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Lecture – 33 Redox Chemistry of Soils – Continued

Welcome friends to this third lecture of week 7 and in this week we are talking about the redox chemistry of soils. In the previous 2 lectures, we have talked about the basic concept of redox reaction and what is redox potential and then we have talked about redox potential and pH relationship. Also we have talked about the redox potential as well as pe relationship. Remember pe is basically the negative logarithm of electron concentration.

And this pe also indicates, you know pe and Eh are basically used simultaneously to denote the redox condition of a system, specifically in anoxic soil like submerged soils and depending on the logarithmic logarithm of the equilibrium constant and their pe values we can define what should be the dominant oxidant species and what should be the reductant species available for this system and also we have discussed the stability lines or difference oxidized and reduced species couples.

And based on that we have seen you know at which condition which form will be more dominant. For example, we have seen that the iron line that is Fe3 Fe2+ line is basically the border line between this oxic and anoxic system, and whatever species which are present above this line tries to be remain in the oxidized form, although their thermodynamic equilibrium is tends towards you know reduction and vice versa for those species which are present below this line just like the sulfide.

So, and also we have discussed you know what is the implication of these high pe values and low pe values and these lines and we have seen that the manganese oxide which has high higher pe values than the arsenic 3 and arsenic 5 and plutonium and other species, they can oxidize those species by getting itself reduced, this manganese oxide because of the higher pe values. Now, in this lecture, we will be talking about calculation, how to calculate the log of K0 and pe?

What is their actual relationship and then we will be trying to discuss the actual chemistry of

submerged soils and also I will try to discuss the practical implication of these eh values as far as the soil chemistry is concerned.

(Refer Slide Time: 03:29)

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Calculation of log K° and p)e
Thus Eq. (10)	
$pe_{-} [(\log K^{\circ} - \log (\text{Red}) + \log (\text{Ox}))/n] - m/n \text{ pH},$	
reduces to Eq. (11) $pe + pH = \log K^{\circ}$.	
and at pH 0, Eq. (12) $pe = \log K^{\circ}$ results	
Relating $\ln K^{\circ}$ to ΔG_{r}° , one can employ Eq. (13),	
$AC^{\circ} = BT \ln K^{\circ}$	
$\Delta q \sigma_r = -RT m R$	

So, let us start with this calculation of logarithmic of logarithm of equilibrium constant and the pH. Now, we have seen that the reduction half-reaction below basically shows the reduction of Fe3 to Fe2+. You can see FeOH 2+ + electron + one proton we get Fe2+ H2O. So, basically from +3 we are getting +2, so it is basically reduction from Fe3 to Fe2+, ferric form to ferrous form.

Now, in this reaction there is one electron transfer as you can see from +3 to +2. So, n = 1. So, if you remember, you know our previous you know equation of equation 8. So, for your convenience let us go back and see what is, what was equation 8. So, if we go back, our equation 8 was K0 equal to concentration of reduced species over concentration of oxidized species multiplied by e to the power or electron to the concentration to the power n and H+ or proton concentration to the power n.

So, here e, this electron is 1, and if we consider this then so in this reaction if we put the e value of e = 1 then ultimately and also consumption of 1 proton. So, electron of transfer of one electron means consumption of one proton, so here m = 1. So, basically Fe3+ and Fe2+ is an imposed condition, if we consider this an imposed condition the concentration of ferric is equal to the concentration Fe2+, then this whole equation will turn into this equation that is equation 10.

Now, equation 10 says pe equal to then this is a logarithmic term minus m by n pH. We know that this is equation 10, this whole thing will be you know reduced to this pe + pH = log of K0, we have also seen that in our previous lecture. Now at pH 0, we also know that pe = log of K0 and relating this natural logarithm of K0 to this Gibbs free energy we can get this equation. So, these all these things we have discussed in our previous lecture, so now what is new?

(Refer Slide Time: 06:02)

Calcu	llation of log K° and pe
UWe know	$\Delta G_t^{\rm o} = \Sigma \Delta G_t^{\rm o} \text{ products} - \Sigma \Delta G_t^{\rm o} \text{ reactants.}$
Solving ΔG_r° for $\Delta G_r^\circ = [(-91.3)]$	or Eq. (1.1), 42 kJ mol ⁻¹) + (–237.52 kJ mol ⁻¹)] – [(–241.85 kJ mol ⁻¹) + (0)] (1.2)
= [-328.8	16 kJ mol ⁻¹ + 241.85 kJ mol ⁻¹]
= -87.01	kJ mol ⁻¹ .
Using Eq. (14)	$-\Delta G_r^{\circ}/5.71 = \log K^{\circ},$
	$\log K^{\circ} = \frac{87.01}{3.71} = 15.2.$

Now, we know that the Gibbs free energy the whole reaction is basically the difference between the Gibbs free energy of products and Gibbs free energy summation of the Gibbs free energy of the reactants. Now, if we solve these reactions, so if we put these values of the free energy of these products and free energy of the reactants, we will get this value that is - 87.01 kilojoules per mole. Now, using this equation 14, we can see that minus delta G0 r by 5.71 equal to log K.

We have seen that also in our previous lecture. So, now we know the value of delta G0 = 87.01. So, basically it will be 87.01 by 5.71, so that will be value of 15.2. So, for this half-reduction reaction from Fe3 to Fe2+, we have calculated the value of log K0 = 15.2. How we have calculated again? We have seen, we have calculated based on the free energy, calculating the free energy.

And once we calculated the free energy, we are basically inputting that value into the equation 14, which you have already seen previously. Now, we have calculated it is 15.2.

(Refer Slide Time: 07:35)



Now, this value for log K0 is the same as we have seen in our table for the, you know reaction of equation 1.

(Refer Slide Time: 07:45)

Calculation of log K°	and p	e	
$1/2\text{Fe}_{3}O_{4} + e^{-} + 4\text{H}^{+} = 3/2\text{Fe}^{2+} + 2\text{H}_{3}O$	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
$1/2Fe_{2}O_{3} + e^{-} + 3H^{+} = Fe^{2+} + 3/2H_{2}O$	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
$Fe^{3+} + e^- = Fe^{2+}$ cvt 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
$1/3$ KFe ₃ (SO ₄) ₂ (OH) ₆ + e^{-} + 2H ⁺ = Fe ²⁺ + 2H ₂ O + 2/3SO ₄ ²⁻			
+ 1/3K*	8.9	6.9	2.9
$[Fe(CN)_6]^{3-} + e^- = [Fe(CN)_6]^{4-}$	_	_	6.1

So, you can see in this table in this table, this FeOH whole 2 to Fe2+. So, for this reaction, we know that the log K value was 15.2. So, this value of log K0 is one shown already we have seen in the table for this reaction in equation 1. So, once we calculate the pe at pH 5 and 7, one would use the equation 11. So, what we know from the equation 11? Equation 11 we know that $pe + pH = \log of K0$.

From there we have seen that at pH 0, pe will be equal to logarithm of K0 or equilibrium constant. So, this is the mother reaction, this is basically the original you know relationship $pe + pH = \log$ of K0. Now, for pH 5, substituting the value of 15.2, so we know the value of

log K0 = 15.2 and pH 5. So, we get a value of pe of 10.2 and for pH 7 similarly inputting the values we are getting the value of 8.2.

So, we can see, we can verify these values with the table which you have seen 15.2, 10.2 and 8.2. So this is how we calculate the value of log of K0 as well as the pe at different pH levels. So basically, we have to use two different formulas; one is for the Gibbs free energy. If we input the Gibbs free energy for that reaction, we will calculate the reaction Gibbs free energy.

The reaction Gibbs free energy can be input to get the value of log of K0 and from there, if we put input the value of log K0 into pe, pH, and log K0 relationship for different pH, we will get this value of pe and then we can verify these values.

(Refer Slide Time: 09:38)

Poise

The poise of a redox system is the resistance to change in redox potential with the addition of small amounts of oxidant or reductant. Poise increases with the total concentration of oxidant plus reductant, and for a fixed total concentration it reaches a maximum when the ratio of oxidant to reductant is 1

Now, another very important term we will, we generally come across when we discuss the submerged soil is called the poise. Now the poise of a redox system is the resistance to resistance to change in redox potential when the addition of small amounts of oxidant or reductant. Again, the poise of redox system is the resistance, so it is a kind of a buffer. So, it is a basically resistance to change in redox potential with the addition of small amount of oxidant or reductant.

So, when we add oxidant, it it slows down. The poise basically try to you know to counterbalance the change which is which is basically initiated by this oxidized oxidant and vice versa for the reductant. Now, poise increases with the total concentration of the oxidant plus reductant and for a fixed total concentration it reaches a maximum when the ratio of

oxidant to reductant is 1 okay. So, this is called poise.

It is basically a resistant or buffer which basically acts to resist the change in redox potential when we are adding a particular small amount of oxidant and reductant and its value becomes maximum when the ratio of oxidant to reductant is 1.

(Refer Slide Time: 11:05)



Now, what is the measurement and use of redox potential? Generally, in case of soil, the measurement of redox potential is usually done with platinum electrode and the electrode will transfer the electron to or from the medium, but it should not react with the medium. Remember that once the platinum electron platinum electrode is combined with a half-cell of the known potential, now reducing system will transfer electron to the electrode.

However, vice versa in case of oxidized system it will remove electron from the electrode. So, redox measurements are most reliable for flooded soil and sediment I have already told you in our previous lecture that although we talk about oxidation potential or you know in case of different chemical reaction, however, in case of soil, for example in case of flooded soils and sediments, we more talk about the reduction potential.

(Refer Slide Time: 12:06)

Measurement and Use of Redox Potentials

Oxidized soils have redox potentials of +400 to +700 mV

Seasonally saturated soils have redox potentials of +400 to +700 mV (oxidized) to highly reduced (-250 to -300 mV)

Now oxidized soils generally have a redox potential of +400 to +700 millivolt okay. In case of oxidized soil, in case of oxic soils you see that or in case of aerobic conditioning you will see the redox potential generally vary from +400 to +700 millivolts and in case of seasonally saturated soils, they have a redox potential of +400 to again +700 millivolt in case of oxidized system to highly reduced system which varies from -250 to -300 millivolts.

So, you can see that in case of oxidized system, the redox potential generally is positive, ranges between +400 to 700 millivolts, in case of anoxic, in case of, you know seasonally saturated soil when it is, when it is aerobic in aerobic condition it vary again it shows the same 400 to 700 millivolts. However, in case of reduced condition when all the pore spaces are filled by water, then you can see then it is highly reduced and showing the redox potential of -250 to -300 millivolts.

(Refer Slide Time: 13:19)

Implication of Eh

If redox potential data are combined with other information such as depth to the water table and oxygen content of the soil helps to know the wetness of an environment

Wetland sites that have low redox have had long periods of flooding and soil saturation

Redox data are also useful in understanding the morphology and genesis of the soil

Soils that undergo alternate oxidation and reduction cycles are usually mottled

Now, what is the implication of Eh? Now, if the redox potential data are combined with other information such as depth to the water table and oxygen content of the soil, it basically helps to know the wetness of an environment. Obviously, this redox potential is more you know highly used in case of defining the condition of an anoxic soil or in other words the chemical dynamics or chemical condition or you know chemical condition of a flooded soil or submerged soils.

So, basically the wetness of an environment can be detected by using these Eh values with the help of some other indicators. Now wetland sites that have been, that have low redox potential have had long period of flooding and soil saturation. So, obviously the wetland soils which are all the time you know which are which are saturated with the water for long time, they have a tendency to produce the very low redox potential.

And remember that redox data are also useful to understand the morphology and genesis of the soil, obviously. A particular type of soil when it is developed under the under the waterlogged condition, we will see that in case of submerged soil what type of you know morphological features we can see. We can see the bluish coloration, we can see mottling. So, these types of features, these types of color features are very prevalent in case of, you know, waterlogged soils.

So, the redox data are also useful to understand the morphology and genesis of the soil. So if you see the redox data of that soil, we can identify okay this environment may have created this type of soil. So soils that undergo alternate oxidation and reduction cycles are easily mottled, we will see that picture in a in a while. So, basically in alternate oxidation reduction in case of soil basically changes their color, we call it mottling.

So, these soils are you know, these mottled soils are very much prevalent in case of these alternating you know wet and dry cycle, wet and dry these mottled colored soils are basically found in case of these soils which are under, which undergo these seasonal oxidation and reduction.

(Refer Slide Time: 15:46)



Now, you know the different redox conditions will of course not only affect the chemical status of the plant nutrient but also the activity of the various microorganisms. Now, because soil organisms are composed of approximately 90% of water, the redox activities are expected to be confined within the borders of the stability of the water. So, obviously, you know not only the soil chemical reaction, but also biological activities also being you know controlled by this redox by this redox potential.

Now, these organisms which are present in the soil do not oxidize directly but acts as a redox catalysts and basically they mediate the oxidation of substance or the reduction of oxygen.

(Refer Slide Time: 16:36)

Implication of Eh

Sulfate-reducing bacteria, mediating the reduction reaction, become active only when Eh decreases below 0 mV.

In general, aerobic soil organisms thrive in normal or oxic soils, where the drainage is excellent (low electron activity), and anaerobic organisms flourish in waterlogged or anoxic soils where the drainage is poor (high electron activity).

Wet or suboxic soil (medium electron activity) may contain facultative anaerobic organisms or a mixture of aerobic and anaerobic microorganisms.

Now, sulfate-reducing bacteria, just for an example let us talk about sulfate-reducing bacteria. So, sulfate-reducing bacteria mediate the reduction reaction from sulfate to sulfide, become active only when the Eh decreases below 0 millivolt. So, unless the Eh of that system goes below 0 millivolt, this sulfate-reducing bacteria will not be effective, and once it is effective it will then change the oxidized form that is sulfate to reduced form that is sulfide which you have already seen.

Now, in general aerobic soil organisms thrive in normal or oxic soils whereas where the drainage is excellent that is obviously that means low electron activity, when the drainage is excellent that means more oxygen, more oxygen means less electron activity that means less electron activity means you know there will be aerobic conditions of the soil organisms, the aerobic soil organisms will grow in that condition.

And anaerobic organism flourished in waterlogged condition where all the oxygen are basically exhausted, by you know they have been replaced by the water. Also, they also so these organisms basically flourish in waterlogged condition, these anerobic organisms which do not require any oxygen for their growth, so they will flourish in the waterlogged or anoxic soil where the drainage is poor there is high electron activity.

Now wet or suboxic soil that is medium electron activity may contain facultative anaerobes organisms or a mixture of aerobic and anaerobic microorganisms. Facultative anaerobes means those which are inherently, so facultative anaerobes means those organisms which can thrive in both aerobic and anaerobic conditions, so it is called the facultative anaerobes okay.

So, these facultative anaerobes will be, will survive in this wet or suboxic soil okay, and basically a mixture of aerobic and, basically they show a mixture of aerobic and anaerobic organisms and most predominantly the facultative anaerobic organisms.

(Refer Slide Time: 18:52)



Another implication for this Eh in the soil can be illustrated using this using this using this graph you can see here. So, this basically shows an illustration of the variation in redox potential you know, when when reduced iron is oxidized by an oxidizing agent. So, suppose this reduced iron that is Fe2+ is oxidized to Fe3+ by some oxidizing agent, now you see if we if we if we if we plot the percentage of Fe3+ present in the x axis and millivolts or Eh in the y axis, then you will see a curve like this.

So, this curve in the figure indicates that oxidation of Fe2+ causes the redox potential to rise. So you can see when the concentration of Fe3+ is increasing that means conversion from Fe2+ to Fe3+ is increasing. As a result, there is also increase in redox potential as you can see, it is increasing.

(Refer Slide Time: 20:00)



Now, now when 50% of Fe2+ is produced and present, the redox potential equals to 770 millivolts. So, we can see here at 50%, we know when the 50% of Fe3 is produced and present, the redox potential corresponding redox potential is around 770 millivolts. So, this can be verified statistically by assuming that the half-cell of reaction is basically this and it is characterized by a standard potential of E0 770 millivolts.

Now, we have seen the redox potential for this reaction was formulated as $Eh = E0\ 0.059\ \log$ of concentration of Fe3 by Fe2+. So we know that here Fe2+, Fe3+ 50% we have seen here. So here by putting these values into this reaction, we will see $Eh = E0\ +0.059\ \log$ of 1. So from there, we can see a value of $Eh = E0\ =\ 0.770\ \text{volt}$. So, these reactions, this you know simplification can be done from this graph.

(Refer Slide Time: 21:20)

Implication of Eh

- Drastic changes take place in the physical, chemical, and biological conditions of soils with development of poor aeration or waterlogged conditions.
- Oxygen content decreases rapidly in poorly aerated soils.
- Respiration of plant roots and microorganisms will rapidly consume the remaining oxygen in soil air. Therefore, oxygen content decreases with a decrease in Eh.
- At low Eh values, the dissolved oxygen in soil water will then be used by the microorganisms, and at very low Eh values, even the combined oxygen, in the form of ferric oxides, nitrates, and sulfates, will be attacked.

Now, what are the other implications of Eh? You know drastic changes takes place in the physical, chemical and biological condition of soils with development of poor aeration and waterlogged condition. Obviously, obviously when there is a poor you know aeration and waterlogged condition, there is drastic changes in physical, chemical and biological condition because you know chemical reaction will be there because of the you know absence of oxygen.

And also biological organisms will not be, the composition of biological organisms will change depending on the aeration status. Now, oxygen content decreases rapidly in poorly aerated soil. So, when the soil is poorly aerated, the oxygen content decrease will decrease rapidly and the respiration of plant roots and microorganisms will rapidly consume the remaining oxygen in the soil.

Obviously, when an oxic soil become anoxic or you know or become waterlogged, the oxygen which is trapped inside the pores are easily or very rapidly utilized by the aerobic microorganisms which are present in the soil or by plant roots. So, therefore oxygen content decreases with a decrease in Eh obviously. So at this low Eh values, the dissolved oxygen in the soil water will be used by the microorganisms.

And at very low Eh values even the combined oxygen in the form of ferric oxides, nitrates and sulfates will be attacked. So, basically when there will be no oxygen present at highly reduced condition, these nitrates, sulfates will be will be used as a terminal electron acceptor by the microorganisms for their survival so because they don't have the oxygen over there okay. So, this is how these you know these changes of these redox potential show the profound influence in the chemical, biological and physical properties of the soil.

(Refer Slide Time: 23:30)

Implication of Eh

A notable chemical effect resulting from waterlogging is the conversion of insoluble iron and manganese oxides into soluble Fe(II) and Mn(II), respectively. The reactions can be represented as follows

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Fe_2O_3 + 6H^+ + 2e^- \leftrightarrow 2Fe^{2+} + 3H_2OMnO_2 + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O
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□ Consequently, in those poorly aerated soils in which reduction processes prevail, iron is found as Fe²⁺ iron, manganese as Mn²⁺ nitrogen as NH₄+ , and sulfur as SO₃²⁻ ions. On the other hand, these ions are present in thr oxidized state in well-drained soils (e.g., as Fe³⁺, Mn⁴⁺, NO₃⁻, and SO₄²⁻).

Now, a notable chemical effect resulting from waterlogging is a conversion of insoluble iron and manganese oxide into soluble Fe2+ and Mn2+ okay. Now, you know we generally see that when there is a waterlogging, the Fe2O3 or ferric oxide will reduce to Fe2+ by taking 2 electrons and then manganese oxide MnO2 basically convert to Mn2+, so it is reduced. So, both Fe2+ and Mn2+ basically are formed.

And you know these Fe3 form and Mn3 forms are basically insoluble in nature and when they convert into Fe2+ and that means when they convert from manganic to manganous and ferric to ferrous they will be converted from insoluble form to more soluble form. So, consequently in those poorly aerated soil in which the reduction process prevails, iron is found as Fe2+ and manganese is found as manganous and nitrogen will be found as ammonium and sulfur will be found as sulfide ion.

On the other hand, these ions are present in the oxidized states in well-drained soil like just like in the oxidized state they will be present as Fe3, Mn4 then nitrate and sulfate. So, basically, these are some of the very important element which shows a profound influence of Eh in their conversion in the waterlogged soils and as a result their availability to the plant also changes. Remember when they become more soluble, the plant can absorb them through their roots.

So, again, in the aerobic condition, this iron will be present as Fe3+ form, manganese will be present as manganic form Mn4+, nitrogen will be present as oxidized nitrate form and sulfur will be present as sulfate form sulfate form. However, in the reduced condition when the Eh

is very low, then the iron will be present as Fe2+ form, manganese will be present as Mn2+ form and nitrogen will be present as present as anaerobic NH4 or ammonium form and sulfur will be present as sulfite form.

(Refer Slide Time: 26:12)

Implication of Eh

□Biologically, decreasing oxygen content in soils produces drastic changes in the population of soil microorganisms. At low oxygen content, anaerobic microorganisms (*Actinomyces sp.*) may prevail over aerobic microorganisms.

In medicine, the redox potential is applied for the detection of certain diseases. Low values of the redox potential around the gum increase the risk of gingivitis, a gum disease

So, biologically decreasing oxygen contained in soil produce drastic changes in the population of soil microorganisms we have discussed it. Now at low oxygen content, anaerobic microorganisms like anaerobic, some Actinomyces species may prevail over aerobic microorganisms. Now, this Eh also not only they have application in soil, but also they have application in other disciplines also.

For example, in medicine, the redox potential is applied for the detection of certain diseases and low values of the redox potential basically, you know, low values of redox potential around the gum increase the risk of gingivitis, which is a gum disease. So, you can see this redox potential not only controls different soil reaction, but also it has you know application in other sectors also.

(Refer Slide Time: 27:06)

Submerged soils

Submerged soils – soils that are submerged in water for a sufficient period of time to give the distinct horizon development differentiating from other soils

□The submerged materials influence □The type of soil which develops from it □The type of aquatic life and crops it supports □Capacity of these sediments to act as sink for terrestrial waste

Now, let us start a very important chapter that is submerged soils. The submerged soils are you know the soils which are submerged in water for a sufficient period of time to give the distinct horizon development differentiating from other soils are known as submerged soils and the submerged materials basically influence the type of soil which develop from it, the type of aquatic life and crops it supports, and capacity of these sediments to act as a sink for terrestrial wastes.

Now, this submerged soil can be, you know they have different types of, we have different types of submerged soils. One of the important submerged soils is paddy field or rice fields. Another type of submerged soil is wetlands. So, these wetlands these submerged soils have their typical you know chemical dynamics and we can see different types of features or properties of these soils, not only their chemical nature but also their physical appearance.

So, so based on that, you know these submerged materials basically influence the type of soil which develops and also type of aquatic life and also the capacity of these sediments to act as sink for terrestrial waste. So, guys, let us wrap up our lecture here and in the next lecture we will be talking more about these submerged soils and we will see what are the other properties of the submerged soils. Thank you very much.