now. So the line for EC is the often considered as the dividing point between the aerobic which is oxidized and anaerobic which is basically reduced soil okay.

So in anaerobic soil basically whatever is above this line is considered is in the oxic condition or oxidized condition, aerobic soil condition and whatever species which are present below this line are considered in the anoxic condition or in case of reduced condition. Now in aerobic soil, oxidized species stay oxidized even though thermodynamic tendency is towards reduction.

So obviously, although the oxidized species tends to reduce themselves easily, but you know in the aerobic soil oxidized species try to stay oxidized okay as indicated by their high pe values. Below this iron line, so whatever below species are there below this iron line, these reduced species are prevalent, even though the thermodynamic tendency is towards oxidation. So obviously, just like just opposite to the oxidized species.

When the when the when the below the iron line when the reduced species are there, the reduced species are will be also have more tendency to get oxidized. However, they tend to be in the reduced condition as compared to the oxidized condition. So, you can see this is basically a kind of a border line above which the oxidized species try to stay as in oxidized form and the species which are below this line try to stay in the reduced form.

So, basically again this is showing the stability lines between the oxidized and reduced species for several redox couples. Obviously, solid phases of manganese, iron are at unit activity and the activities of other species are designated if not equal to, if not equal within a couple. So, you can see here different couples are there, different redox couples are there for manganese, for nitrogen you can see, for chromium and so on and so forth from iron.

And then from sulfur, you can see different redox couples are there depending on different conditions. So, these basically shows their stability.

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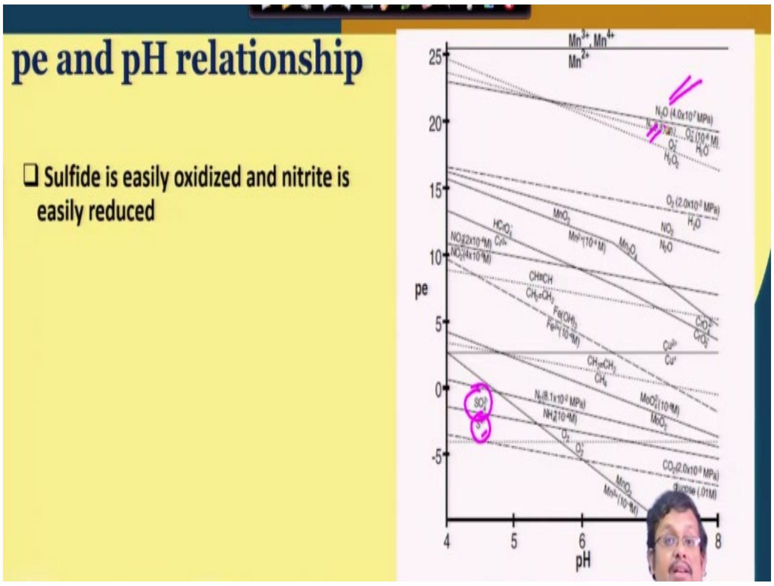

pe and pH relationship

- ❑ Sulfide is easily oxidized and nitrite is easily reduced

So if we move ahead, we will also see one important thing that this sulfide here, this is sulfide. So this sulfide and sulfate, so this is in oxidized and reduced, so basically this is a redox couple. So this is the line, stability line. So we can see that sulfide is easily oxidized and nitrate is easily reduced because this sulfide or sulfate these couple remain below this cutoff line or the, or the border line that is Fe3, Fe2 borderline.

So, basically here the sulfide is easily oxidized as compared to the nitrite, you see here the nitrate which is you know obviously easily reduced to other nitrogenous form like nitrogen. So, this is how we can we can we can we can define the state of oxidation reduction of different couple, different you know redox couples based on their pH and pe relationship.

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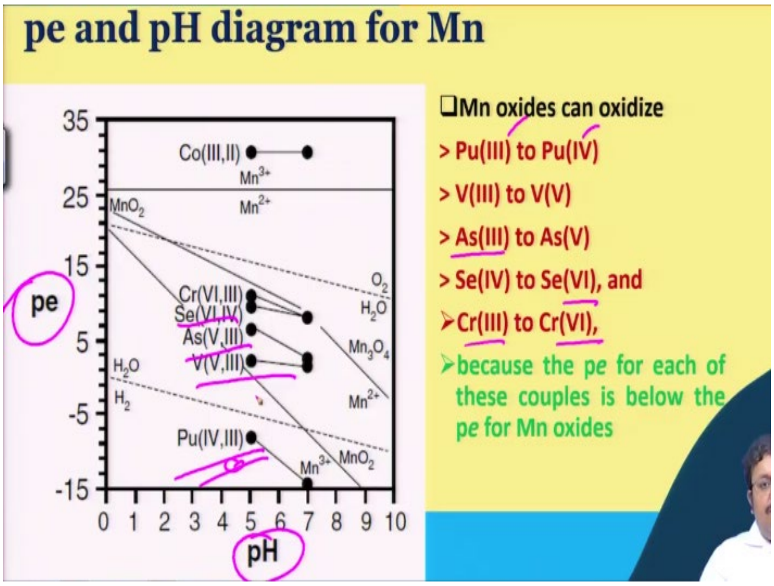

pe and pH diagram for Mn

❑Mn oxides can oxidize
> Pu(III) to Pu(IV)
> V(III) to V(V)
> As(III) to As(V)
> Se(IV) to Se(VI), and
➢Cr(III) to Cr(VI),
➢because the pe for each of these couples is below the pe for Mn oxides

So, also we can see here, this is the pe and pH diagram for manganese. We are plotting the pH in the x axis and plotting the pe in the y axis and these are line for different species of you know different other species like this for chromium, selenium, arsenic and vanadium, plutonium. Now we can see that the manganese oxide can, can, you know can oxidize Pu3 to Pu5. As we can see, Pu3 to Pu5 it can oxidized and also vanadium 3 to vanadium 5 it can oxidize.

This As3 to As5 that is arsenite to arsenate it can oxidize, then selenium 4 to selenium 6 it can oxidize, and also it can oxidize from chromium 3 to chromium 6. We will see these in more details in our next lectures how these different you know conversion happens. So you can see that, you know, these different, so because you know at different pe versus pH relation, we can see that the conversion of different oxidized form of this plutonium, vanadium.

And then arsenic, selenium and chromium you know mediated by manganese oxides now because the pe for each of these couples is below the pe of manganese oxide. So, it is very clear. These, the pe values of these, you know, of these each couples that is chromium 3, chromium 6, selenium 4, selenium 6, arsenite, arsenate and then vanadium 5, vanadium 3, all their pe values are basically below the pe values of manganese.

So, as a result of that, manganese has more tendency to get reduced and when it is reducing, simultaneously it is oxidizing these species. So that justify why manganese oxide can oxidize these species from one you know oxidation state to another oxidation state. So guys, I hope that you have learnt something new in this lecture. Let us wrap up this lecture here.

And we will start from here in the next lecture, that is third lecture of week 7 and then we will see in details about you know submerged soils and other aquatic soils. Thank you very much.