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<u>Course Title</u>

Environmental Degradation of Materials

Lecture – 21
Broad Subject: Cathodic and Anodic Protection

By
Prof. Kallol Mondal

Dept. of Materials Science & Engineering

Let's begin again, we end up in discussing we were discussing corrosion protection by electrochemical methods, and we have also seen that there are two sections, one is cathodic protection, another one is anodic protection, we started the cathodic protection, and we saw that where we can go for cathodic protection and some of the places we cannot go for cathodic protection, for example we have seen that the locations where the structure is above water line or above the surface of the earth that cannot be protected, because since there is no electrolyte.

Now another place where, if we have a shielding effect that case we cannot go for cathodic protection, another case where we have non-conducting solution, for example, oil which is non-conducting, non-conducting oil we cannot go for cathodic protection. Now another place where if the system is highly corrosive okay if the electrolyte is highly corrosive then we should not go for cathodic protection, so in order to have cathodic protection there we need to spend a lot of current, we need to spend a lot of money.

Now we saw those two cases, now let us start with the principles of cathodic protection, principle of cathodic protection, now while we discuss principle of cathodic protection we'll take help of mixed potential theory again. Now we have seen that if the structure, this is the metal object which is to be protected cathodically we have an auxiliary electrode and we connect it to a cathode terminal of external source so that we make this metal object which is to be protected a cathode. And now we see that electron will flow this way and current will flow this way and the circuit will be completed like this the current will flow like this and it will go like this, so positive to negative terminal and the current will go out of the auxiliary electrode and enter into the metal, okay when we have cathodic protection. Now since this is cathode, okay, so and the current is entering into the metal object so that means another concept of, another criteria for cathodic protection is we have to see that the metal object the current should enter into the metal object which is to be protected, so there are three cases one is cathode, metal object is to be made cathode, second is the metal object is to be connected to a cathode terminal for of an external DC source, another criteria for cathodic protection is we should see that the current should enter into the metal object, so that the metal object is protected. So one other is electrons should flow into the cathode or the metal. And third is current will enter into the metal.

Now if we come to mix potential theory let us get into this particular this board, we will plot potential versus log of current density. Now there is, let us take a simple system where both the cathodic and anodic polarization are activation controlled, so this is my anodic polarization line this is my cathodic polarization line, now if we see that this is the free corrosion potential, now if you keep this is metal +M, so actually N+ this is the anodic side, so that's what I have written anodic reaction, metal is going to the metal ion and this is E reversible potential, okay, if the metal ion concentration is unit activity so we can write it as E0 and this is my I0 which is the exchange current density at the metal surface and that's what I have to write M, I0 of M. And this is another reaction which is I0 for the cathodic reaction, C for cathodic reaction and if it is hydrogen evolution reaction then I0 should be written as I0 (M) that means the hydrogen evolution is taking place on the metal surface.

Now this is my free corrosion potential, this is E Corr and this is my I Corr, if we keep it like this so the system will corrode, maintaining this current density at a particular temperature and pressure. Now if we would like to introduce cathodic protection that means we have to supply electrons to this system, this system if we can supply electron, okay or if we can introduce negative current or IC, if we increase the IC, this is my IC which is cathodic current density or cathodic current density during the cathodic polarization of particular cathodic reaction and this is my IA, this is my IC. Now if we increase IC, what would happen? If we increase IC, the system the polarization will be enhanced and the polarization line, the cathodic polarization line will try to take the direction as shown in this figure.

Now let say I have, this is my corrosion potential if we measure the potential of this electrode at this condition we will see this potential is shown, now this point onwards will have extra cathodic polarization because the current value we are supplying cathodic current, so let say I have reached to this potential, and this is my polarization, this is my polarization, okay, the value of the polarization, now at this point my IC is this is my IC, and this is my IA, and IA is nothing but the corrosion rate because IA is indicating anodic current density, so my applied current would be this much, this is my I applied which is nothing but IC – IA, since IC see is considered to be negative current, so I put a mod value so that this is the value of I applied, at this value of I applied I will have this much polarization and this is my current density for the corrosion, okay, so this is my new corrosion rate. Actually my corrosion rate was here which is I Corr, which is I Corr, now IA which is the new one, let say this is N means new, so this is new, so IA new is less than I Corr, so I have reduced my corrosion, I have reduced the corrosion rate of the metal object in the particular solution, this is very concept of cathodic protection, okay, so I have to somehow take the potential the corrosion potential, potential to a lower value compared to the E Corr value and I will get rid of, we can reduce the corrosion rate to a great extent, and since this is a log scale so if we reduce it by, you can reduce, we can reduce it by maybe 2 to 3 order magnitude, okay, so we can have a very good corrosion protection.

Now if we keep going along this line if we keep going along this line and this is my position of I0 and ER, okay, and I0 is nothing but the current density corresponding to the reversible reaction for the forward and backward reaction. Now if we keep going like this, I keep decreasing the I Corr, IA, okay, but at the same time we are increasing the I applied, we are increasing the I applied, and these I applied will be increasing with respect to the log scale so the I applied would be a very large value if we keep going down. Finally we can reach to this value, this value, okay, so which is nothing but the I Corr would be IA would be = I0 of metal on metal surface, fine, at that point we can see that the corrosion rate would be minimum for the metal object, okay, and this particular point would be called as the complete protection. Now beyond complete protection, so complete protection means a very large I applied, so I have to send a huge current to the system, huge negative current to the system, and that negative current the amount of negative current would be so large it could be of the order of 10 to the power 4 to 5 ampere per centimeter square which is a large current so we should not do that rather we should stop somewhere in between in order to have a realistic corrosion control.

Now what happens if we go down? If we go down you can go down, if we go down what would happen? I will see that it's becoming cathodic reaction this is also cathodic, okay, so this part of this metal polarization is a cathodic polarization of metal ion is going to make a elemental metal, so below this complete protection instead of having a better corrosion protection we may get, there could be a situation for amphoteric metal for aluminum or zinc like this amphoteric metal there could be a corrosion again, okay, the corrosion could be like this, ZnO + H2o + 2h minus, it can go to ZnOH 4 – 2, okay, so instead of having protection zinc ion can go into this complex ion which is dissolving again. So instead of having corrosion protection we can have corrosion, and this could be termed as a cathodic corrosion.

So we should not go beyond that, actually we should stop in between in order to have a realistic protection at a realistic amount of money which is to be spent. So corrosion protection by cathodic means is basically taking the potential to a negative side at the same time sending the negative current and taking the I Corr value which is the anodic current density to a much lower value, okay, this is the principle of cathodic protection on the basis of mixed potential theory, mixed potential theory. Now once we know this we should see that how many ways we can say negative current to the system, okay. Now there are two ways, there are two ways, one is sacrificial anode and second one is impressed current, impressed current cathodic protection, and this is in short we call ICCP. So let us see first this particular method, in this method what we do, we have let say a pipeline which is to be protected and this pipeline is buried pipeline this is the art surface and this is the pipeline, you know we have to protect this pipeline from corrosion or to control the corrosion rate, what we do, we connect it to another anode material which could be magnesium or zinc or aluminum, we can connect it to the magnesium electrode or zinc electrode, or aluminum electrode and this is the steel, the material of the pipe is steel, why we connect it to this magnesium, zinc, and aluminum, because those are highly electronegative compared to steel in the electrochemical series, fine.

Now once we have, we connect this thing, now this is forming a galvanic series, now this is forming a galvanic series, now this becomes anode, and this become cathode so now we have made it cathode in this system and here we are not supplying any external current, okay, so the current is coming into the system, okay, so this is anode, so electron will go this way and current will pass this way, so the concept of having cathodic protection that electrons should go to the material which is to be protected and the current should enter into the system from electrolyte, okay, so that's what we are having so this material is cathode and also we are supplying current or we are sending current and the current is entering into the system and the electron is entering into the system through the wire, conducting wire, so this system where we are not using any external current source or power source and this system is called sacrificial anode, why? While we have this protection, this magnesium, zinc or aluminum they will corrode, they will corrode and steel pipe will be protected.

Now this is exactly similar like what we, why we use zinc coating on steel or steel sheet, that means galvanization, we use we use galvanized steel, there we have a steel plate on top of that we use zinc coating, and zinc is acting as anode and steel will be acting as, steel surface will be acting as cathode, and this is a protection which is called sacrificial anode, because the anode material is getting sacrificed and giving protection to the steel.

Now in this case this kind of situation we can have it in protecting water tank, okay, hot water tank and the system would be like this, the water tank we can also have a protection for example, this is my water tank, this is my water tank, I need to protect it using sacrificial anode method, now this is also steel material and this is, let say some water, hot water is kept, now we can do it like this, we can have a hood which is also made of steel and from that hood we can hang one magnesium rod, this is magnesium rod. So now once we hang magnesium rod, this magnesium will be acting as anode, and this would be cathode, current will go like this and enter, this is current enter into the steel tank and the steel tank would be protected.

Now when we see that the steel tank is protected because the current is entering from the anode through the electrolyte to the steel object, but at the same time wherever the current is leaving the magnesium rod that part will be corroded, so here the current is leaving, so this part is corroded, so this one more point, you please remember this one that when the current leaves the metal object, okay, so that point is vulnerable for corrosion. Now this is one more situation, now once we have this knowledge that we can use it for sacrificial anode method the aluminum, zinc and aluminum zinc aluminum magnesium, so we need to see what are the characteristics of those anode material, because one point is when you are using this we need to know that what point we can go for this method, okay, where we should go for this method, okay, how long we can have protection, okay, and then what are the current value that it can supply to the system, okay, those informations are necessary informations, okay.

So now let us get into those part, one thing is anode material and cathode material, cathode which is steel pipe, these two there should be sufficient potential difference between these two, okay, so if we have sufficient potential difference between these two of course this will be negative, this will be positive, then only we can go for this method, okay. Second is, it should have a sufficient electrical energy contact it means let say sufficient electrical energy contact, it means let say a particular anode material the rating is given like this, let say it's meant as, it means ampere hour per kg or per pound, it means that if we send, let say this is the system, this is my cathode, this is my sacrificial anode, SA this is SA mean sacrificial anode, if we supply 1 ampere of current then 1 kg of anode material, how long it can give protection, how long it can give protection if we send 1 ampere of current to the cathode material, okay. So this is nothing, this is called, this is basically the idea of electrical energy contact, okay, electrical energy contact hour I could say, contact hour, so how long it can protect this system if we send 1 ampere current from sacrificial anode to the cathode material okay, so this should be sufficiently high.

The another point is which is a very important that cathodic protection by sacrificial means we should go for wherever we do not have external power source, some remote places if we don't have an external power source then we should go for this sacrificial anode material, no power source, electrical, so there we should go for this sacrificial anode method. Now what should be the criteria for anode material? Now we see that the zinc is very good anode material for steel protection we see that magnesium is a very good protection, very good material for anode, for anode in case of sacrificial anode method, aluminum is also very good but there are some issues with aluminum. Now aluminum there is a tendency for the aluminum to go into passive state, now if it goes to passive state if aluminum let us say in case of aluminum if it goes to passive state, then there could be a serious problem, then instead of acting as cathode, acting as anode aluminum going to passive that case instead of acting as anode it will act as cathode, so that time if we have a steel with aluminum, this is anode. Now if we have passive layer on top of this, since this aluminum is a highly passivating metal, so that case instead of anode this will become cathode and this becomes initially it was cathode later it will become anode and we all know that the anode material in a galvanic couple corrodes. So instead of getting protection, this will corrode.

So what should we do? Generally many a times or most of the cases or all the cases we have this sacrificial anode on top of that we put a blanket, and this blanket, inside that blanket we put some material, that is gypsum, we put gypsum or coke bentonite, this kind of material is placed on top of this sacrificial anode, and in case of aluminum we put NACL, okay, so what it does? It is called backfill, this is called backfill. The function of backfill is let's say in this side we have steel, iron, now we have connected it, now let's say the current is coming like this and entering like, if we do not have the backfill there could be a situation the some part of the channel of the soil material is highly conducting, the some part is highly conducting, some part is less conducting with or very high resistance, so which side the current will flow? Current will take the path of highly conducting path, which is the narrow position, so that part and we have seen that wherever the current is coming out from the system of the anode material that part will be corroded, so the current is preferentially going through this particular part, okay. So we have more corrosion here, now it may happen like that this entire part will be corroded and the lower part is detached, but the electrical connection or the conducting where is connected on top of this so this part only give the protection, this part is invalid. So that is what we go for the backfill, what it does, the backfill provide conducting surrounding, uniform conducting surrounding so all throughout the surface the current is leaving the anode material and there will be uniform distribution of current over the entire anode surface and the anode surface will be corroding uniformly, okay, that is a very essential criteria for this design of this sacrificial anode system.

Now another part is if we have this sacrificial anode it should be used for a shorter duration, okay, if we go for a very, very long duration we have to see that time to time we have to replace this anode material we have to monitor all those anode material part and all those things, so generally we should go for a shorter version of prediction, okay, and at the same time the electrolyte should be less corrosive, if it is very highly corrosive the anode material will be corroded very fast and the protection will be lost, so this is the part of sacrificial anode method, okay.

Now there is one more method which is called ICCP, which is called Impressed Current Cathodic Protection which exactly follow this, okay. Now here what I do, we have a pipeline let say this is buried pipeline, okay or some water tank, let say, let's consider a water tank here a big water tank which is buried or sump tank material tank, steel tank which is buried and this tank is to be protected cathodically, now that case we have a rectifier which sends DC current, this is positive terminal, this is negative terminal, we connect this steel material or steel tank to the rectifier and the negative terminal is connected to this, and the positive terminal is connected to auxiliary anode, okay, and this is cathode, this is auxiliary anode, since we have connected it to positive terminal and we send DC current, so the current is going like this it is leaving this anode surface and entering into the cathode surface. Now if this tank is a very large tank, okay, so this part the current is gradually entering, now if we consider away from this section where we have this auxiliary anode we see that the current is traveling a larger distance, fine, and also if we consider this part the current has to move a further large distance. Now instead of that and if the current is flowing like this the current will move like this, this path it will take, so though we can have a protection on the surface but this surface will not be protected to that extent.

Now we have a technique to avoid to have a uniform protection, but here if you see this rectifier is sending uniform current, constant current to this anode material and this anode is from the anode material current is coming out and entering into the steel material or the steel tank. Now here also since the current is entering this part will be protected, okay, and here also I am sending negative current IC to this system, fine. Here the cathodic and anodic reaction would be different, because this part is auxiliary anode and since we are using external power source the auxiliary anode material should not corrode it should stay for longer period, that’s what we generally use platinum or titanium, and now it is platina is titanium is coming up as a very good auxiliary anode material which will not corrode and which will act as anode, its function would be just to supply current to this system.

Now in order to have a complete protection what we do, we put another auxiliary anode here, A means auxiliary anode, now we what we'll do we’ll connect it to this part, this positive site, okay, see if we connect to the positive side the current is also going to this through this and leaving the surface and entering to the surface, so we have complete protection. Now when we have this thing you know that time we should be careful that this connection which is connecting wire, basically the wire is conducting wire is connected to the auxiliary anode as well as the cathode material which is the steel structure, we should have a proper insulation. Proper insulation means there should not be any local cell formation, let say this is copper wire and this is steel, so copper would act as cathode, steel will act as anode in this local zone, if we expose this joint to the electrolyte, so we should have a proper insulation in this portion so that there should not be any other galvanic couple in the protecting, in the steel structure.

Now another point is this current value is to be chosen in such a way that most of, all the time this steel structure is in the solution or the electrolyte which is basically the soil electrolyte, okay, that time there could be a various number of reactions that can form on the surface, there could be a several local cell formation on the surface which can be cathodic, which can be anodic, now we have to see that whatever anodic reactions are happening this current should cover up that anodic reactions so that all the time the current will flow into the system and go out through this electrode to this connecting rod, this is called impressed current cathodic protection, and here of course you see that all the time you have to spend, you have to send current so the external power source is required and this is also little costly because here you have to also take care of auxiliary anode material which must have a very good protection against self-corrosion in the system, okay, so that it can function for a longer period. And third thing is of course here also you see the backfill is kept, backfill always make the current which is coming out from the system it makes it uniform distribution of the current.

Now this is ICCP, now ICCP has various advantages, okay, the advantage is basically it can serve a longer protection, okay it can make it uniform, it is not dependent on the material, on the corrosion behavior or the corrosion rate of the anode material in the sacrificial anode case we need to see what is basically the ampere hour for that particular anode material, but here we should not bother about that because once we fix the anode material which is not self-corroding in the system and if we can keep on sending this current we can have a protection, okay, but it is a little costly method because you need to have external power source, but this can have some other problem which is related to stray current. Stray current related problem there could be possible, how is it is possible? Let say some company has gone for a protection of steel tank which is buried steel tank, now some other company which has led oil pipeline just below this entire system, okay, this is oil pipeline which is led by another company, now this is not protected by this system, what would happen? Now once it sees that there is one or another conductor which is passing through this system the current will also try to move into the system, okay, so if current enters into this system the current has to leave somewhere and here also the current is entering, current is entering. Now this current will leave and this material let say this material is coated and since it is buried there could be a possibility that some part would be, there will be no coating, okay, some part would be exposed to the electrolyte, okay, so the current will leave from this surface and enter into the system. If current enters leaves this pipeline and enters into the system this part is protected because current is always entering into the system, but what happens here? Since the current is leaving the system, this part would be corroded. And this is you know highly potential field, so this will also will be polarized and current will enter into the system and current will leave from this system to this metal electrode.

So we see that the current is entering into the nearby pipeline and the pipeline here also current is entering and it is leaving from the pipeline surface to this system, so these part, this part, this part are vulnerable for corrosion. Now if it is painted, if the some part is exposed because of the wear and tear, erosion, so this metallic surface is exposed only, so the huge amount of current will pass through this system and the current density around this region, since this is a very small area a large current, the current density would be huge here, so gradually there would be a lot of corrosion and finally there could be a possibility of leak, okay, so this leakage lead to oil loss.

Now this entire thing, basically the corrosion which is happening in the pipeline surrounding, nearby pipeline is because of this stray current and this is basically nothing but the stray current and this is called stray current corrosion. How to protect this? Because you never know, and you will not be able to know that how long this pipeline will stay and when it will be, it will start leaking.

Now the protection would be simply if we can make this pipeline be the member of, if we can make this pipeline to be member of this tank system, so how you can make the pipeline be the member of this cathode? You just connect this pipeline with the steel tank with a conducting wire and the surrounding part of the conductor should be insulated properly. Now if we connect it so current of course will start coming here because this is you know very highly, it’s a basically a current field, okay, so the potential field, so the current will always enter here, here also current will enter, so if current enters into the system, no problem, we have protection but when it leaves that time it goes through the conductor and it goes into the steel tank, so no case where the current is leaving this system of the pipeline to the electrolyte that situation we are stopping, and if we can stop this situation we can protect this pipeline also, fine.

The classic example of this, this is a pipeline oil pipeline there are instances that this pipeline is leaked and there is a huge oil loss because of the stray current because another company has set one ICCP on top of this pipeline, another example is in cases in cities where you have tram line, okay, the tram line below the tram line if water pipe is going that water pipe can also come under stray current corrosion, because the tram line, the top part when it goes that time it develops potential field and the current will pass through the, current will enter into the water pipeline and it leaves the pipeline and goes to another surrounding metal object, so there you can also have corrosion due to this stray current, stray current effect and the protection is you in case of pipeline you connect it with the steel tank which is being protected with the help of ICCP.

Now let us see what are the advantage of impressed current cathodic protection, one advantage is its versatile, it's versatile and it can be applied with a wide variety of situation, let say difference in electrolyte conductivity or different electrolyte, okay, metal object can be a large object which can be protected for example pipeline and this tank both can be under protection because of this ICCP because the current value is much larger compared to the sacrificial anode method.

Second is, it is also effective in high resistance, high resistance soil, okay, very, very highly resistance soil, so if the resistance is very large so the current flow would be less, okay, that there will be resistance to the current flow, there will be but, since we are supplying current from the outside source we can control the current value and have the protection.

Now third is let say I have steel tank and on top of that we have a small coating, let say paint, non-conducting coating, fine, or if we have or let say I have zinc coating, there if we employ this ICCP, the current value which will be needed to protect this would be very small, now let say some part of the coating would be out, if the some part of the coating is out then the current value will be needed as per the expose area, so we can monitor depending on the current what you are sending via this external power source if we see that the large current is required that means we will be coming to know that there is a problem with the coding, okay, so the coating can be monitored or the coating quality can be monitored.

So these are the advantages, what are the disadvantages? Of course it requires external power source and I would not say that is disadvantages, I would say this is an requirement, but it needs since we are having external power source the cost of having all those systems together would be very large, okay, so that is one, there could be a possibility, so what are the disadvantages? One is high cost, second is there is a possibility of stay current corrosion, now so the another point is let say when you are supplying large current now this is cathode, this is anode, you have connected it to positive and negative terminal, so if you are supplying large IC to this system and if there is hydrogen ion, the hydrogen ion can take this electron and form H2 gas and it can also have hydrogen atom and then there could be a possibility of hydrogen related embrittlement effect in the steel, this is another problem. So these are the disadvantages of ICCP, and also we have explained about I explained, we have also seen sacrificial anode method and these are the two methods by which we can go for cathodic protection.

Now there is one more protection mechanism which is also falling under electrochemical ways of corrosion protection, that is anodic corrosion, anodic protection. Now anodic protection in case of cathodic protection we make the steel structure of the structure which is to be protected a cathode, but in this case the structure will remain as anode, but still we can have protection, how it is possible? This is possible in case of active passive metal. Now coming back to this figure which is the mixed potential based theory for cathodic protection, now let say since we are saying that this is anodic protection that means instead of cathodic polarization we should go towards the cathodic polarization side, now if it is activation control and if it is active metal then if we go towards the positive sized which is nothing but the anodic polarization, we will see that gradually we keep increasing the IA, IA will be increased as we go towards the positive side from this equal point. Now if we increase IA, that means we are not getting any protection rather we are increasing the corrosion rate of the metal. Now if it is instead of active, if it is passive, if it is passive metal or active passive metal, then what would happen, okay, now let us get into that part we will modify this figure a bit. Now if this is active passive let's say, if it is like this, we know that active passive if we go towards the anodic polarization side the active passive metal after reaching, after reaching I critical, I critical it will the current value the anodic current density will go towards the left side and finally it will attain the passive region this is nothing but the passive region, fine. And let say the situation is like this, okay. And this is my cathodic polarization line, this is my anodic polarization line, and with this we have also seen that if it is mixed potential theory, now the system will go to this point and it will remain there, now if by forcefully if we take the anodic potential or the potential of this metal object or the metal object towards the positive side further positive side what you have to do, you have to send extra current, so that current is decided by difference between IA –IC, this is my IA, this is my IC, this is IA. So gradually if we see, if we keep on going like this we will see that gradually I am increasing my applied current, fine, now if we keep on increasing my applied current, so actually you will see that the anodic current density is increasing, the anodic current density is following this track. And if we plot the anodic current density with I applied up to this point let say this is 1, 2, 3, 4, 5, 6, up to 6, so I applied and IA, I applied if we keep on increasing IA is also increasing like this, so my corrosion rate will also increase because IA means the corrosion rate, corrosion off or the anodic dissolution current for the metal object or metal.

Now we are also going towards positive polarization direction, we are increasing the positive polarization that means the daily is gradually increasing. Now some what if we can take it to this point if we take the potential to this point and that time what would be my I applied, my I applied would be this much, okay. So from this if we jump to this may I applied would come to this level, this is my starting level, now my I applied would be this much, so it would be little less, this is my I applied, and what would be my IA there? IA would be like here, so as we go on increasing the anodic polarization we are seeing that initially the IA is increasing with increase in I applied but later once we go to this section which is the passive zone my I applied would also go down at the same time my IA also will go down, okay. So IA will be coming to this, so I am putting it as a red point, okay, and this is the point we have reached and if we maintain this potential, these potential if we can maintain what would happen? I will always experience my corrosion rate would be in the passive region and we have also seen that if we can take it to the passive level the material corrosion rate would be very, very small, okay, this is the very concept of anodic protection, somewhat we have to take the potential to the passive range, and if we take it to the passive range we will see that there is a very, very small anodic current density which is equivalent to the corrosion rate of the metal object, and that corrosion rate would be very, very small.

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Camera
Ram Chandra
Dilip Tripathi
Padam Shukla
Manoj Shrivastava
Sanjay Mishra

Editing
Ashish Singh
Badal Pradhan
Tapobrata Das
Shubham Rawat
Shikha Gupta
Pradeep Kumar
K.K Mishra
Jai Singh

Sweety Kanaujia
Aradhana Singh
Sweta
Preeti Sachan
Ashutosh Gairola
Dilip Katiyar
Ashutosh Kumar

<u>Light & Sound</u>
Sharwan
Hari Ram

<u>Production Crew</u>
Bhadra Rao
Puneet Kumar Bajpai
Priyanka Singh

<u>Office</u>
Lalty Dutta
Ajay Kanaujia
Shivendra Kumar Tiwari
Saurabh Shukla

<u>Direction</u>
Sanjay Pal

<u>Production Manager</u>
Bharat Lal

an IIT Kanpur Production