**Concrete Technology**
Prof. B. Bhattacharjee
Department of Civil Engineering
Indian Institute of Technology, Delhi

Module - 8
Lecture - 34
Durability of Concrete: Rebar Corrosion

Welcome to module 8 lecture 4. So, we looked into carbonation and chloride and initiation of corrosion, that is depassivation by these two agents in the last lecture. Today we will look into and also in the beginning in the previous lecture, lecture before the last, we looked into corrosion, introduction to corrosion, we also explained that what it is? This is actually an electrochemical process and all that. So, we will follow up from there more about corrosion today.

(Refer Slide Time: 01:02)
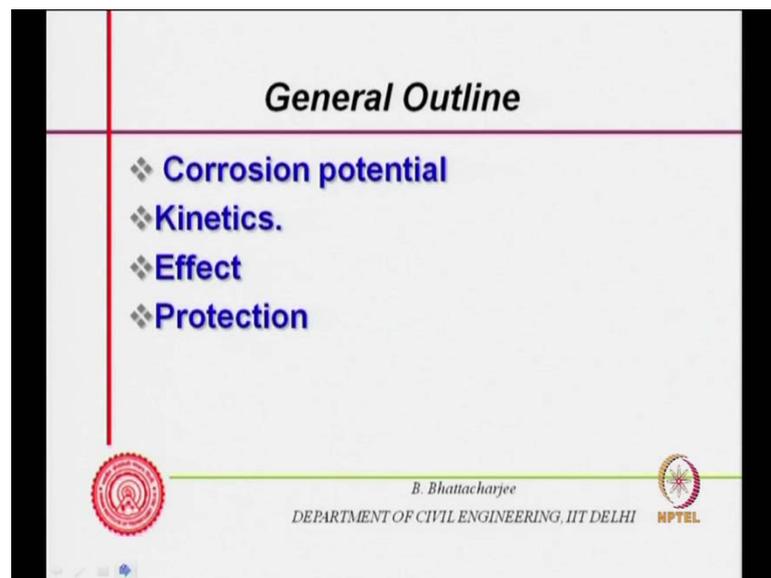
So, what we would do is we will look at corrosion potential, because it is an electrochemical process; we will look at kinetics and effect and protection. You see if you recollect we talked about there will be anode and cathode formation within the metal. So, if this is my metal, so there will be someplace where there will be anode formation. So, let us say this is my anode, and this is my cathode. So, in anode Fe goes out into the solution, Fe dissolves to Fe plus plus and 2 electron. Now, electron moves along this direction to the cathode and reacts with oxygen and water, oxygen and water

forming hydroxyl ion, and Fe goes into solution, reacts with this hydroxyl ion forming Fe OH 2, etcetera, etcetera. So, you have anode and the cathode.

(Refer Slide Time: 01:12)

Now, since the electron is moving along this direction, and we talked about there is a double layer; there is a potential at the metal and potential at the electrolyte. There are two potential we talked about; let us denote them by phi. So, phi m a is the potential in the metal at anode; that means I am talking of this potential, phi m a; and phi m a must be less than phi m c, why? Because electron is moving along this direction, so phi m c must be greater than phi m a, where phi stands from the potential at the metal, right. So, we said that you know there is a variation of the potential from the metal surface to the solution, and we talked about two, three models you know, and finally Stunts model and all that.

So, we talked about. So, we are talking of the potential here and since electron moves from here to here. So, this potential must be more than this potential. So, phi m c is greater than phi m a, and if you come here the positive ion moves along this direction. In other words phi electrolyte a at the anode must be greater than phi electrolyte at the cathode. So, potential here at the anode is less than potential at the cathode, and if you come to the electrolyte potential at the anode is greater than potential at the cathode. So, electrolyte potential because f e ion is moving along this direction, electron is moving

along this direction. So, now if I subtract the potential phi m a minus phi e a that is at the anode itself, let me just draw it again let me just draw it again.

(Refer Slide Time: 04:24)
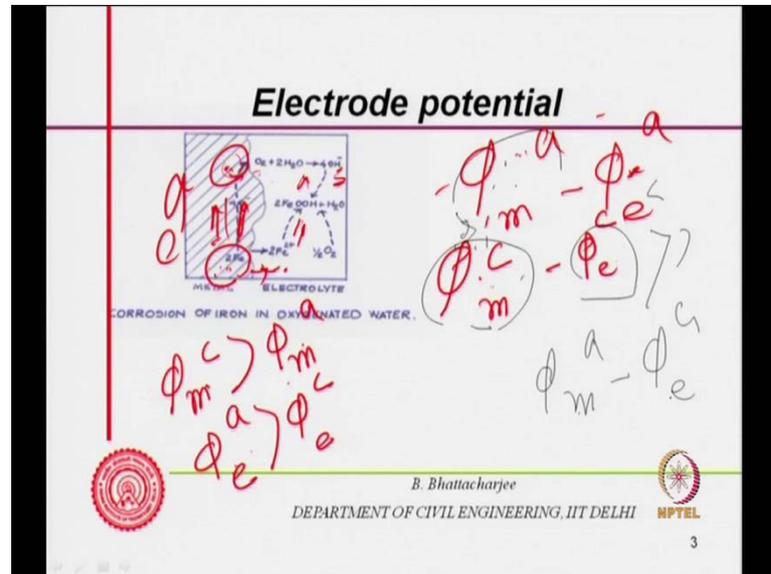
You know at anode itself let me just write it; let me just write it at the anode itself. Find out the potential difference phi metal anode minus phi electrolyte anode. Now phi metal anode, this is one potential and other potential is phi metal cathode minus phi electrolyte cathode. So, if I consider this two potential now phi metal cathode was greater than phi metal anode. So, this is greater than this, this is greater than this, this is greater than this, this is greater than this, and I am subtracting and this is greater than this, and this is greater than this. So, you see phi this is greater than this is greater, this is bigger than this, this is bigger than this, this is bigger than this.

So, this is greater than this is greater than this, and this is smaller than this. So, I am subtracting a larger value from a smaller value, larger value than a smaller value and here from a larger value to a smaller value. So, I am subtracting larger value from a smaller value; I am subtracting here smaller value from a larger value. So, in other words what I can say is this will be greater than the phi m a minus phi e a. The difference in potential at the anode between the metal and the electrolyte electrode will be less than that in cathode; that is what we are trying to say, and we define this as electrode potential.

So, what is electrode potential? phi m minus phi e; that is electrode potential, and we have seen that e a is less than e c. e a is less than e c because that is shown by this expression; that is shown by this expression phi m a minus phi e a is less than phi m c minus phi m you know phi e c. So, phi m a minus phi e a is less than phi m c minus phi e c. So, electrode potential which is e a is less than e c. So, e a is less than e c. So, electrode potential at the anode is smaller than is lower than electrode potential at.

So, that is what we call as electrode potential. It is the difference between the potential of the metal minus you know in the electrolyte at any electrode. Now how do I measure that? I cannot directly measure this; I can only indirectly measure it. I cannot directly measure this potential between the electrolyte in the metal; it is impossible to measure this, at the inter phase potential difference is difficult to measure. So, what we do we measure it indirectly and using some external electrode some reference electrode.

Now the potential of the reference electrode that is taken as zero is hydrogen electrode. So, a hydrogen electrode is one which has got a platinised platinum, and you pass hydrogen in distilled water, you pass hydrogen at one atmosphere pressure at unit activity concentration of hydrogen is unity, potential is zero and is standard hydrogen potential. So, standard hydrogen potential is measured under a standard condition when you have got a platinised electrode in hydrogen situation which is constituent of activity being one and at atmospheric pressure you know that is called standard hydrogen

potential and we call it as zero. So, the reaction is H 2 gets broken down into H plus plus plus 2 electron.

(Refer Slide Time: 07:27)

So, this is a kind of an you know this H 2 breaks down into 2 H plus ion hydrogen ion plus electrode and corresponding to this reaction the potential is taken to be zero. All other potentials are measured with respect to this. For example, the most commonly used one for reinforce concrete is copper copper sulfate electrode, and for this the copper copper sulfate electrode this value is 0.32 volt with respect to standard hydrogen electrode, 320 millivolt minus 320 millivolt. So, hydrogen electrode is considered zero, copper copper electrode is minus 320 millivolt or minus 32 volt.

So, if you measure with respect to copper copper sulfate reference electrode then you want to express it in hydrogen electrode terms, you to make this kind of difference addition or subtraction as required, right. So, copper minus two electrode of course, it will be plus. So, if it is the direction is this copper copper to coppers minus two electron is then I will call it plus 0.32 volt, and if it is copper breaking down to copper and two electron. So, I will call it minus 32 volt, right; it depends upon which side is the electrons are, right.

(Refer Slide Time: 09:39)
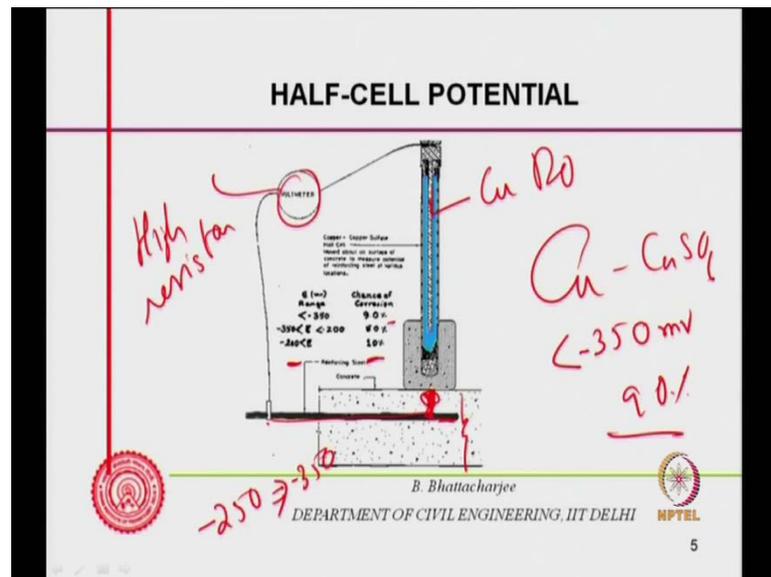
So, for concrete system the STM 876; this gives you a reference electrode copper copper sulfate reference electrode, copper copper sulfate, copper copper sulfate reference electrode where you have weighted sponge here. This is saturated copper sulfate solution, this is a copper rod c u rod copper rod connected to a high resistance volt meter, and one point is connected to the rebar exposed rebar; this is your reinforcement bar, and this is the concrete; this must be weight enough. So, the potential between this point and this reference electrode is measured by this volt meter, and this is the half sulfur. This we call it half cell potential, because this is the half cell.

The other cell is formed by the rebar and the electrolyte here concrete pore solution, and if this potential measured is less than minus 350 millivolt the chance of corrosion is 90 percent. According to their empirical observations in chloride read and concrete, so they found it if it more negative than minus 350 millivolt chance of corrosion is 90 percent, ninety percent of the time. But if it is between 250 and 350 millivolt minus 350 minus 250 to minus 350 millivolt there will be 50 percent chance; that means it may be corroded or it may not be, and if it less than more positive than minus 250 then chance of corrosion is only 10 percent. So, by doing a survey over actual site one can actually demarcate the areas of high risk active corrosion and low risk active corrosion using this; however, this is also used for laboratory measurement as well.

Now what is the basis of this? So, you go to little bit of thermodynamics and talk in terms of potentials which comes. Now you see the reaction takes place; actually here electrochemical reactions are taking place. So, reaction takes place and in the reaction what takes part is the free energy. Now what is free energy? Some energy would be bound with the entropy; some energy would be bound with the entropy and that is what is available for reaction, right. So, if some energy goes in changing the entropy that will not be bound for available for reaction. So, if it is only isothermal process there will be no internal energy, because it is only temperature is not changing.

So, there is no change in internal energy, right, of the system as long as it is in same temperature, but chemical reaction if it is occurring internal energy of the species reactants on the products could be different. But some of the difference can be consumed you know it might go in changing the entropy. So, remaining energy is what we call as free energy, but more important for us and this is available for an isothermal process that is for our reaction. But what is more important for us is when it is same pressure the free energy that is available.

Now it is the enthalpy because it is the total internal energy total heat content of the body which can change. So, delta h it could be the change, but delta h will not be responsible or will not be contributing towards the reaction, because some of the energy will be associated with entropy change from thermo dynamics. So, G is called free energy and it

is H minus TS. This is energy associated with entropy, and this is free energy is vortex part in what it is exchanged in or what influence is the reaction processes chemical or electrochemical reaction processes.

(Refer Slide Time: 13:47)

So, if I have n moles of A reacting with b moles of B and the product form is n c moles of C and n d moles of D. This is a kind of reaction that is occurring then delta g; there is a change in the Gibb's free energy that is G products minus G reactants that governs whether the reaction will progress or not. For example, if this is you know high and this is low; so, this will be negative, and in that case the reaction can proceed spontaneously, but if this is high this is low you have to supply that energy. So, one can write delta G you know in this manner because free energy per mole is known. So, n c G C one can write in this manner n c G C minus n d G D, etcetera, etcetera, and at standard reference condition we call it delta G 0 which would be n c G C at the standard, zero stands for standard reference condition of possibly one, concentrations are 1, etcetera, etcetera; under standard condition it will be given like this.

So, therefore, one can write if for a given species let us say L species like A or B n L G L minus g 0; it can be shown that it is actually n L RT ln by a L. a l is the activity, or it can be replaced by concentration in most of the cases. At many cases ideal laws are followed by concentration where real cases activity would be aware of situation, alright, but we will replace this by concentration. You can understand this because since the constant

pressure situation. So, pressure constant pressure situation you know the volume change will take place. So, p d v is the work done would be and one can write p as RT by v, and when you integrate it you will get ln v 2 by v 2, etcetera, etcetera, and 1 by v can be expressed in terms of concentration and that is why it comes RT ln this way. So, from chemical thermodynamics one can derive this.

(Refer Slide Time: 16:06)

I think we will not go into this derivation, but what we will be interested in delta G G products minus G reactants can be written for this expression can be written like this delta G can be written as delta G 0 RT ln; concentration activities are replaced by concentration, and they would be written in this manner like we did from here like we said for here it can be and this can be in fact written as RT ln concentration of you know species L to the power n L. So, for any species for A B C D, I can write four such equations G L minus G 0 or delta G minus delta G 0. So, I can write for delta G minus delta G 0 and rest all since I have replaced the activity by concentration I can write it like this.

Now this was actually free energy, and this can be written using ferrous slope for charge transfer where charge is involved; you remember the potential is basically the energy on one charge and if I have z is the number of electron transfer that takes place or the valency of that you know species that is taking part in an electrochemical reaction, F is the number of coulombs charge associated with one gram mole; this is associated with

one mole, this G is associated with one mole. So, z multiplied by F will be the total charge associated with one mole and E is the potential for unit charge. So, E multiplied by E is the potential is the energy, actually work done for unit charge. So, multiplied by the total charge can be related to delta G. So, when I am dealing with charges it will be zFE.

So, this reaction can be written if z electron is involved the electron is involved in the electrochemical reaction this reaction can be written as zFE is equals to minus you know minus zFE is equal to zFE E 0 where E 0 is something analogous to z this or equivalent to this zFE is 0, and this concentration still remains same, because electron concentration one need not take. So, one would get by dividing by zF all the sides RT by zF you get what is called Nernst equation. So, what it shows is the electrode potential when the charge transfer is taking place in an electrochemical reaction charge transfer takes place. The electrode potential can be written in terms of standard electrode potential that is electrode potential under standard condition and can be expressed in terms of the concentration of the species involved in the reaction.
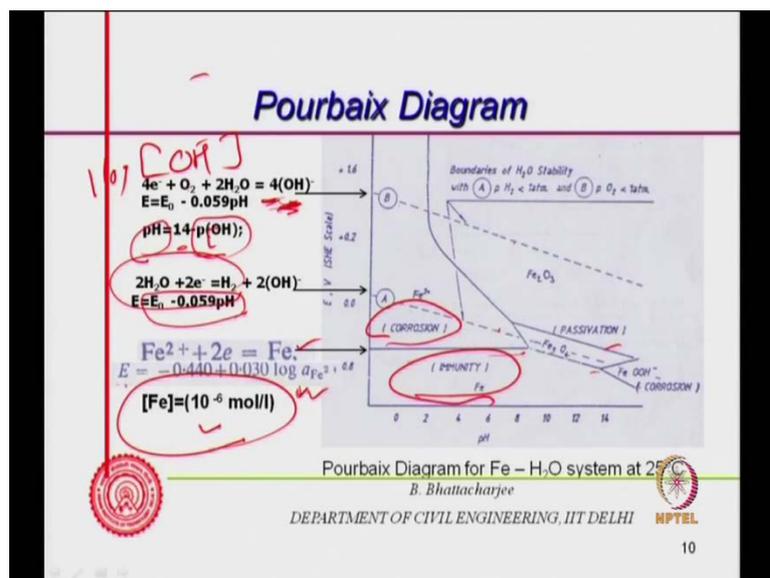
(Refer Slide Time: 18:58)

For example, if I have you know like R is equals to F equal to and temperature RT because it was RT divided by zF, right. So, 2.3 because it was ln; ln can be converted into log. So, it will be 2.303 you know RT by F it is 059 and I can write expression as E 0 0.059 z this, and for hydrogen of course, for hydrogen in case of hydrogen we can

write this, because we know hydrogen this value is zero; E 0 is 0 standard because we take it to be zero under standard condition you know that is one atmospheric condition unit concentration and so and so forth, and for any other hydrogen ion concentration the electrode potential will be given by this where this is the hydrogen ion concentration and this is the pressure related to activity and all that.

So, for concentration of pressure being unity this will be SHE will be zero. For various other reactions these values are available. I just want to make one point. For example, lithium this is negative, but if you come to gold, Au stands for gold, it is 1.498 positive, silver it is positive, platinum it is positive, which means that as long it is negative the reaction will occur spontaneously or it will occur you know, but if it positive it will not. So, noble metals have got their electrode potential positive. They do not form a node; the dissolution of this reaction do not take place there readily while in case of other ions such as Fe this reaction would occur, it would act as anode.

So, you connect Fe with gold, Fe will automatically become anode, and gold will be cathode. Similarly platinum any one on this side of hydrogen if you connect to any one on this side they will tend to be cathode, and the one more negative than hydrogen will tend to be anode, and this is important in sacrificial anode selection and all that; for typical cathodic reaction in case of Fe iron corrosion this is plus 401.

(Refer Slide Time: 21:19)

Pourbaix Diagram for Fe – H$_2$O system at 25°C
B. Bhattacharjee
DEPARTMENT OF CIVIL ENGINEERING, IIT DELHI
10

So, one can actually calculate this one's for various reactions. For example, you know this reaction Fe dissolved into Fe that is the iron dissolution at anode; this reaction one can find out e, and one would write it like this you know the Fe ion log of Fe ion concentration or activity of Fe iron will play a role, and if I put Fe ion concentration as 10 to the power minus 6 I will get it e as a constant, and this is essentially this line. So, e is constant if I put some concentration values of Fe because this is concentration this will relate to concentration 2.303, etcetera. You know we have already written zero point zero if you come to this equation 0.059 by 2 or 0.059 by 2 here in case of iron reaction because Fe dissolves into Fe plus plus plus two electron. So, you put here two it will be 0.03, and here the Fe ion concentration will be there.

So, if you put Fe ion concentration as 10 to the power minus 6 moles per liter you will get this line. So, if the concentration is more than this it means the corrosion is occurring; if it is less than this the corrosion is not occurring. So, one can identify theoretically zone of immunity and zone of corrosion. Similarly for various other reactions one can get these curves and which product is stable that one can find out using Nernst equation. This diagram is called Pourbaix diagram. Now if you look at this line this is actually this line is for you know oxygen evolution. So, the equation here this line corresponding to this reaction; this line corresponds to this reaction water oxygen forms cathodic reaction for hydroxyl ion. This line is for cathodic reaction, alright.

Now if you calculate out pH OH can be replaced OH ion concentration can be replaced by pH actually, because we know the concentration of when you write down the Nernst equation for this I will have concentration of hydroxyl ion. So, concentration of hydroxyl ion that is OH can be replaced by this can be replaced by concentration of hydrogen ion and I know the log hydrogen ion negative of log hydrogen ion concentration is pH. So, pH can be replaced by 14 minus p O H, or in other words p O H because this will be log of hydrogen ion concentration and negative of log of hydroxyl ion concentration that can be written in pH terms. So, you can see that is linearly varying with pH, E is equal to E 0 0 9 pH.

So, there is similarly many other for various other reactions you can get pH varying equations. For example, this reaction which can be a cathodic reaction under certain condition hydrogen evolution reaction, for this you get this line this dotted line bottom line A bottom line A, for this reaction you get B. So, you get actually equation related to

pH. So, it varies with pH linear equation with pH. So, various other reaction similarly which are function of where hydrogen ion concentration or hydroxyl ion concentration is involved you can get equations, and this diagram is called Pourbaix diagram given by Pourbaix. Here in this zone iron concentration is very little and thought to be immune zone.

In this zone iron concentration is relatively high and he arbitrarily chooses this value; if it is more than that this is corrosion. This is corrosion where this iron is stable; in this zone this specification Fe 3 O 4 is stable and so on so forth. So, zones of pH and potential combination where various products are stable or you know possible product formation of that can take place can be seen from Pourbaix diagram. So, it shows that at high pH' s values high pH values you may have somewhere around this values. Depending upon the potential you might have stable specific layer formation like Fe 3 O 4. Some other cases this may form and some other cases low pH corrosion can occur and so on so forth. So, that is Pourbaix diagram, and that tells us on what potential and pH range what kind of product formation can occur.

(Refer Slide Time: 25:52)
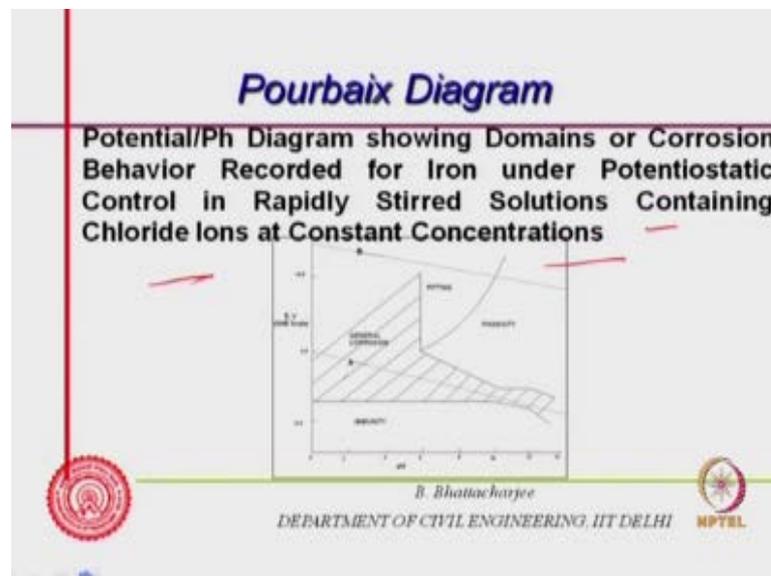
Similar diagram is available for chloride also potential pH diagram showing domains of corrosion behavior for you know solution containing chloride ion at constant some constant concentration.
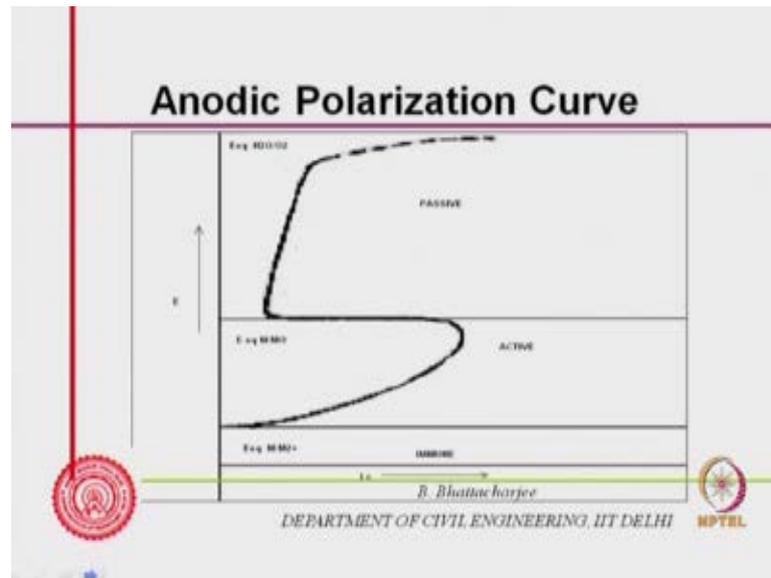
So, this kind of diagrams can be obtained theoretically, but you can obtain from experimental situation also. For example, when you do something called anodic polarization; that means you supply current to an electrode, we will just talk about this a little bit more later on, and you find that the corrosion proceed in the beginning and then suddenly the current reduces; we will come back to this, we will explain this again further. So, you can have zones of active corrosion passive situation where oxides are formed, current has got reduced. Corrosion rate is measured in terms of current because you know we talked of charge transfer Fe ion dissolving. So, when current is less corrosion rate is less.

So, suddenly corrosion current has become less because of oxide has been formed that oxide layer has been formed, and then this is called passive zone, this is called transpassive zone and so on so forth, immune zone is below this, and etcetera, etcetera. So, one can actually experimentally also determine something similar to Pourbaix diagram and verify this scenario for various concentration situation. So, experimentally determine zone of corrosion is also possible.

(Refer Slide Time: 27:09)
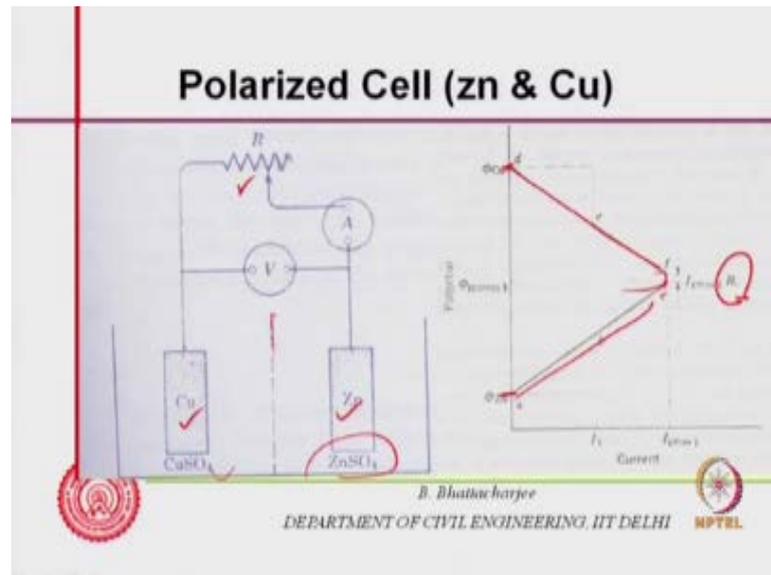
Now this was as far as potential is concerned. Now when you connect we go to the galvanic cell again. Supposing I have got copper and zinc and you remember you know it is in copper sulfate solution there is boundary here of course, zinc sulfate solution and we said that their potential will differ, and when we connect them actually current will flow. If I put a resistor now I will see there is a potential change. So, originally potential if I measure it without this resistance this is a high resistance volt meter. I will find a potential difference or potential here also I can measure with respect to some reference electrode and here also with respect to some reference electrode you know, and this is the zinc potential copper potential when I have measured them with respect to some standard reference electrode and put them here.

When I have connected them then the potential difference between them will change and it will become i R, the current passing through them and i R. So, there is change in the potential; there is change in the potential depending upon the R and this is i R. So, this is actually we call the potential here has got actually polarized; it has got changed. So, when actual current is passing potential actually changes, because what happens there is an electrical double layer at the boundary, and some current has to pass through that as well, and you know some current has to pass through that. So, finally, some loss of drop would be there as well. So, finally, the i R drop across the resistance would be much less than this difference; it will be much less than this difference, because there will be some drop across the electrical double layer, and that is why the polarization occurs. So, this i

R drop across the resistance we call it as Ohmic polarization because I have collected a resistance this is occurring.

(Refer Slide Time: 29:00)

Now this occurs in galvanic cell. This can occur even in case of corrosion cell. It can occur when concentration of one of the reaction reactants you know reacting species is less. For example, oxygen is less the cathodic current may not pass and therefore, the corrosion process will become slower. So, this is called concentration polarization. If the resistivity between the media you know when there is two corrosion, corrosion anode and cathode in the corrosion cell, if there is a resistance within that media is high then the current passing would be relatively less, i R drop across the resistance will be less, right.

So, the corrosion current will be controlled by this resistivity or resistance of the media, and that is actually is occurring Ohmic polarization. But sometime I might apply current from outside voltage or current from outside and that is called activation polarization, and that is used to study actually you know study or measure corrosion rate, etcetera, etcetera, this activation polarization is used. But that gives us also the understanding because the kind of polarization that would occur that actually depends upon original condition or original corrosion that process that was going on in the corrosion cell.

Activation Gibbs energy

When ion participate in oxidation or reduction reaction at an electrode, it must discard any solvating molecule & migrate through the electrode solution interface & adjust its hydration sphere as it receives or discard electron.

A species already at the inner plane must detach and migrate in to bulk.

B. Bhattacharjee
DEPARTMENT OF CIVIL ENGINEERING, IIT DELHI   NPTEL

Now this activation when I am applying more additional current from outside when this ion is actually participating in oxidation or reduction reaction it must discard any molecule solvating molecule to which it was there. So, if was necessary to some molecular or some situation it must discard there or get out of it and migrate through the electrode solution inter phase and adjust its hydrogen sphere as it receives for discarding electron. So, either it will discard electron. Supposing if it is a metal, from metal it goes to a solution.

So, it discards all you know if it is a solid solution in the metal, it discards the solvating molecule, come out of that, migrate and move to the solution and if it is taking electron or giving away electron then it must change its hydration sphere and so on, so forth. And in this process actually it needs some energy would be needed. So, a species already in inner plane must detach and migrate in to bulk. So, if it is in the inner plane or the metal it must migrate into the bulk. If it is already in the solution it has to come it must discard its solvating molecule, and then you know get into pass through the interface and get into the bulk metal.

(Refer Slide Time: 31:44)

So, both these cases would need some energy, and this activation energy would be needed. So, energy is required for transition from one state to other. So, we call it activation energy. So, if I am supplying current actually I am giving activation energy. So, let us say this was the energy state originally, and you have to supply some energy in order to jump from this state and come back to this state, right.

(Refer Slide Time: 32:08)

So, activation is required. So, jump from lower level to you know this state to other sate and net current actually species it works both ways, net current supplied current density

will be the anodic process current of anodic process minus the cathodic current; if I am supplying current in a given way I have pushed it up. So, actually both this process will continue simultaneously and net current will be given by zF some constant multiplied by the concentration of oxidant concentration of reluctant. Actually first order reaction essentially you know this come out from the fact that I will just come to this; I will come back to this.

(Refer Slide Time: 32:54)

First order reaction molar concentration reaction double layer from first order reaction actually his product flux is proportional to k into species flux you know its proportional to k into species flux. So, therefore, some constant first order reaction rate is proportional to concentration of the reactant.

So, that is why some k is coming in and from Arrhenius equation one can find out this k as this relationship is there ln is equal to ln k you know this is the kind of relationship and one can find out k is proportional to activation energy divided by RT. So, kinetic energy increase with T and activation energy is given by directs the reactants towards the product. So, anyway it is a function of temperature, and it can be shown that k is e to the power E a divided by RT, okay. So, this is the progress of reaction, the reactants has been pushed up. This jumps from that you know and comes to the product level.

So, that is activation oxidant; these are the molar concentration of the oxidized and reduced you know reactants or reduced out layer outside double layer, reduced material

outside the electrical double layer. First order reaction is proportional to k species; therefore, rate of oxidation and rate of reduction can be written like this. So, at any metal place both anodic and cathodic current work simultaneously; both would be working simultaneously, and net current will be the difference between these two. So, oxidation current is given by this or you know reduction for this reaction the active anodic current will be like this, and cathodic current be given be given like this, and at equilibrium thes two currents are; same therefore, no net current is passing.

(Refer Slide Time: 34:50)

Kinetics

Rate constant k of electrode reactions has the same exponential form

current densities are

$$i_c = zFB_c e^{-\frac{\Delta G_c^*}{RT}} [Ox] \quad for\ Ox + ze^- = Red$$

$$\&\quad i_a = zFB_a e^{-\frac{\Delta G_A^*}{RT}} [Red] \quad for\ Red = Ox + ze^-$$

net current density

$$i = i_a - i_c = zFB_a e^{-\frac{\Delta G_A^*}{RT}} [Red] - zFB_c e^{-\frac{\Delta G_c^*}{RT}} [Ox]$$

B. Bhattacharjee

DEPARTMENT OF CIVIL ENGINEERING, IIT DELHI   NPTEL

But if I am supplying some current then some currents would be passing through it, and this k can be replaced by according to Arrhenius reaction I can replace by the free energy divided by RT which is activation energy, and for this case also I can replace this by activation energy i a and i c can be replaced like this zF some constant into e to the power activation energy divided by RT and b a activation energy to the power RT. Net current will be difference between this two, and one can write it like this. Net current at the electrode if I am applying current then it will be given by this.

(Refer Slide Time: 35:29)

Kinetics: Tafel's equation

ΔG^{*}_{a} & ΔG^{*}_{c} can be replaced by $-\alpha FE_{a}$ & βFE_{c} respectively

$$i_{c} = zFB_{c}e^{-\frac{\beta FE_{c}}{RT}}[Ox] \qquad equilibrium\ current\ density$$

$$i_{a} = zFB_{a}e^{\frac{\alpha FE_{a}}{RT}}[Red] \qquad i_{0} = zFB_{a}e^{\frac{\alpha FE_{a}}{RT}}[Red] = zFB_{c}e^{-\frac{\beta FE_{a}}{RT}}[Ox]$$

$$\frac{i_{c}}{i_{0}} = e^{-\frac{\beta F(E_{c}-E_{0})}{RT}}$$

$$\frac{i_{a}}{i_{0}} = e^{\frac{\alpha F(E_{a}-E_{0})}{RT}}$$

$E_{a} - E_{0} = \eta_{a}$ & $E_{c} - E_{0} = \eta_{c}$ are over potentials; taking log of both sides results in Tafel's equations. β s are Tafels constants

$$\eta_{c} = \beta_{c} \log \frac{i_{c}}{i_{0}}$$

$$\eta_{a} = \beta_{a} \log \frac{i_{a}}{i_{0}}$$

B. Bhattacharjee

DEPARTMENT OF CIVIL ENGINEERING, IIT DELHI   NPTEL

But delta G can be replaced by some alpha F E a because you know some f into alpha into E a activation energy activation potential energy can be related to the potential in this manner. Similarly beta F E c that we have discussed earlier, and we can write it in this manner alpha beta F E c divided by RT and alpha F E a divided by RT you know in this manner we can write it. Equilibrium current density if the equilibrium these two will be same. So, if I call this as i 0 I will get this kind of relationship these two will be same z F e B. So, this will be E 0, and this will be E 0, this will be also E 0. And then if I write i c by i 0, i c by i zero when it is not at equilibrium then at any other current when there is a net current flowing you know.

So, this will be i c by i 0 can be written like this because z f will cancel out it; it will be left with e to the power beta F E c minus e 0 and E a minus E 0. So, if I shift it from an equilibrium potential to some potential I will give additional by giving activation energy; this sorts of a relationship will be followed. This difference is called over potential; they are called over potential. So, if I have supplied some additional current I will actually change its activation energy, and the activation potential will change. Difference between the equilibrium potential to the new potential I call it over potential and what I see is i c by i 0 or i a by i 0 is given by this kind of an equation.

If I take log of both sides I get what is known as Tafel's equations. So, n c I will get nu c. Nu c is nothing but over potential, this is nu c, and this is nu a, and if I take it ln or log of

both the sides I will get some constant I call it Tafel's constant, anodic constant, cathodic constant and log of i c by i 0. So, these are called Tafel's law. So, if I apply current I will find that actually log of current versus over potential varies linearly, because this is a linear plan log of cathodic and anodic potential over potential it would actually in a single electrode if I do that I will get this sort of relationship.

(Refer Slide Time: 37:56)
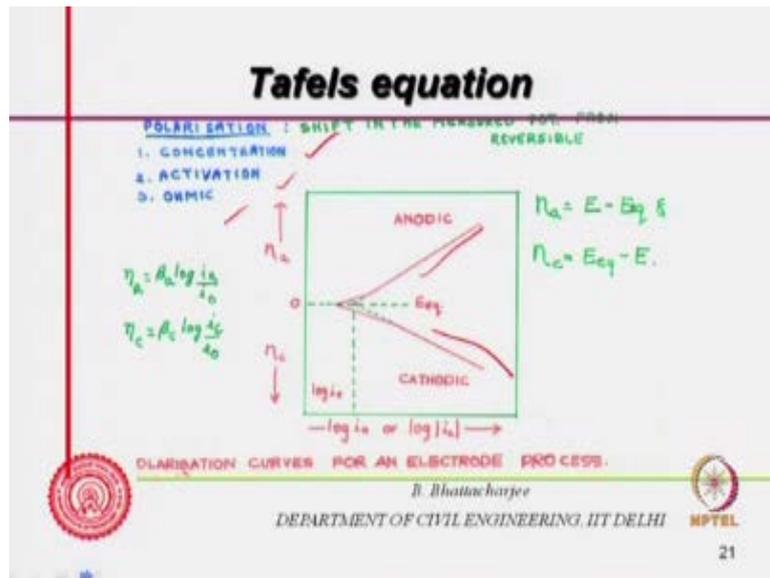
(Refer Slide Time: 38:10)
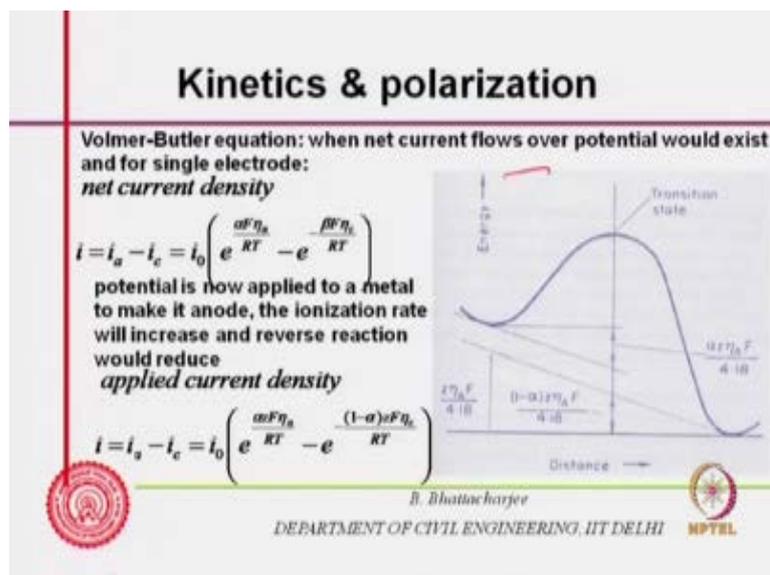
So, these are called Tafel's relationship. So, that is how I would see anodic and cathodically if I polarize I get this sort of curve, right. So, this is activation polarization,

and as I already said concentration and activation and Ohmic polarization we have already defined them.

This was activation polarization. Now Volmer-Butler equation of course gives you for a single electrode the net current equation, and this is related to this. What it says is potential is now applied when we apply to the metal, the ionization rate increases and reverse reaction will reduce. So, if I apply in a given single electrode if I try to increase anodic current cathodic current will reduce and the relationship of beta and alpha will be beta is equals to 1 minus alpha. So, that is how this is Volmer-Butler equation for single electrode.

(Refer Slide Time: 38:52)
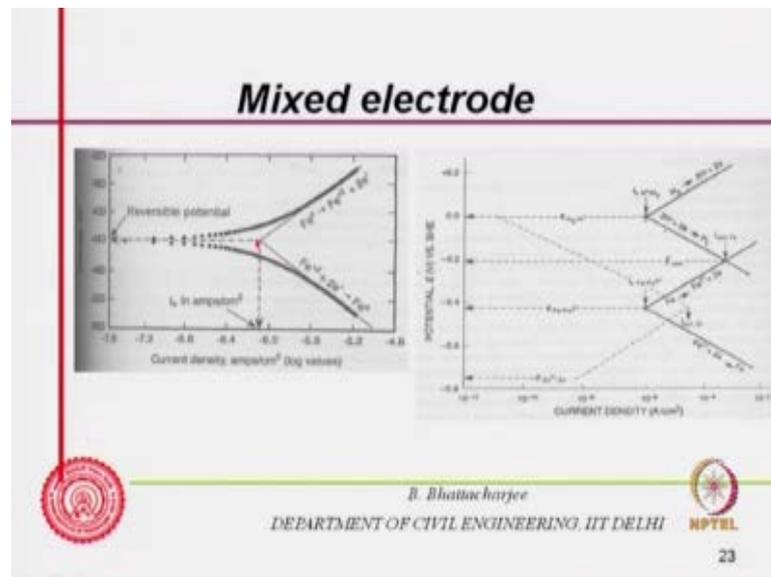
But real electrode single electrode both anodic and cathodic reaction goes on simultaneously and actual potential will depend upon those, but in react corrosion shell you have actually anode and cathode where both anodic and cathodic reaction are going simultaneously, but depending upon where it is polarized it will act like cathode or it will act like anode, and mixed electrode situation is what is modeled for actual corrosion process. So, actual corrosion process is cathode is a single electrode anode you know mixed electrode situation is talked about.

(Refer Slide Time: 39:28)

Now where it is related? This activation polarization can be used for measurement of corrosion. So, rate measurement linear polarization technique is used where I actually part of apply some current from outside over a small range where it has been observed that although it follows Tafel's relationship in the long run when I polarize over a very short range of potential change it follows a linear line.

For example, over this range it follows linear relationship up to this where this follows log logarithmically linear this just directly linear and in this zone I can use polarization resistance and I can use Stern-Geary equation to find out the corrosion current density. So, I corr is given by B divided by R p where R p is called polarization resistance which is nothing but delta E over delta I for small current applied such that please this do not change more than plus minus 20 millivolt such that this does not change more than plus minus 20 millivolt and B over R p, beta is called Stern-Geary constant. You know R p is the polarization resistance and it is given as beta a beta c where these are Tafel's constant which we discussed plus beta a beta c. So, relationship between Tafel's constant is something like this.

The other technique is to get this. So, R p can be obtained by applying current small current in a galvanostatic polarization or you know potential static polarization method over a small current, and there are instruments available which is of course commercial. Instruments are there to find out the corrosion current density even in c 2, although their

reliability one has to see how good they are. There are several question related to this, but that is not a part of our discussion right now. Only I wanted to mention that corrosion rate can be found out by linear polarization technique where you have small over potential n a nu a or nu c within plus minus twenty millivolt and this nu c slope of the line Tafel's line in this zone where nu a nu c do not exceed 20 millivolt that line gives us R p; slope of that line gives r p and I corr is B over R p. B is Stern-Geary constant given by this formula.

But this r p also I can find out from AC impedance spectroscopy and in this one the electrical double layer or the inter phase of the bar and the surrounding is modeled as a capacitance and the polarization resistance. So, when you apply current the polarization resistance you are applying all D C current by the way here all direct current. So, when you apply an alternating current the capacitance because there are two metal; there is an inter phase, it will have a capacitance; it can store the charge and release the charge. So, this has got a capacitance. So, R c is the concrete resistance. So, if this is my reinforcement bar and this is my concrete surrounding the R c is here R c and at the interface I will have R p as well as capacitance.

So, these are parallel. So, I have got actually R p and parallel to this is the capacitance of the interface, and this is the equivalent circuit simplest of the equivalent circuit assumed. So, when you apply an A C current through this when we apply an alternating current through this, and we vary the frequency from this variation of frequencies we can make two kind of plots; one is called Nyquist plot, another is called Bode plot, and from those plot again you can find out R p, and then I corr is B divided by R p. So, corrosion current density can to be also found from S-G impedance spectroscopy as we call it, but I do not have time to discuss them really in details.

Well, there are several other methods for corrosion rate measurement in-situ electrochemical method, coulostatic method; there are several of them. You know electrochemical noise method; there are n number of them, but most popular is the Stern-Geary method, l p r method and next is this that is why I said. But if you are looking at mass loss gravimetrically that is how much mass loss is occurred, the mass loss will be proportional to I the current, time, atomic weight z and F. You know from Faraday's law that we are assuming, and if I divide I by area corrosion current density then R the

corrosion current density per unit area. So, R will be the rate per unit area. So, it will be the kind of mass per unit depth that is going in.

So, this can be shown to be R can be related to actually it can be related to by dividing by density in micrometer per year in terms of 3.27 atomic weight of the material, z is the number of electron transfer involved. So, in case of Fe this will be 56, this is will be 2, this value will be 28 and one can find out if you measure the corrosion current density, density of the material in case of steel is 7.85 and therefore, one can actually find out how much is the penetration depth per micron per year or it is also written in 10 to the power minus 6 inch per year mills per year and so on so forth.

(Refer Slide Time: 45:02)
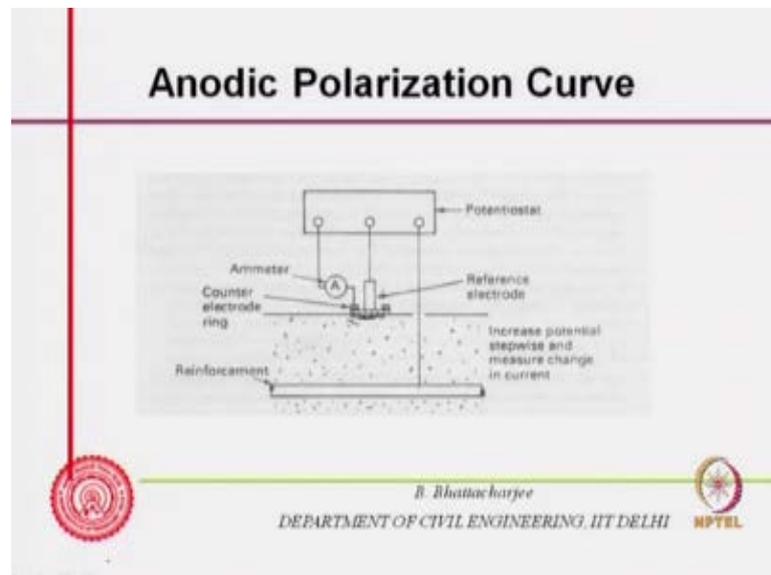
So, these are how you express. Now anodic polarization I was talking about; you apply current from outside through a potentiostat circuit to this you know this you apply current through auxiliary electrode, and this is the reference electrode and change the measure the potential change in the reference electrode, and that is what you use even in l p r method, but you have lot of other arrangements, gadding, etcetera, etcetera to take care of certain special things. So, if you are doing a polarization over a wide range over a long range of potential it is actually a kind of a semi destructive or destructive test while l p r measurement we do over small range of potential. Anodic polarization curve that I showed earlier to identify the zones of corrosion we do it over a large range of potential.

(Refer Slide Time: 45:51)
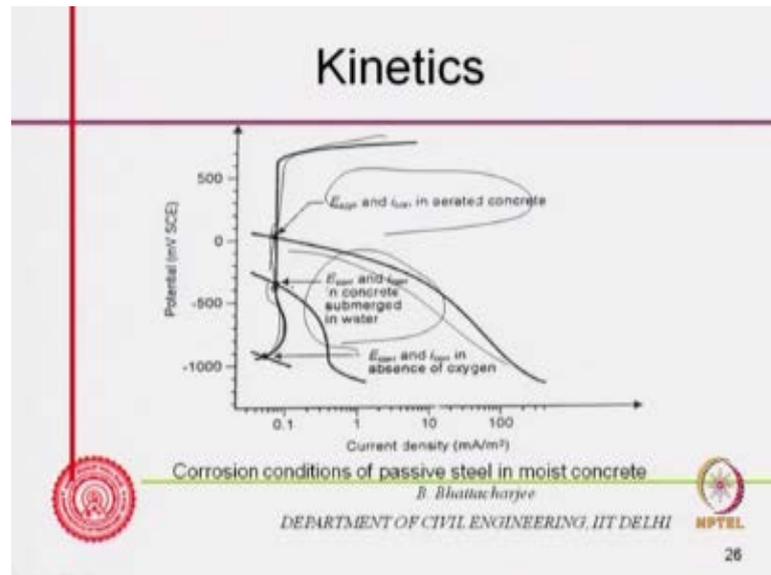
And you get this kind of curves you know potential curve. For example you might get this sort of anodic polarization curve, cathodic polarization curve in this manner, and you can actually find out where this is your equilibrium potential; this could be your equilibrium potential. So, it is in aerated concrete is here; it is in submerged water concrete this kind of behavior. So, one can study the behavior, and as the potential changes how it will behave.

(Refer Slide Time: 46:43)
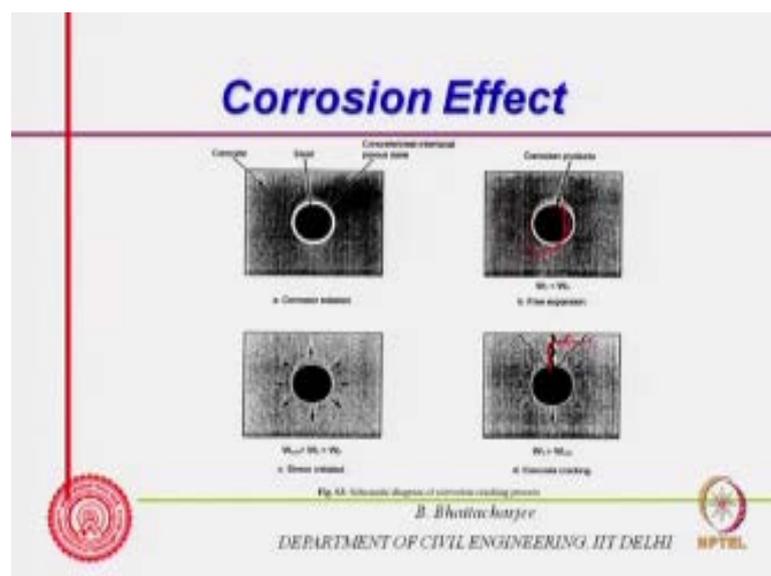
So, if corrosion rate is increasing some cases it might get passivated; that means if oxides are formed and then it stops, but at a very high potential actually that might get broken down and so on so forth. So, behavior of the electrode can be studied by kinetic behavior of the electrode can be studied by anodic polarization curve; one of them I showed earlier, and it can be studied by you know potential static studies.

Let us see the effect of corrosion general corrosion. There are two types of corrosion pitting corrosion and general corrosion. Pitting occurs if the chloride is coming from outside; if chloride inference is coming from outside. Now in pitting the mass loss is very severe; rebar it loses its dimensions like this. As I showed earlier in one of the slides in the previous lecture there is a kind of mass loss could be occurring here. So, lot of mass loss that is pitting.

So, if the chloride is coming from outside anode is localized then it is pitting. So, pitting is local; this is local. Loss and the dimension change will be very very high, But other cases general corrosion. So, general corrosion mass loss is not very high but what happens is the corrosion product particularly of this product red rust $FeO\,OH\,H_2O$; let me write it here again $FeO\,OH\,H_2O$. In other words which you can write as $Fe\,OH_3$ is red rust.

This occupies volume much larger high volume higher volume, then Fe. So, what happens is it occupies a large volume and therefore it exerts pressure to the surrounding concrete, exerts pressure. First it fills in these pores, exert pressure to the surrounding concrete and finally cause cracking of the covered concrete. So, general corrosion results in cracking of the covered concrete, and this can happen from carbonation or chloride coming from inside in gradients. But for external chloride sometime you may have pitting corrosion; if one place the chloride has gone, other place it has not gone that location pit formation would be there, and actually total rebar may be lost totally.

This could be very dangerous in FISH test concrete because of the FISH testing were loose lost its dimension is under stress; it may be even causing a brittle kind of failure. So, typically you can see this general corrosion it causes first cracking in a beam, loss of mass. In case of slab internal crack its sagging and loss of mass.
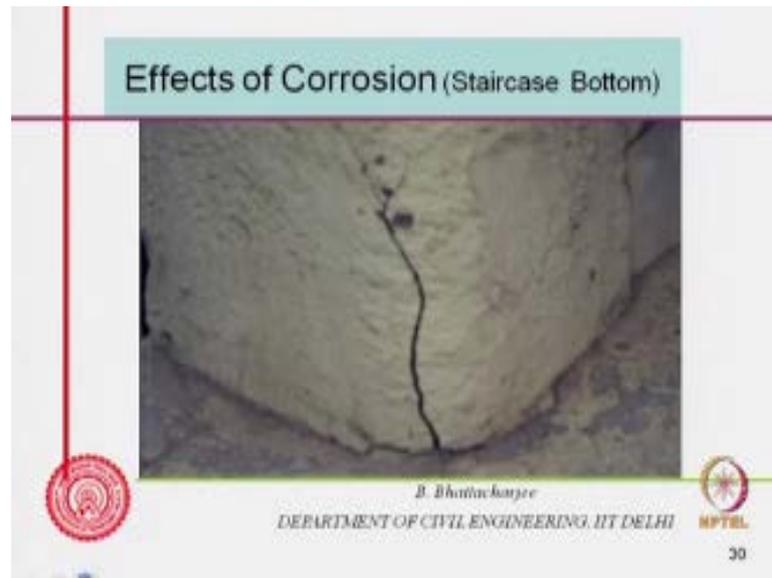
(Refer Slide Time: 49:13)
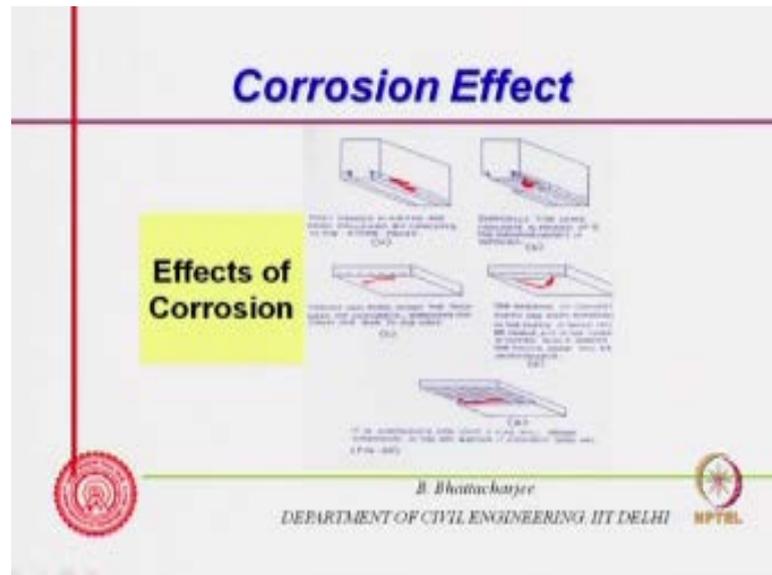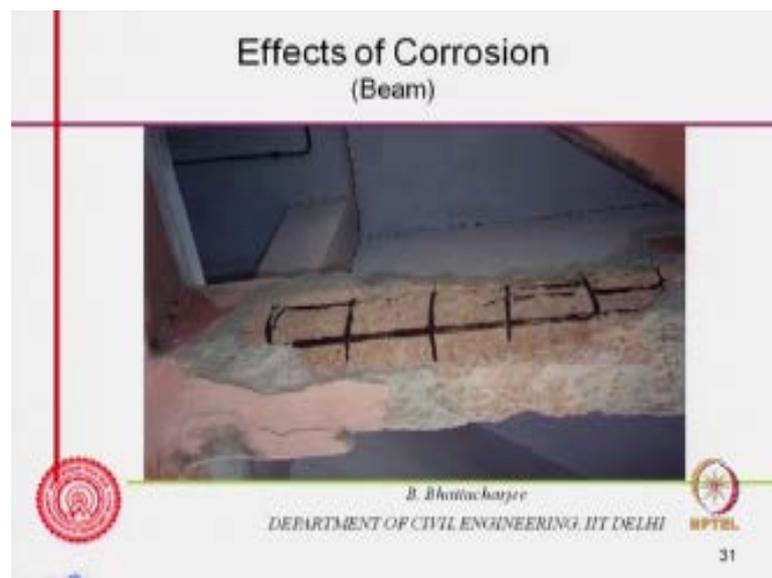

(Refer Slide Time: 49:27)
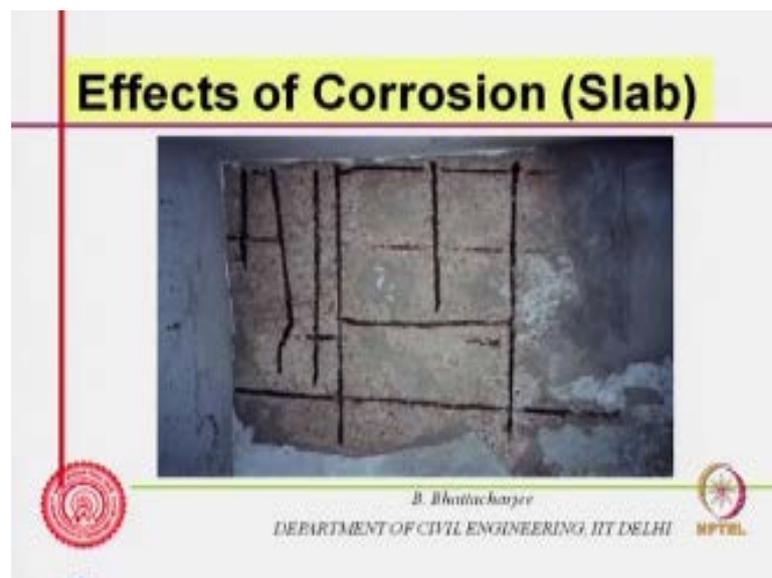
And this is what practically we can see in many cases the slab general corrosion it is gone from internal chloride. This is a case from internal chloride; the whole steel is gone. There is another case. In case of a staircase already repaired by doing some grunting. Again crack because of the corrosion inside. This is of course a beam gone fully; this is the sunshade gone completely.

(Refer Slide Time: 49:38)

(Refer Slide Time: 49:47)

Corrosion protection

❖ Quality Concrete in the cover-crete, elastic modulus, tensile strength and adequate cover depth are the primary requirements together with protection against moisture ingress (water proofing).
■ Use of blended cement may improve the protection.
■ Use of corrosion resistant rebar can be another way.

B. Bhattacharjee
DEPARTMENT OF CIVIL ENGINEERING, IIT DELHI   NPTEL

So, there are several cases one would find. How do I protect? Quality of concrete in cover-concrete, elastic modulus, tensile strength and adequate cover depth are primarily required for corrosion protection, but moisture is one thing which you should keep out, so good water proofing. Use of blended cement improves the protection because blended cement exhibit better resistivity of concrete. Sometime they improve protection even though decalcification time may not increase I mean may not increase in for carbonation, but still overall it might provide better kind of protection.

Corrosion protection

❖ Coating & surface treatment of concrete.
■ Coating of rebar.
■ Corrosion inhibitors.   *sacrificial anode*
■ Cathodic protection and other electrochemical measures   *Impressed current*

B. Bhattacharjee
DEPARTMENT OF CIVIL ENGINEERING, IIT DELHI   NPTEL

Use of corrosion resistance rebar like rebar with alloy such as copper, chromium, etcetera in small percentage, you know like there are corrosion resistance rebar. Then coating of the surface treatment of concrete; coating of rebar like epoxy coated bars, fusion bonded, corrosion inhibitor like sodium nitrite, molybdate, acrylic corrosion inhibitors. There are varieties of inhibitors which are available, but these are yet to be proven; many things are yet to be proven, but you can have something called cathodic protection where you apply current from outside to oppose the corrosion current. That could be impressed current system or impressed current or sacrificial anode. This is used in ship metallic ship. So, you put aluminum which is actually anodic compared to steel, and therefore, aluminum is actually steep; it is steeper waste aluminum or whatever you can use. I mean it is a costly process as such.

So, aluminum will be lost but it will protect the steel. So, that is called sacrificial anode. If you are applying some current from outside through batteries some cases of bridges the reinforcement bar it has been done actually such that it actually change the potential to such level that it is immune potential, or in other words you are applying current. In that case cathodic protection, these are cathodic protection. So, it is impressed current system. Coating of rebar I said coating or surface treatment, but these are all costly process.

(Refer Slide Time: 52:50)
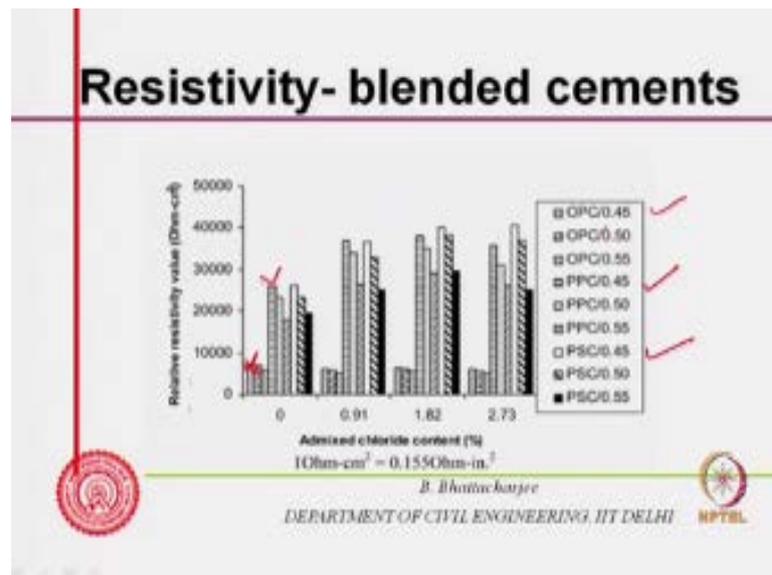
So, just to conclude our discussion resistivity of blended cement I was talking about. You see this is a diagram showing for OPC Ordinary Portland cement and Portland Slag cement. This is kind of a relative resistivity, and you can see the least air for OPC, you know these are for OPC. Next one is for different water-cement ratio or for admixed chloride. So, when you have added chloride at from outside, right, and you have actually these ones are for other cement for different water-cement ratios for situations like this. So, blended cement actually shows exhibits. So, these are for blended cement for three water-cement ratios. This is for 0 percent chloride; this is for OPC 0.45, 0.50 and 0.55.

This is for PSC 0.45, 0.50, 0.55; slack cement 0.45, 0.50, 0.55. No chloride, but if you have high chloride resistance is this does not change much, this did not change much, but this is relative resistance change was there in PSC and OPC. So, you can see the gas chloride; this blended cement performs much much better. Well, carbonation of course initial phases it may not be same, but resistivity still is better even in case of carbonation also, because resistivity is independent of whether it is carbonated concrete or uncarbonated concrete. So, kinetics is controlled by resistivity, because we talked of volume polarization and so on. So, this finishes our discussion.

(Refer Slide Time: 54:38)
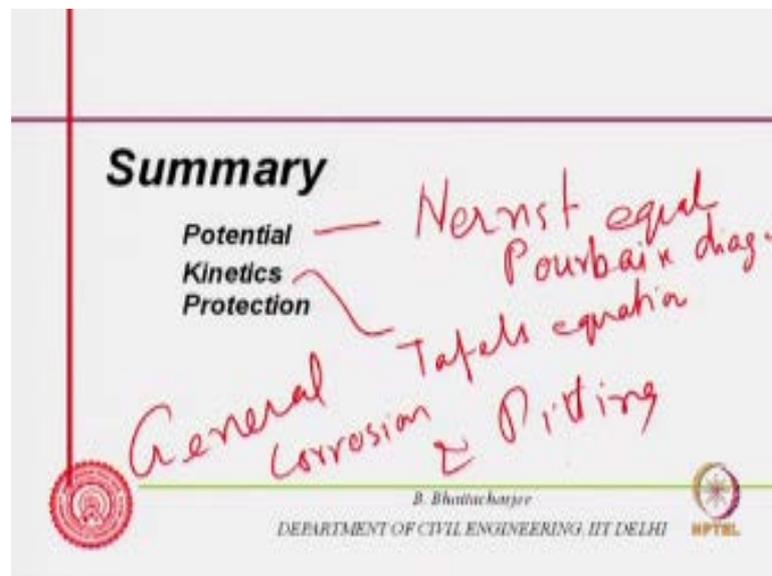
We can summarize; we actually discussed about potential, and in the potential we talked about Nernst equation, Pourbaix diagram, etcetera. Then we talked about Tafel's equation, and then we talked about effect of corrosion; we identified general corrosion

and pitting corrosion. This is only with respect to enforcement corrosion. There are many other corrosion when it comes to steel as such like gravies corrosion, stress corrosion, cracking, so on and so forth. But with reference to corrosion this comes with chloride, external chloride; this is generally for internal chloride and carbonation, and then we talked about protection measures. Good concrete is the first thing; I think I must have mentioned this, but I am rementioning it before stopping.

Quality concrete and cover-concrete, elastic modulus is important. Good quality concrete is very important. Elastic modulus because it is related to cracking; we will look at it in the next class. Tensile strength and adequate cover depth; these are very very important. So, good concrete is very important; good concrete is very very important and elastic modulus of the concrete that is strength of the concrete and cover depth is very very important. Actually quality of construction plays a big role. So, with this I think we will finish off; we will look at the corrosion a little bit in the next class, and then we will look into the general strategy for durability of concrete in the last lecture of this module.

Thank you.