

Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning (NPTEL)

Course Title

Manufacturing Process Technology – Part- 2

Module -17

Material Removal Rate of ECM

by


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Hello and welcome to this manufacturing process technology part 2 modules 17.

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**Manufacturing process
Technology-Part II (Module 17)**

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We were talking in the last module about the ion transport theory and we assume that in an iron environment there are many positive and negative ion centers and each positive ion center has a cloud of negative ion centers around it and vice versa, so there are various motions which happen in such a system which is otherwise electrically neutral the first motion that can think can be imagined is basically the random walk or the thermal motions of the ions which would be completely randomized excuse me.

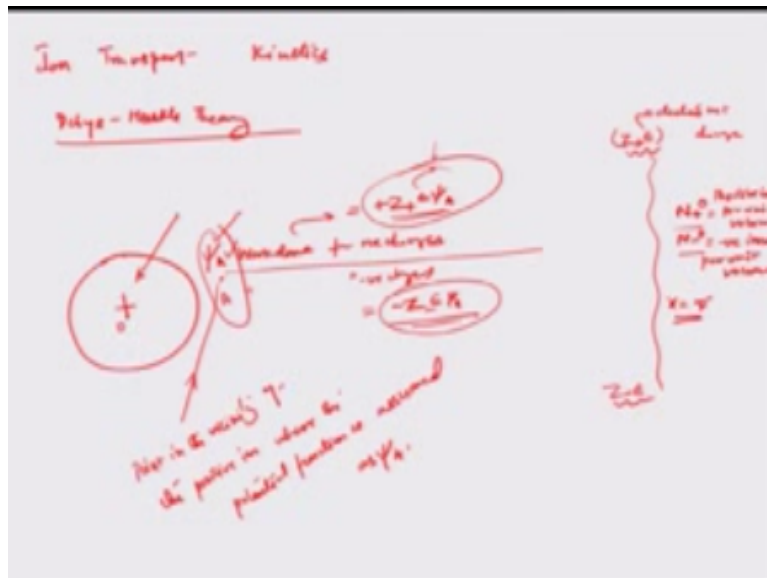
The other motion that it suggested is basically you know sort of clouding of the opposite charges around the central ion of interest of the opposite type so if supposing the central line is positive

we should have an ion cloud formulation around eight of the negative ions and vice versa and in the third module what we saw is that if we put our electrical potential in such a system there is a tendency of the electrons or the negative ions to move towards he positive electrode and vice versa.

And in the process of wait all these ion clouds around atmosphere kind of gets reformulated and disrupted you know from place to place so it is like a hopping mechanism that discharges would follow so that the bulk movement of positive charge happens towards the negative electrode and vice versa, so we also started understanding how we can actually develop a potential function around the charge around the charge based on an otherwise electrically neutral medium.

Where we can assume a certain density function at a distance of infinity from a central charge of interest and in this context we laid out this.

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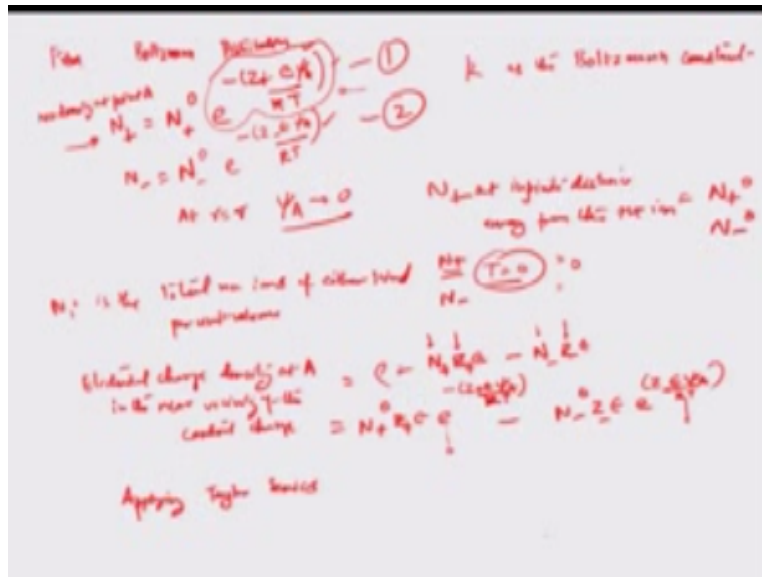


Famous you know divide hierarchical theory and try to you know started to sort of derive it that let us say there is a central ion of interest which is positively charged and around a point you know around this charge is a point A where the potential function is given by ψ_A we also assume that there are about close to $n + 0$ and $n - 0$ positive and negative ions per unit volume at a distance radius $R = \infty$ from this particular ion of interest the positive ion of interest.

And having said that we tried to sort of find out that if we wanted to bring a positive charge which is having $z+$ valency or a negative charge which is having $z-$ valency near this I and at the point A from the point infinity the total amount of work that is done for the positive charges would be then given $+z + \epsilon$ times of ψ_A as is the potential function at A and E is the electronic charge which is 1.6×10^{-19} coulomb and similarly for the negative charges an identical kind of work would be done by the positive charge by the system given by $-z - \epsilon \psi_A$, okay.

So this point A is actually a point in the vicinity of the positive ion where the potential function is assumed as ψ_A ,

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So if we apply the Boltzmann distribution here so from Boltzmann distribution n_+ plus could be obtained as $n_+^0 e^{-z_+ e \psi / k}$ times of t and n_- minus which is actually the number density near the at the point A so we can call of this as number density at point A okay where the potential function is ψ_A is given by $n_+^0 e^{-z_+ e \psi / k}$ k is the Boltzmann constant so I am NOT going to go into the derivation of how we arrived at this but we will just merely explore whether the boundary conditions are obeyed you know as far as this equation is concerned okay.

So we have a k as the Boltzmann constant and we can assume here that at a distance R equal to infinity these ψ_A would typically go to 0 which would make the n_+ plus at infinite distance away from the positive ion as n_+^0 and $n_- = n_-^0$ putting the value of $\psi_A = 0$ putting the value of $\psi_A = 0$

in these two equations 1 & 2 okay and similarly at a certain temperature which is a very low temperature.

Let us say at absolute zero temperature $T = 0$ this factor here would be very small okay and so the n plus or the charge density at the point A because of absolute zero temperature would be actually equal to zero which is also a true assumption in this particular case, so if I consider the you know subscript I in a manner so that N_i is the total number of ions B is negative or B is positive of either kind per unit volume.

And we wanted to find out the electrical charge density at the point A in the near vicinity of the central charge this would come out to be equal to $\rho = n^+ z^+ + \epsilon$ plus is the valency on the positive ion minus of $n^- z^- - \epsilon$ where again n^- is the number density of the negative charge Z^- minus is the valency on the negative ion, so we can actually write this down as $n^+ z^+ + \epsilon e^{-z^+ \psi / kt} - (n^- z^-) (z^- - \epsilon e^{-z^- \psi / kt})$ so therefore it is plus Z^+ minus $\epsilon \psi / kt$ this is ψA .

The potential at the point A near in the near vicinity of the charge which is the central charge so if I were to apply Taylor series here so that the higher order expressions of the series representation of the exponential function can be neglected.

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We know $e^x = 1 + \frac{x}{1} + \frac{x^2}{2!} + \dots$
 neglect the higher order terms $e^x \approx 1 + x$
 similarly the Taylor series for e^{-x}

$$\rho = N^+ z^+ e^{-(z^+ \psi / kT)} - N^- z^- e^{-(z^- \psi / kT)}$$

$$\approx (N^+ z^+ - N^- z^-) - \frac{N^+ (z^+)^2 \psi}{kT} + \frac{N^- (z^-)^2 \psi}{kT}$$
 (Note: $N^+ z^+ - N^- z^- = 0$)
 (Note: $N^+ = N^- = N$; (charge is distributed equally))

$$= - \left[\frac{N^+ (z^+)^2 \psi}{kT} + \frac{N^- (z^-)^2 \psi}{kT} \right]$$

$$= - \frac{2N z^2 e^2 \psi}{kT} = \rho$$

We can sort of you know approximate the exponential function we know that X is represented as a series function by $1 + x/1! + X^2/2!$ so on so forth so if we neglect the higher order terms we can easily have e to the power X being represented as $1 + X$ and we put that back into this particular equation for the net charge density let us say equation 3 so putting the Taylor approximation in three will result in $n + 0$, so ρ basically that overall electrical charge density $n + 0, z + \epsilon (1 - z + \epsilon \psi /kt) - N - 0, z - \epsilon(1 - z - \epsilon \psi A/ kt)$.

So if we open this up we are left with an expression $n + 0 Z + \epsilon - (n - 0) (z - \epsilon)$ is one term $-(n + z + \epsilon^2 \psi A / kt - (N - 0 (z - \epsilon^2 \psi A / kt))$, so the first term here based on the principle of electro neutrality which holds true at infinite distance you can assume that there is no influence of the central charge at a distance R equal to infinity from the charge itself so there is exactly equal number of positive and negative charges you know therefore this whole expression here $n + 0$ and $n - 0$ are same to each other.

So this is the average number density of the charges at R equal to infinity so this becomes equal to 0 okay and we are left with only two terms here which is $n + 0, (z + \epsilon)^2 \psi A / kt + N - (Z - \epsilon^2 \psi A / kt)$ so we can represent this as $-N_i$ with σ where σ is \sum of all different charges varying between 1 to let us say N charges, where N includes both positive as negative charges $Z_i^2 \epsilon_i^2 \psi A / KT$ and this becomes equal to the charge density ρ at the point in the near vicinity of the positive central charge of interest as represented.

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$$\rho = -\sum N_i z_i^2 \left(\frac{e^2}{kT} \right) \psi \quad \text{--- (4)}$$
 To determine potential ψ is related to ρ by - Poisson's equation.

$$\frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} = \frac{-\rho}{\epsilon_0} \quad \text{--- (5)}$$
 For spherical coordinates $\psi = \psi(r)$ in spherical coordinates transformation to cartesian is $\psi = \psi(r)$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) = \frac{-\rho}{\epsilon_0} \quad \text{--- (6)}$$

$$= \frac{+4\pi}{\epsilon_0} \sum N_i z_i^2 \left[\frac{e^2 \psi}{kT} \right]$$
 Let us assume $\psi = K \left[\frac{4\pi}{\epsilon_0} \frac{e^2}{kT} \sum N_i z_i^2 \right]^{1/2} \psi$

$$\left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) \right) = K^2 \psi \quad \text{--- (7)}$$

So if we wanted to look at the expression that comes out let us just record it here ρ becomes equal to $-\sigma$ and $\sum Z_i^2 \epsilon^2 \psi_a / kT$ let us call it equation 4, and this will be referring to because would be needing this to really solve the potential equate the equation you know involving the potential function and try to find out what is the potential at A based on some of these assumptions. So if we look at the electrostatic potential ψ_a it is related to the ρ or charge density function at A by Poisson's equation and this can be represented here by $\partial^2 \psi_a / \partial x^2 + \partial^2 \psi_a / \partial y^2 + \partial^2 \psi_a / \partial z^2 = -4\pi / D$ so let this be equation 5.

So we first apply a sort of coordinate transformation here try to get it converted into a spherical coordinate you have to remember that the central ion of interest is actually a spherical ion at least that is what we are assuming it to be, so we use a coordinate transformation to convert into spherical coordinates.

So here obviously we consider this to be a symmetric distribution of charges which is really creating a potential function which is also a symmetric distribution and it is only a function of R so it is a function of radius R. So assuming that so we have this equation right here converted into $1/r^2 \partial / \partial r (r^2 \partial \psi_a / \partial r)$ times of r^2 becomes equal to $-4\pi / D$ or in other words I can substitute the value of ρ from equation 4 right here I can write this as $-4\pi / D \sum N_i Z_i^2 [\epsilon^2 \psi_a / kT]$ so this becomes plus minus of minus so this actually represents now the final form of the equation.

So if we want to solve it let us assume a term K which is actually given as $4\pi / D \epsilon^2 / kT$ goes in constant times $\sum N_i Z_i^2$ just for the sake of convenience we are assuming this is in any even constant okay, so we can represent this whole expression here $1/r^2 \partial / \partial r (r^2 \partial \psi_a / \partial r)$ as $K^2 \psi_a$ so this equation here right here you can call this equation 7 has a general solution.

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General solution

$$\psi_a = A \frac{e^{-Kr}}{r} + A' \frac{e^{Kr}}{r}$$

we can apply the boundary conditions to solve for the unknowns A & A'

$r \rightarrow \infty, \psi_a \rightarrow 0 \rightarrow A' = 0$

$$\psi_a = A \frac{e^{-Kr}}{r} \quad (4)$$

$$\rho = -\sum N_i Z_i^2 \frac{e^2}{kT} \psi_a$$

$$= -\frac{\sum N_i Z_i^2 \frac{e^2}{kT}}{r} A e^{-Kr}$$

$$K^2 = \frac{4\pi}{D} \frac{e^2}{kT} \sum N_i Z_i^2 \quad (2) \rightarrow -\frac{DK^2}{4\pi} \frac{Ae^{-Kr}}{r}$$

Provided by ψ_a as a function of r is $Ae^{-Kr}/r + A'e^{Kr}/r$ so this is the general solution and we can apply the boundary conditions here to solve for the unknowns which are the coefficients A and A' so we already know that there is one boundary corresponding to r tending to infinity where the ψ_a becomes equal to 0 there is no influence of the center line of interest at distance infinity from the ion of interest itself so in that event this possibility only can happen if A' is 0 because at r equal to infinite distance this will go to infinity and this will go to 0.

And so therefore definitely A' has to be 0 and other words ψ_a can be represented as $A e^{-Kr}/r$ okay, so if I substitute this value back into equation 4 which was about the density function so the density here was represented as $-\sigma N_i Z_i^2 \epsilon^2 \psi_a / kT$ and I represent the value of ψ_a into the expression so this becomes equal to $-N_i Z_i^2 \epsilon^2$ by Boltzmann constant kt times of $A e^{-Kr}/r$ and already we know that the value of K^2 has been represented as $4\pi/D \epsilon^2/kT \sum N_i Z_i^2$ from the last equation.

So this whole term right here $N_i Z_i^2 \epsilon^2 kT$ can be written down as equal to K^2 times of $D/4\pi$ okay, so I would like to now substitute this back into this expression for ρ , so the ρ becomes equal to $-DK^2/4\pi \cdot Ae^{-Kr}/r$ and this is how you define the value of the charge density ρ . So our goal now in this whole process would be to establish this unknown which is A and this can be again you know brought by creating a sort of charge balance equation because we know that otherwise the medium is electrically neutral.

So if I had a central ion of interest which is positively charged and there is ion cloud around it so obviously for electro neutrality sake the values of the charges of the central ion should match with that of the ion environment in which the ion is present okay, so for electro neutrality sake.

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For determining the total negative charge (assuming central ion is positive) of the atmosphere about a given ion as $-Z_i e$. The total charge in the atmosphere around the central ion can be determined by a spherical shell of thickness dr and distance r from the central ion.

$$\int (4\pi r^2 dr) \rho = -Z_i e$$

$$\rho = -\frac{AK^2}{4\pi} D \frac{e^{-Kr}}{r^2}$$

$$\int_0^{\infty} 4\pi r^2 \left[-\frac{AK^2}{4\pi} D \frac{e^{-Kr}}{r^2} \right] dr = -Z_i e$$

$$AK^2 D \int_0^{\infty} r e^{-Kr} dr = \frac{Z_i e}{-A}$$

Integrating by parts

For electro neutrality the total negative charge assuming the central ion to be positive of the atmosphere about a given ion as exactly $-Z_i e$ okay, the total charge in the atmosphere around the central ion of interest can be determined by a spherical shell of thickness dr and distance r from the center line okay, so we can have this positive charge sitting right about here and we can also have basically a radius function you know A and we can also have spherical shell around this which is at a distance R from the central ion and have a thickness dr .

Okay represented by the volume elemental volume times charge density function okay so if we assume only one central ion and posterior around it we have the elemental volume of this small

spherical shell as for $\pi r^2 dr$ you know so with this dv times of ρ as the total charge in the spherical shell.

If I integrate the shell from the value A all the way to r equal to infinity which is assumed to be for completeness you know a single ion balance complete balance so a to infinity this should be essentially equal to the charge density minus $Zi\epsilon$ okay and this is more so because obviously the ion here of the central you know of the central ion here would be having exactly the same magnitude of charge at the atmosphere around it.

There is no more positive ion in the whole system that is what we are assuming we are assuming on the one central positive ion okay in this whole, whole, whole division so therefore we substitute the value of ρ from the previous step in this expression here we get ρ from the previous step was minus a square of $k/4\pi$ dielectric constant d to the power of minus kr/r so if I substitute that here we get in they do infinity $4\pi r^2$ times of minus a capital $K^2/4\pi D$ $e^{-Kr/r}$ times of dr should be equal to minus $Zi\epsilon$ so the 4π goes away the r goes away.

And we are left with an expression a square of k times of d integral a to infinity re^{-Kr} to the equals $Zi\epsilon$ so if I am able to solve this value with the known terms because I already know what is the valence which is into question I already know what is the K value I already know what is this function here you know between E and infinity the dielectric constant of the medium so I would be able to solve for the unknown which is K in this particular which is a in this particular equation.

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$$\int_a^b f(x)g'(x) dx = f(x)g(x) \Big|_a^b - \int_a^b f'(x)g(x) dx$$

$$f(x) = r, g(x) = e^{-kr}$$

$$f'(x) = 0, g'(x) = -\frac{e^{-kr}}{k}$$

$$\int_a^\infty r e^{-kr} = -\frac{r e^{-kr}}{k} \Big|_a^\infty - \int_a^\infty \left(-\frac{e^{-kr}}{k} \right) dr$$

$$= 0 + \left(\frac{r e^{-kr}}{k} + \frac{e^{-kr}}{k^2} \right) \Big|_a^\infty$$

$$= \frac{1}{k^2} \left[\frac{e^{-ka}}{k} + \frac{e^{-ka}}{k^2} \right]$$

$$= \frac{2e^{-ka}}{k^3}$$

So let us now integrate this expression by parts kind of recall that the integration by parts expression says any integral $\int_a^b f(x)g'(x) dx$ can be represented as $f(x)g(x) \Big|_a^b - \int_a^b f'(x)g(x) dx$ right so our first function is in our case of the value r and our second function $g(x)$ in this particular case is e^{-kr} meaning there by that you know the, the first function $f(x)$ is r and the second function $g'(x)$ okay.

Because $g'(x) = -\frac{e^{-kr}}{k}$ becomes equal to minus e^{-kr} times $\frac{1}{k}$ okay so that is how $g'(x)$ can be represented so if I put this or substitute this back into this by parts formulation we have integral $\int_a^\infty r e^{-kr} dx$ which we need to calculate in the last step becomes equal to minus $r \frac{e^{-kr}}{k}$ between limits A and B minus of and so now we have one expression which is $\frac{r e^{-kr}}{k}$ which is one so we have only minus of e^{-kr} times $\frac{1}{k}$ times of dr integral A to infinity this B is infinity.

In our case so that is how we write this expression and when we solve for this particular integral this comes out to be $\frac{r e^{-kr}}{k}$ between limits a and infinite okay so this thing is solved here and the first expression which comes out corresponding to infinity are equal to infinity is 0 minus of minus that is positive $\frac{a^{-ka}}{R}$.

And the second calculation the limits here becomes equal to plus $\frac{e^{-ka}}{k^2}$ okay so that is how you solve this by parts and if I substitute this back into the expression that was obtained earlier which was $\frac{1}{k^2} \left[\frac{e^{-ka}}{k} + \frac{e^{-ka}}{k^2} \right]$ whose solution is given as $\frac{a^{-ka}}{K} + \frac{e^{-ka}}{k^2}$ equal to Zie I would have a solution for the value A .

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Handwritten mathematical derivation:

$$A = \frac{Zi\epsilon e^{ka}}{D[1+Ka]}$$

$$\psi_A = \frac{A e^{-kr}}{r} = \frac{Zi\epsilon e^{ka-kr}}{D[1+Ka]r}$$

At $r=a$

$$\psi_A = \frac{Zi\epsilon}{D[1+Ka]a}$$

[used the higher power of r]

$$= \frac{Zi\epsilon}{D} \left[\frac{1}{a} - \frac{K}{(1+Ka)} \right]$$

im. unit

$$\frac{Zi\epsilon}{D} - \frac{Zi\epsilon K}{D(1+Ka)}$$

effective radius $r = \frac{1}{K}$

$$\frac{Zi\epsilon}{D} \left(\frac{1+Ka}{K} \right)$$

And this can be represented here as further said $Zi\epsilon e^{ka} / D(1+Ka)$ okay in other words if I put this back into the expression ψ_A is recorded as a^{-kr}/r which is equal to said $Zi\epsilon e^{ka}$ times of e to the power of minus $kr / D(1+Ka)$ times of our so obviously that is how you can have your potential function in a point A which is in the near vicinity of the main charge equation further if I wanted to sort of see what is the contribution from the ion and what is that from the atmosphere.

I can resolve this in a manner that it can be calculated at the point r equal to a if I substitute that here these are going to go away and we are left with the potential function at the surface of the charge as $Zi\epsilon / D(1+Ka)$ times of A and if I wanted to further resolve this into partial fraction I would be left with two terms here I can write this down as $Zi\epsilon$ by D times of $1/a$ minus capital K by $1 + \text{capital } ka$ okay.

So obviously the first term would be due to the ion itself so that is the contribution from the eye on itself but what we are interestingly seeing here that there is also a contribution from the atmosphere back to the ion on which can be represented as $Z_i \epsilon K / D(1 + k_a)$ in other words I can also represent only this part as $Z_i \epsilon / D$ times of $1 + K_a$ okay so this right here is the effective radius you can say just because this was the radius of the ion of the centerline this could be the effective radius of the ion atmosphere.

So as you are able to see here that when we are talking about the central ion of interest and a point round a which is at the surface here there is a contribution from the ion itself there is also a contribution from the atmosphere itself the ions radius obviously is a given by this part of the potential function at the surface corresponding to r equal to a and the other part here comes from the environment.

Is given by the and an effective radius which is $1 + K_a / K$ so with this I would like to end this particular module but in the next module I am going to look at how you can apply instead of a single charge if I had an ensemble of charge on a surface can we really find out a potential function close to the surface because of the series of such charges trapped within the solid electrode so with this I would like to end this particular module thank you so much.

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