Corrosion – Part I
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Lecture – 17
Concentration Cell Formation and Galvanic Series

Hello everyone let us begin lecture 17.

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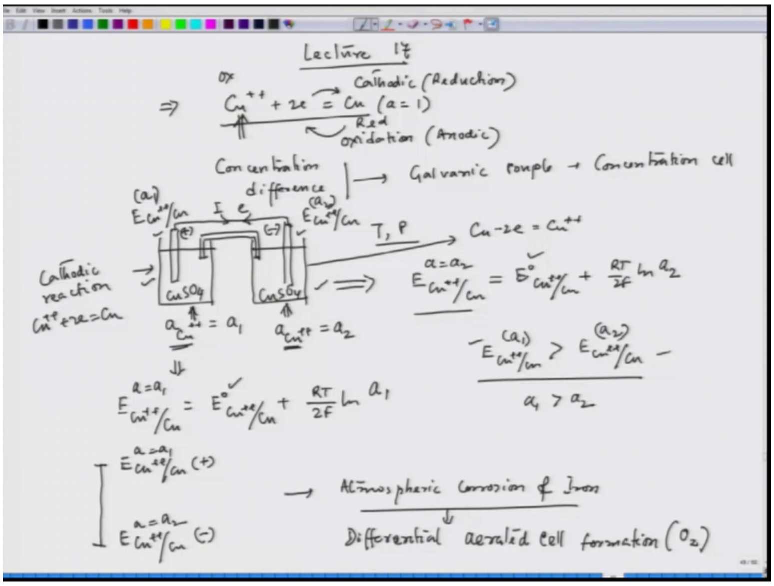

Lecture 17

$\Rightarrow$ $Cu^{++} + 2e = Cu \; (a=1)$ Cathodic (Reduction) / oxidation (Anodic)

Concentration difference $\longrightarrow$ Galvanic couple $\rightarrow$ Concentration cell

$a_{Cu^{++}} = a_1$ $\quad$ $a_{Cu^{++}} = a_2$

$Cu - 2e = Cu^{++}$

$$E^{a=a_2}_{Cu^{++}/Cu} = E^{0}_{Cu^{++}/Cu} + \frac{RT}{2F}\ln a_2$$

$$E^{a=a_1}_{Cu^{++}/Cu} = E^{0}_{Cu^{++}/Cu} + \frac{RT}{2F}\ln a_1$$

$$E^{(a_1)}_{Cu^{++}/Cu} > E^{(a_2)}_{Cu^{++}/Cu}$$

$a_1 > a_2$

$E^{a=a_1}_{Cu^{++}/Cu}$ (+)

$E^{a=a_2}_{Cu^{++}/Cu}$ (−)

$\rightarrow$ Atmospheric Corrosion of Iron

$\Downarrow$

Differential aerated cell formation (O_2)

In lecture 16, at the end we started talking on concentration cell, let us discuss this Concentration Cell little bit and then we try to understand some of the corrosion phenomena related to concentration cell development. So, when we talk about concentration cell; that means, that it is actually talking about difference in concentration of the ions that are forming in the solution or electrolyte or one of the species that are taking part in those electrochemical reactions.

Let us consider one particular reaction which is copper plus plus plus 2e this is copper this is a cathodic reaction. Now this is cathodic or reduction, the backward reaction is nothing, but oxidation or anodic. Now here I can see this is a copper pure metal and if it deposits; so, the activity I can consider to be 1. So, when we talk about concentration cell for this cathodic or anodic reaction, for this particular half cell reaction we have to consider the concentration difference of this particular species.

Now let us construct a cell; so if we construct a cell let us say. So, now when we talked about the concentration difference that lead to a galvanic couple, which lead to a cell called concentration cell. Now, if we construct the cell let us say this is a copper sulphate and we have a copper electrode with activity of copper plus plus is equal to let say equal to a 1.

And then we have another cell another half cell we can construct same solution, but here activity of copper plus plus is equal to a 2; temperature and pressure are constant; that means, they are not changing. And then because of this activity a 1 and a 2; they will develop a potential.

So, the potential that would developed here would be E copper plus plus copper same as ox slash red; that means, oxidant slash reductant equal to E 0 copper plus plus copper plus R T 2 F l n; a of copper plus plus by a of copper. Because in this reaction if we see this is oxidant and this is reductant; now since we are considering this is to be 1 because it is depositing. So, we are left with only this part this one; so now, instead of a plus plus we can write a 1, similarly this is for this cell.

Similarly, for this cell we can write E copper plus plus copper equal to E 0 copper plus plus slash copper plus R T by 2 F ln a 2; similar way we can have this Nernst equation. So, here activity equal to a 1 here activity equal to a 2. Now the potential; that means, the potential developed at this electrode respective 2 cell; 2 half cells, we can have a relation between these two; that means, whether E copper plus plus copper a 1; greater than E copper plus plus copper a 2; that means, a 1 and a 2 they are basically the activities of those copper of the copper ions in this respective half cells.

When it is true? When a 1 greater than a 2 because these 2 are same for both the cases. So, now, once we have a difference in concentration of copper plus plus in both the half cells; then we see that the potential at this electrode which is E copper plus plus copper a 1; that means, the activity of copper ion and E copper plus plus copper a 2; this becomes positive compared to this, this becomes positive. So, now, if we have a series in the series if we try to plot them this is E copper plus plus copper a equal to a 1, this is E copper plus plus copper a equal to a 2.

So, of course, then this would become my positive electrode, this would become my negative electrode because once we complete this cell by connecting a salt bridge; this is my salt bridge. And then if we connect this 2 electrode then will definitely see that since this one this potential lies on top of this potential, then we have a current flow from left side to the right side.

So, the left side whenever we have a current flow then the current always flows from the positive electrode to the negative electrode. So, this would becomes my positive this would become my negative and electron would flow this way. Cathodic reaction would take place in this electrode which is nothing, but copper plus plus 2 e equal to copper. And anodic reaction would take place on this electrode which is copper minus 2e; minus 2e equal to copper plus plus.

Now we see that because of the concentration difference of C u plus plus ion; we have developed a potential difference and that potential difference is leading to current flow. And also this current flow it relates to the galvanic series, galvanic difference galvanic potential difference between these 2 half cells; so, this is the concept of concentration cell. Now the concentration cell what we see here the same concentration cell can be developed in atmospheric corrosion of iron.

Now, whenever we try to talk about atmospheric corrosion of iron; this sometime happens due to differential aerated cell formation, due to difference in oxygen perception. So, let us look at this part little more careful.

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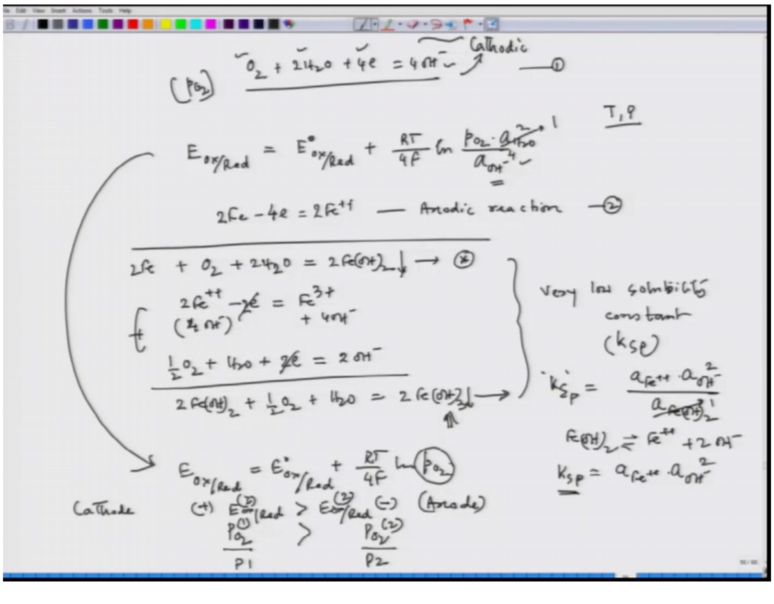

(p_{O_2}) $O_2 + 2H_2O + 4e = 4OH^-$ — Cathodic — ①

T, P

$$E_{ox/Red} = E^\circ_{ox/Red} + \frac{RT}{4F}\ln\frac{p_{O_2}\cdot a^2_{H_2O}}{a^4_{OH^-}}$$

$2Fe - 4e = 2Fe^{++}$ — Anodic reaction — ②

$2Fe + O_2 + 2H_2O = 2Fe(OH)_2\downarrow \rightarrow$ ⊛

$2Fe^{++} - \cancel{2}e = Fe^{3+}$ $(4OH^-)$ $+ 4OH^-$

$\frac{1}{2}O_2 + H_2O + \cancel{2}e = 2OH^-$

$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O = 2Fe(OH)_3\downarrow \rightarrow$

Very low solubility constant (K_{SP})

$$K_{SP} = \frac{a_{Fe^{++}}\cdot a^2_{OH^-}}{a_{Fe(OH)_2}}$$

$Fe(OH)_2 \rightleftharpoons Fe^{++} + 2OH^-$

$K_{SP} = a_{Fe^{++}}\cdot a^2_{OH^-}$

$$E_{ox/Red} = E^\circ_{ox/Red} + \frac{RT}{4F}\ln \boxed{p_{O_2}}$$

Cathode (+) $E^{(1)}_{ox/Red} > E^{(2)}_{ox/Red}$ (−) (Anode)

$p^{(1)}_{O_2} > p^{(2)}_{O_2}$

P1 P2

And when we try to look at before that let us see in the atmosphere what is that cathodic reaction that happens involving oxygen and moisture? Generally in atmosphere we have a situation where the system can be considered, the electrolyte can be considered as of a kind of neutral system. So, if we have a neutral system then we have this reaction; this reaction is possible and this reaction can be considered as cathodic. So, if forward direction we consider then it is cathodic; if we consider backward direction, this is anodic; cathodic. And depending on the partial pressure of oxygen, we have a different concentration cell development.

Now, if we try to write Nernst equation for this; now instead of writing all those pieces here this and this these are basically the oxidant part and this is my reductant part. So, now, we write only ox by red; if we go back to earlier lectures you can see that we can write it as oxygen slash OH minus; that means, oxygen is basically the oxidant and OH minus becomes my reductant. So, this one I can write it as E 0; ox red plus R T by 4 F, since here 4 electrons are involved; so, ln p o 2 activity of H 2 O activity of OH minus to the power 4; so, this is my Nernst equation for this.

Now when we have iron corrosion; then we have this reaction, this is the oxidation reaction that take place. Now if we put multiply by 2; so then it becomes 4 and this becomes 2. Now this is my anodic reaction and cathodic reaction; is this way. So, then if we add them this is 1, if we consider this is 2 then if we add them then we get oxygen iron plus oxygen plus 2 H 2 O equal to 2 Fe OH whole 2.

Now even after that we can have Fe plus 2, it can also go for another oxidation reaction of Fe plus plus 3 plus; this is another reduction process that can take place. Now whenever we are having Fe plus plus; that means, we are considering Fe plus plus along with OH minus. So, if we consider 2 Fe plus plus; that means, we considered 2; 4 OH minus ion along with that; so, it also have OH minus 4 OH minus. Now the same reduction reaction if we multiplied by half, then H 2 O plus 2 e, so, this is multiplied by 2; so, the 2 equal to 2 OH minus.

Now, if we add them again; so, this equation and this equation these 2 if we add; then we get 2 Fe OH whole 2 plus half O 2 plus H 2 O equal to; so because this 2 will get cancelled; so, you get 2 Fe OH whole 3. So, this is this has and these 2 these 2 have very low solubility constant. So, we call it k S P; so; that means, solubility constant because that is what they precipitate. Once they precipitate we can assume that they are going into the activity state 1 because when they are precipitating we are assuming that, they are precipitating in the form of p o; p o form.

So, if we consider the k S P; k S P for this reaction this, this, this one. So, equal to Fe plus plus ion or in the form of activity; I can write a Fe plus plus a OH minus 2 by a Fe OH whole 2, because we are considering Fe OH whole 2 Fe plus plus plus 2 OH minus. So, now, this is 1; so then all the thing k S P equal to activity of a plus plus into activity of OH minus square.

Because we are considering because they are different same thing we can construct for this. Now you see this OH minus percentage is decided by the k S P of that particular face that is forming due to the reaction with oxygen and moisture. So; that means, at a particular temperature and pressure if we have this particular thing and mostly temperature because this particular equilibrium constant depends on the temperature. So, then we can have this one to be fixed because the activity of OH minus will be fixed because that is decided by the solubility product of both the insoluble faces or partially soluble faces.

And since they have a very low solubility product that we can then say that they are partially soluble; so, this activity of OH minus we can consider to be fixed in this particular situation. And activity of H 2 O if it is a pure then it can be also considered as 1. So, now, entire thing boils down to this particular reaction or equation boils down to plus R T by 4 F ln p o 2 the partial pressure of oxygen.

So, now, once we have this relation; we see that if we have a difference in this quantity in at 2 places. For example, if we consider place 1 and this place 2, place 1 and place 2 and if we have P o 2 1 and P o 2 2; then if this is greater than this; then automatically we have E ox red 1 greater than E ox red I can put 2 here. So; that means, we see that because of the pressure difference of dissolved oxygen difference in 2 places, which are electrically connected we see that there is a difference in potential.

And since they are electrically connected; so that means, the place where the oxygen pressure is more than the place where oxygen partial pressure is less; then this place would act as positive electrode and this place would act as negative electrode. So, this becomes cathode and this becomes anode. So, then we see that the concentration cell is developing again. Now this particular concept can be used to understand some of the corrosion phenomena; as we see commonly happen in our day to day life if you see that. So, let us understand some of these corrosion phenomena; first let us understand the corrosion phenomena what happens if we have a raindrop.

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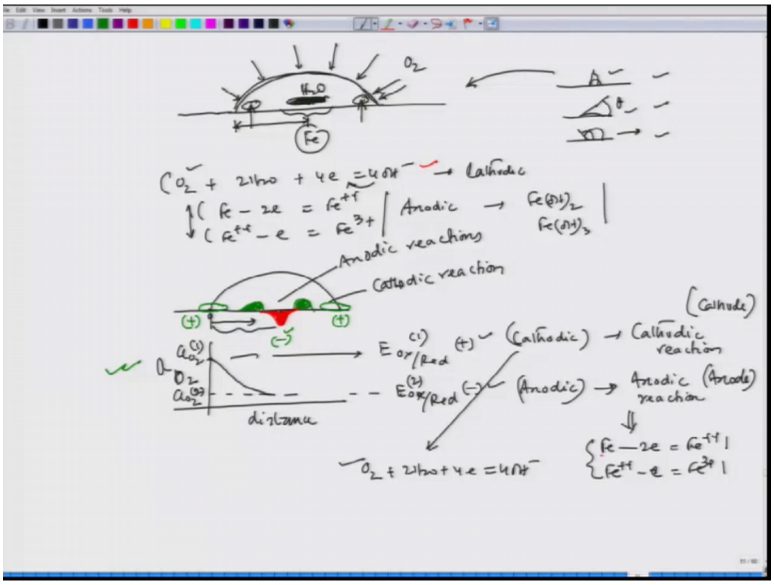

Let us say when the raindrop happens the raindrop is small raindrop and that actually stays on the surface of that metallic object; depending on the contact angle, depending on the nature of the surface, it can have this or it can have this or it can have appearance like this. So, this becomes my hydrophobic, this looks like better hydrophobic because the contact angle becomes this is a contact angle.

This contact angle becomes more than 90 degree and this is hydrophilic because it is trying to absorb water and this is in between this is in between. So, contact angle is this is the contact angle theta. So, here the contact angle is more than 90; here it is more than this angle. So, this is hydrophilic this is hydrophobic this is in between and that is what we have super hydrophobic surface where the contact angle is generally around more than 140 or 145 degree.

And one of the super hydrophobic surfaces basically the lotus leaf; there we if we put a water droplet it dances on that particular surface and that is what water at this that is what; it actually helps in cleaning the particular surface; that means the lotus leaf because when we tilt it the water falls down and that way it takes those dirt particles along with it and then gets rinsed.

Now if we try to see this particular situation; now I can make it a bigger picture like this I zoom it this particular situation I zoom it. So, if I zoom it; so, then this is my H 2 O and if I see the surrounding area, they are in contact with air and this is my iron surface; so, this is my iron surface. So, let me remove that part; so now, once we have this situation then since this is electrolyte, this H 2 O becomes my electrolyte and we have iron and also oxygen.

So, immediately we start having this reaction; as well as Fe plus plus minus E equal to Fe 3 plus. So, these are anodic reactions and this is cathodic. So, initially the partial pressure or the initially the oxygen concentration throughout this water droplet, this water droplet this throughout this droplet; we have almost similar concentration level. So, in the beginning both those reactions will happen statistically uniformly over the surface.

So, now if I consider this section; at this section in the beginning we have both the all 3 reactions and these are actually forming Fe OH whole 2 as well as Fe OH whole 3. Now due to the reaction this oxygen is getting consumed. So, once we have consumed oxygen then of course, there is a from this plane to this particular centre position; we have a concentration difference.

Why that concentration difference is coming? Because the oxygen that is being consumed here or here that is getting replenished by the oxygen diffusion that is coming from here. Because these section this peripheral sections are under direct contact with the air. So, oxygen content in this section remain almost same from the starting of the reaction as well as during continuation of the reaction.

But at this zone the oxygen is consumed because since is a diffusion process that oxygen has to diffuse through this layer; go to this even though it is a small droplet, still it takes time for the oxygen to reach to that particular section. So, now here we have oxygen deficiency and here we have almost similar oxygen. So, now, if I see the plot of oxygen concentration; so now, if I see the plot; so, from this to this if I try to see the oxygen plot between oxygen. So, this is the distance and this is oxygen content, if I see the concentration or activity of oxygen; then at this place the activity would be the maximum.

And then as we go from this to this as the reactions are progressing; we are relaxing time. So, then the oxygen content in this zone would get replay will get depleted in this zone there will be supply of oxygen from surrounding air; so, oxygen concentration gradually goes down. So, this particular line it may have its own plot depending on the diffusivity of the temperature of the atmosphere.

So, even though this water droplet remains momentarily, but still this situation can arise. So; that means, we see the concentration activity of oxygen here this is 2; let us say and this is activity of oxygen this is one position, we have difference in concentration. Once we have difference in concentration if I try to see the E ox red position 1 and this is the position E ox red position 2.

So, this becomes higher than this; so, this becomes positive this becomes negative or this becomes cathodic and this becomes anodic. So, finally, this here we have anodic reaction and here we have cathodic reaction. And we must say that these are basically predominantly cathodic and here we have predominantly anodic reactions. Now for the anodic reactions we can have anodic reactions like this, but for that we have to have supply of oxygen or this OH minus should get decomposed and then form oxygen, but there are 2 more strong reduction oxidation reactions which are these two.

So, in the cathodic zone we have this cathodic zone we have cathodic reactions. So, this becomes cathodic reaction zone and this become cathode, this become anode and here the cathodic reaction would be F minus 2e equal to F plus plus F plus plus minus e equal to F plus 3 plus. And whereas, here we will have oxygen plus 2 H 2 O plus 4 E equal to 4 H minus. So, in this zone we have cathodic reaction and in this zone we have reactions.

The cathodic reaction is this one and anodic reactions are these two. So, whenever we have Fe plus plus and Fe 3 plus; so, they would try to form Fe OH whole 2 and Fe OH whole 3 and they will try to deposit. So, this is the deposit if I consider; so, now, corrosion; that means, this iron is dissolving. So, the iron is dissolving preferentially in this zone; in this zone in the centre part because the centre part becomes my anode. And those iron ions will form OH minus that is forming in this particular reaction and they will form a deposit around this zone, around on this zone.

So, these are my deposit of ferric oxide ferric hydroxide or feroxide oxide. So, the corrosion is taking place in the centre part and the cathode regions or these regions will have very little corrosion because the preferentially cathodic reactions are taking place and why it becomes cathodic? Because we have this situations; so, it becomes a concentration cell and where this is negative part and this is positive and this is positive.

So, this is a typical corrosion phenomenon when have it corrosion phenomena happening inside a water droplet; even though it is a momentarily staying of this water droplet is staying momentarily, but still this corrosion reactions can take place. And with time you would see that there could be a small if we see carefully under the microscope we will see that yes this zone has got attack more than the surrounding zone the annular zone.

So, this is the effect due to concentration cell or the differential aeration cell that is forming because of the concentration of oxygen or the dissolved oxygen in the water or in the electrolyte; so, this is basically we call it a rainwater corrosion.

So, we will stop at this moment. Now, we will continue our discussion in our next lecture.

Thank you.