Marine Construction and Welding

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Module No. # 01

Lecture No. # 20

Acid Pickling

In my student days, I also used to have longer hair. I used to use, what is called that head band during the exam period otherwise, if I write like this, all hair comes in front disturbs you, so I put a head band there. One of my professor also told me, advised me good, nice to keep a good long hair, trying to imitate Jorge Ericson. In those days, Jorge Ericson was - you have heard about Jorge Ericson. So well, take care of your hair, keep it clean; so that is what I am repeating to you.

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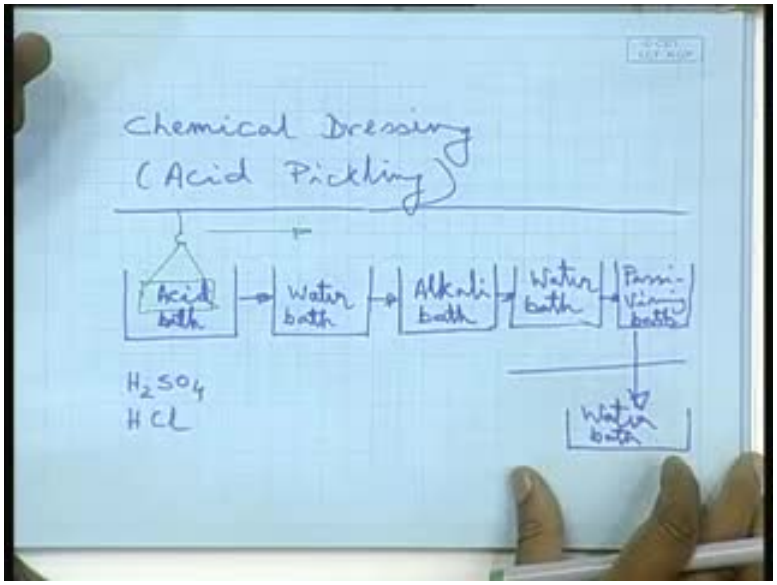

Anyway, from hair dressing to chemical dressing, right? In chemical dressing, we had been talking about mill scale removal. We have seen the mechanical methods, some of natural method frame treatment mechanical and this is a chemical method, so it is referred as chemical dressing or acid pickling. Essentially, we take help of so called

chemical reaction by which whatever oxide layer is there that is dissolved out. So in this process, as the name suggests that means we will have to have some acid bath.

The plate material is to be subjected to a kind of acid bath; there we subjected to some mechanical means, mechanical force by which we remove those oxide layers. Here schematically it would be like this that means, first you take in an acid bath, this acid bath is as shown (Refer Slide Time: 02:00) well, what acid do you think will be suitable?

Somebody says, H 2 SO 4 that is fine, anything else? H Cl, anything else? Well, we do not go for any other complicated acids. Very two common acids H 2 SO 4 or H Cl, one of these are basically used; both have their own positive and negative aspect, we will talk about that little later. So, once acid bath is given, what happens? This ferric salt, they react with the acid and go in to the solution. So this process of going in to the solution that will tell us which acid is more preferable; we will see that little later.

Once this bath is given then obviously, I have to take it out. I will take it out and put it where a wash has to be given, water wash because water wash traces up; because when you taking it out of acid bath, you will have to clean it from the acid; if acid traces driven that will corrode, so a water bath.

Now, what you think should be the next treatment? Not really, because after giving water bath still you are not sure that whether traces of acid is remaining or not, there might be; so if traces remain, they will corrode. So, alkali bath; once again, alkali bath means it should be followed by a water bath, because you will have to clean it.

Here, you can see in short plasting we have seen, there is a question of dirt, dust and noise and here acid, alkali, water quite a messy affair. Well, water bath next, what it should be? Yeah, directly alkali, there lot of alkali will be wasted, you know to protect alkali because then acid will react with the alkali that is why. So after water bath when I am taking then, there can be few traces only, so that is why; but, in the process you need lot of water that is there, but still water would be cheaper than the alkali. So that is how had water been costlier, then probably straight away go for alkali. Like in Germany, a bottle of water is costlier than a bottle of beer. So, you can choose what you want to drink; anyway, so that is how it is.

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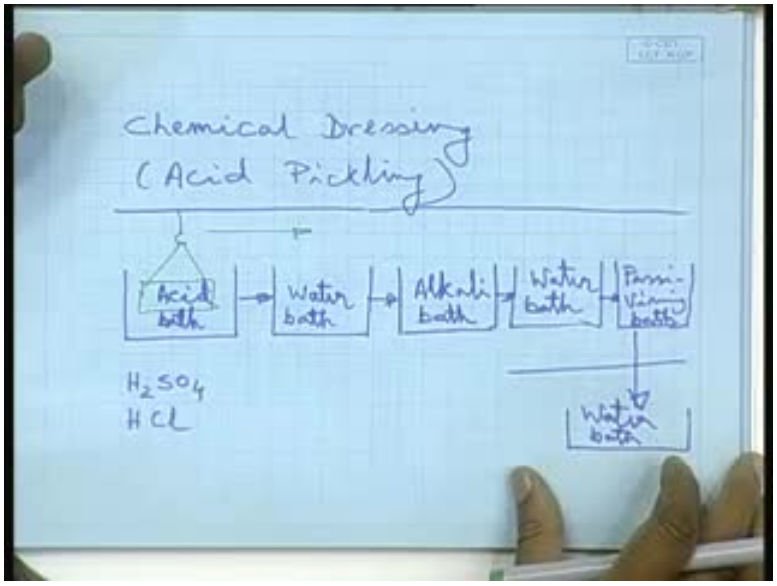

After water bath, what should be there? Not dry immediately because, after alkali bath what we are getting now? We are getting that same steel material as you got from after shot blasting that means, bright cleaned surface; so, some kind of priming. So here, it should be compatible with the process there that spray priming, painting was compatible with the process; so here also, some kind of chemical treatment.

So that chemical treatment is refer to as passivizing bath, you make the surface passive. There we protected it by providing paint, a coat of paint; here I am protecting it by a chemical reaction which is forming a protective layer on the surface, making the surface passive. So that is referred to as passivizing bath; that means the surface is becoming passive.

After it has been passivized, then you just take it out, there is no need of drying because the water will dry off automatically after the passivizing bath. Well, after the passivizing bath one can give kind of another round of water wash; so final water bath and take it out. What happens in this, as you can see the material should be moving over this various baths; so, it can be something like this and it moves (Refer Slide Time: 07:00). That means you have a mechanism, that means this entire one after the other chemical or treatment bath, this will be housed in one big hall having an overhead cringe facility.

So here, you hang the plates, take them, dip them in the bath for the required time, take it out, goes in the next bath, whole process can be programmed and made automated.

Again, this process is also automated process though it is as it as but, well it will take proper precautions. That means, once it is made totally automated so there is not much of need of human intervention inside; like when we are doing shot blasting, nobody is present inside those chambers not needed.

Similarly, even if this can be properly controlled all the process parameters and the whole operation can be made automated, so no physical presence is needed of any worker inside the hall. So, he is not exposed to all these acids, chemicals or the fumes right; so that is how this process works.

So, we come to that. Here, then we see, start with the first sort of operation that is the acid bath. So acid bath, what all things we will have to look in to there? That means, first we will have to choose the type of acid, what acid to be used?

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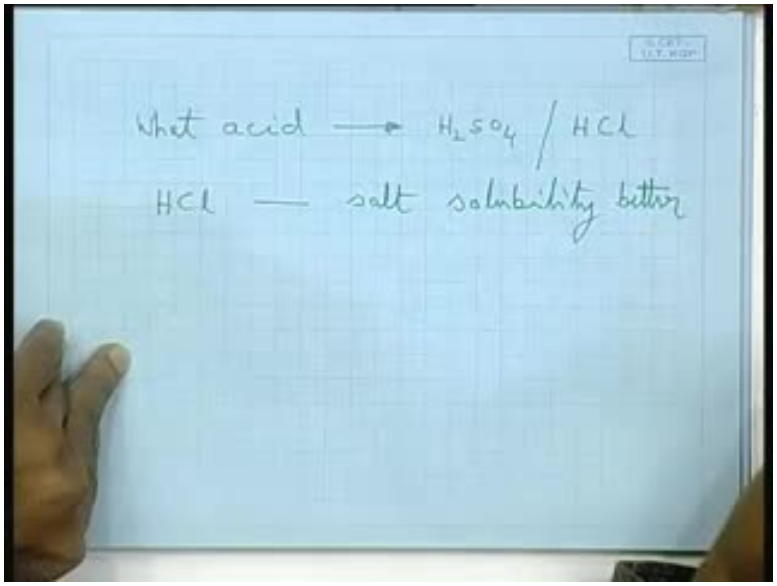

You have already told or we have talked about two possibilities H 2 SO 4 and H Cl. Now, which one, because it should be either this or that; it cannot be both, which one? Well, it is like this. I mean, what is the process happening there? It is essentially reacting with the ferrous oxides and forming some salts. How that salt is removed? It is getting dissolved, so the salt should have a good solubility.

Because it does not have a good solubility then, what will happen? When I dip the plate take it up, it may have reacted but, the salts may be sticking to the surface, yes it has not

got removed. We should be looking for such an acid which will form more soluble salts H Cl is a preferred one, because chloride salts have better solubility than sulphate salts. Chloride salts are more easily soluble, so from that point of view H Cl is preferred. Salts are soluble, salt solubility is better.

Now, what are the other aspects? Other aspects should be how much consumption of this acid, because that is also another factor. In the overall well economics of the process, how much it will consume? Now what we see is, this consumption rate of the acid also depends on - apart from the reaction there are other factors like before consumption if you talk about how much time it takes for the reaction to take place. We find it depends on the temperature of the bath, if you increase the temperature I have a faster reaction rate. So if you increase the temperature, you have a faster reaction rate; so let us take a look first, at how these two acids they react? Then again we will come back to this which acids to be used.

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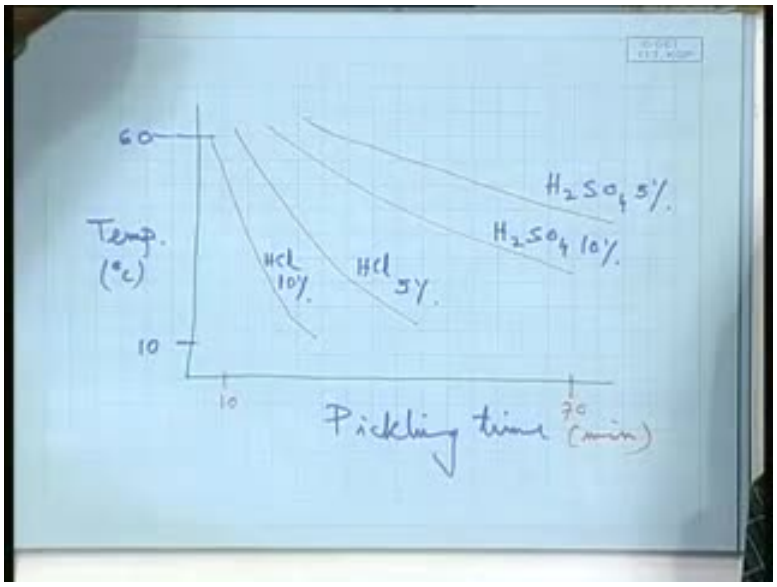

May be through a simple graphical representation, we can see that somewhat like this; this represents H Cl with 10 percent H Cl, 5 percent, this is pickling time, this is temperature (Refer Slide Time: 11:33).

Well, here this plot what we have drawn it is the pickling time. Let me mention it is from around 10 to roughly about 70 minutes. Here, I have tried to show the trends, it is not

exactly you measure from this, it is not an exact but, it is a general trend like this. That means what we see that this percentage is at the concentration of the acid.

So how much pickling time, that is my production time, definitely we would like it have as low as possible because then my production rate is faster. So you see that with the acid concentration reducing obviously pickling time will increase.

With temperature increasing, pickling time is reducing; so obviously, we try to keep higher concentrations as well as at a higher temperature such that I have a lesser picking time. But, well there is a limitation you cannot go on increasing the concentration of acid also, what is observed generally that one uses of the order of 15 percent concentration one starts with, now the process is a continuous process.

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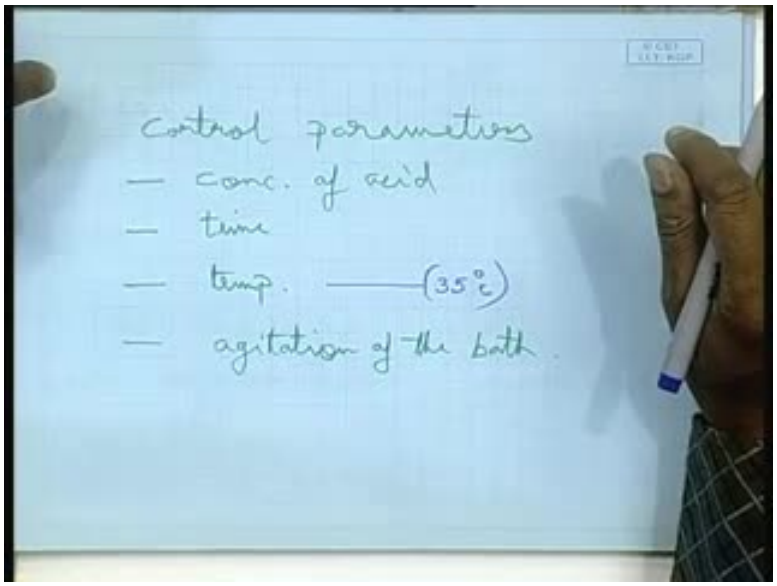

You start with a 15 percent concentration over period it drops; so as it is dropping then what is happening? As it is dropping, your pickling time has to be increased; that means to make the process automated and fully assured that it is exactly just corroding away the scale and not the metal. Like same thing they are the energy of the pellets was such that it is only chipping of the surface mill scale; same thing has to be done, proper process control as towards controlling the parameter.

So, there is a process control parameters. It would be the acid concentration, then the time, the temperature and of course, agitation of the bath. Agitation of the bath by that I

mean, acid has to be continuously stirred, continuously agitated, either agitate the bath or agitate the pluck material that helps in the reaction process and helps in the dual process of the salts.

So, these are the aspects to be controlled and as we can see with time that means, with time the concentration of acid will fall because it will react with the thing. So the pickling time has to increase for a given temperature; temperature will do not temper with, you keep a fixed temperature. Generally, a temperature level of around 35 degree centigrade is used, I mean there is no hard and fast rule about it; but, it has been observed that if we go for H Cl at 35 degree centigrade it is good.

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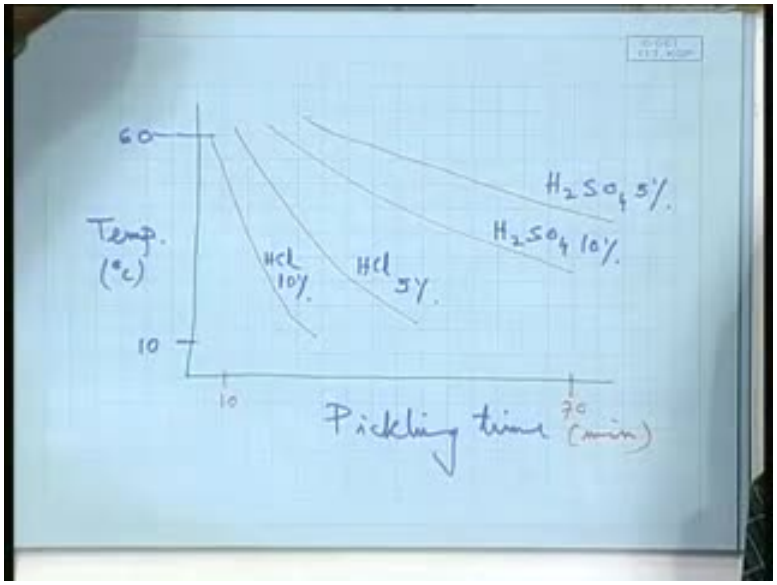

What does that mean it is good? That means, we see a comfortable reaction time and also there is another aspect here, as we that the pickling time is naturally more for H 2 SO 4. So, preferred choice is H Cl but, from the cost point of view H Cl works out expensive because it is more volatile there is loss takes place by air pollution and that loss increases much with increase in temperature. So if I could have gone up to 60 degree centigrade it would have been even better from production point of view but, the loss of H Cl would have been too much.

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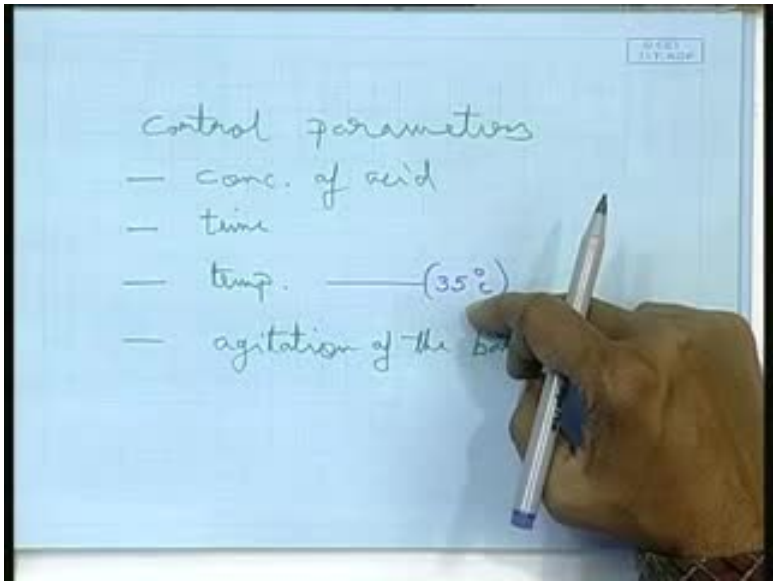

So that is how probably a compromise is that you keep the temperature at a level of 35 degree centigrade wherein, we make a compromise of the loss due to volatile effect of the acid at that elevated temperature. We service the pickling time, the productivity because if I do not have the temperature raised, I may save some of H Cl but, in the process I will have production time elongated, so there I lose.

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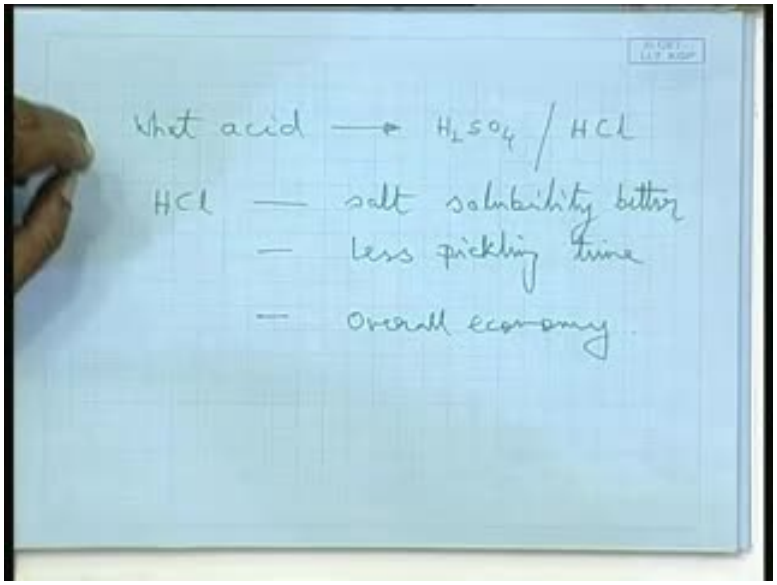

So that is how this temperature is kept at 35 degree centigrade. We see that in this process, H Cl is a preferred one because here the salt solubility is better and also we see

that the pickling time is less. Though the consumption of acid will be more compared to H 2 SO 4 in case of H Cl but, still we will have overall economics works in favor of H Cl, consumption would be more right but, overall economics will be better.

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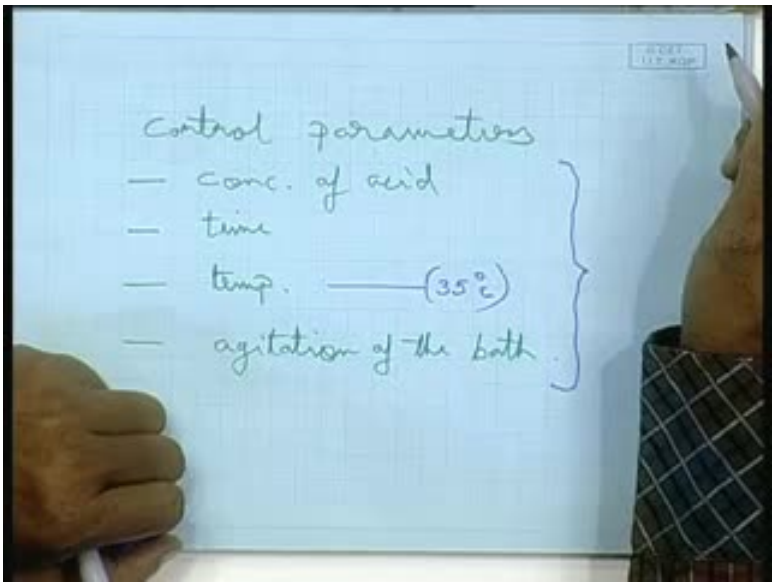

Overall economics can be achieved with H Cl. So that is how H Cl is preferred and now so we see that in this process, the control parameters as we have mentioned that we will have to have a proper process control. That means we will have to have mechanism to monitor the concentration of the acid bath continuously and it has to be properly agitated the acid bath, because if it is not agitated then the concentration on the bath at various points will differ. So there should be a uniform homogeneous composition of the acid all over.

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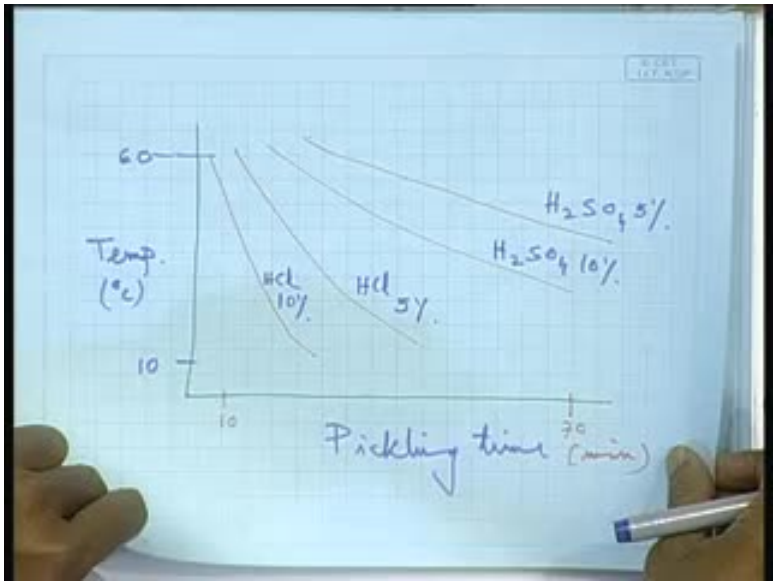

So monitoring of that continuously with time; so you will have to have a proper process developed such that as it monitors the concentration is falling from 10 to say it will gradually fall. It is not a step function, it will gradually fall so accordingly, gradually you will have as it is falling you will have to increase the pickling time.

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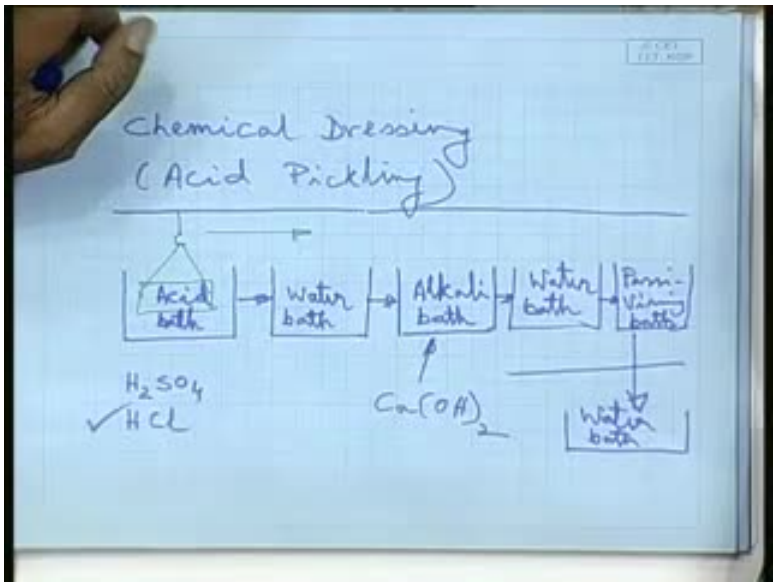

So that should go automated, then only it will function properly. Temperature as we mentioned maintain elevated temperature; depending on what temperature you are maintaining your pickling time, concentration, all those things will be effective. Well, so

that is what the acid bath is. So, we use their, it is preferable to use H Cl, it does not mean that you cannot use H 2 SO 4.

There are places where people use for some reason of their own H 2 SO 4 also possible; if you can afford to have a longer pickling time that H 2 SO 4 may work out more economic that is the thing. If your production rate requires that you will have to produce so much within a certain period of time and which cannot be achieved by H 2 SO 4 then well, one have to go for H Cl, so that is how.

So once that is done you need water bath; this water cleaning is done, this cleaning is flowing water it has to be flowing water, it is not stagnant water because then again cleaning is not done properly. So that is another difficulty of this process; means it should be having good huge amount of water. Obviously, any shipyard will be located in front of any (( )) it will have a water front but, well not necessarily any water can be used it has to be some bit of treated water, not necessarily distilled water but, treated water.

Then comes alkali bath, in the alkali it is essentially alkali of soda ash or calcium hydroxide bath is used because, here the whole purpose of the alkali bath is nothing but, so called neutralize the traces of acid whatever is there. Obviously, go for the cheapest one and possibly calcium hydroxide is one of the easily available and cheapest alternatives which can be used.

This neutralizing bath is, there again the process is same; you will have to just keep it dipped for a certain period of time. Obviously, here time factor is not that important neither a longer time is needed because it is only any acid trace coming in contact with alkali it will immediately react and it is done. That means it is just question of dipping, agitating and taking out; the whole process agitating is such that it gets a good mixing with the plate surface and the alkali bath. Next, water wash and then go to the passivizing bath.

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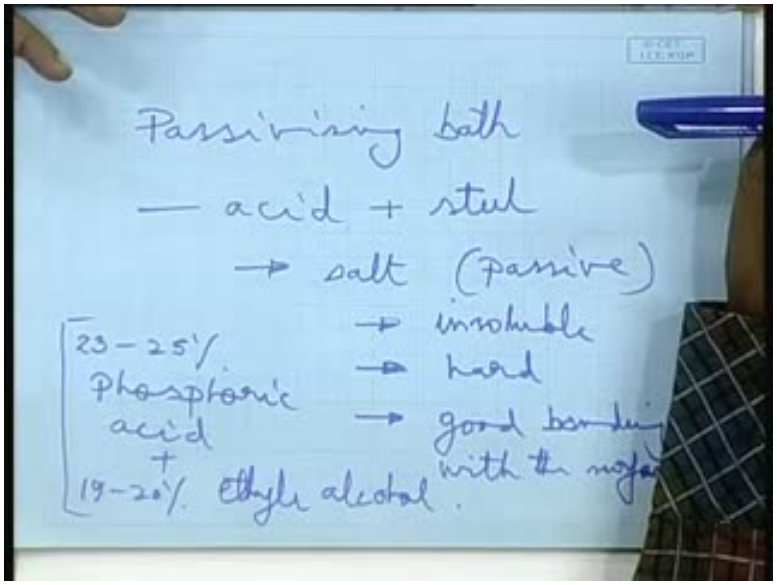

In the passivizing thing, what is used is there are various types of chemicals. It is also a kind of acid bath but, acid which reacts with the steel surface. So passivizing bath that comprises of acid bath; however, which reacts with the steel surface. There the acid was reacting in the previous case with the mill scale. Now, this acid is reacting with the steel surface because after the alkali bath we are getting the clean, fresh, shining steel surface.

So this will form a salt, which will be passive in nature; that salt should be passive in nature and should adhere to the surface. Previously, we used acid such that it reacts with the surface; surface was mill scale and forms a salt which is soluble in water. So here, I have to have the salt forming which is insoluble, which is fairly hard, it is sort of property that means should have the necessary aberration resistance, necessarily hardness should have a good bonding with the surface.

Good bonding with the surface means, the surface layer gets, that surface layer founds that salt and it does not get detached. The surface is kind of it reacts in a sense it gets corroded in that sense but, that corroded material should remain on the surface there we are protecting. That should be neutral in nature; neutral in nature means, we will not corrode further; provide the necessary resistance to corrosion make the surface passive. Subsequent other two properties obviously, it should have that means like after priming, we talked about it should not interfere with the cutting and welding process; same thing is true here also; it should not interfere with that cutting and welding process.

The acid used here is a essentially a phosphoric acid bath with alcohol around 20, around 23 to 25 percent, phosphoric acid in a ethyl alcohol bath of 19 to 20 percent ethyl alcohol. We are talking about passivizing bath, there are various different type of patented passivizing bath; that means, you do not know I mean there is a patented type bath but, one of the common is you use a essentially a phosphoric acid bath with ethyl alcohol.

This gives you the necessary surface which becomes passive towards marine environment, essentially becoming passive towards marine environment. It is protecting the steel from further corrosion but, obviously at the end of construction again the same surface has to be protected with necessary painting scheme, etcetera because it also has a live like that of priming paint. So there by, we say that this is another method of mill scale removable which is acid pickling also a mechanized quiet effective and efficient method.

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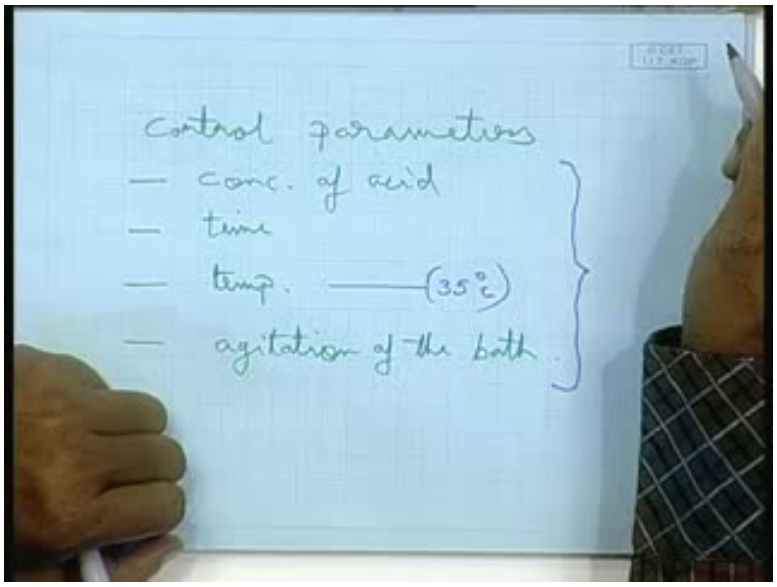

So, what could be the drawbacks in this? Like we have seen in case of your shot blasting the drawbacks were that it could cause work hardening of the surface leading to cracks developing, it could deform the plates. Similarly, here the drawbacks could be that if this process control is not done properly, if we cannot, if we fail to control this parameters same thing there, if you fail to control the parameter angle of impact, the force of impact similarly here, the pickling time corresponding to the temperature and concentration of

acid, it may lead to under reaction. That means, some traces of mill scale may remain or it may lead to overreaction or plate may get corroded.

So that is one difficulty here we have, which needs to be sort of properly controlled. Another difficulty in this is it is essentially much more hazardous compared to your shot blasting process, much more hazardous in the sense, disposal of the consumed acid, the disposal of the consumed alkali.

Because that acid is getting sort of so called consumed, you will have to go on replenishing fresh hydrochloric or sulphuric acid to bring up the concentration because over the use, say from morning 8 o clock shift it starts by 12 o clock if it gone down you will have again add acid and lot of slug is forming; the slug will be acidic slug. That salt which will remain, it has to be removed as it is, so disposal of that becomes obviously some environmental concern as well as the alkali bath; that alkali material also has to be disposed, whereas in shot blasting that problem is somewhat less. Because it is iron oxide which will be the left over in case of which needs to be so called disposed and iron oxide is not environmentally hazarders, it can well go in the soil.

So, that is another problem here. That means it is potentially a little more hazarders, trances and also it requires as we can see too many water baths. So, it needs a huge volume of water, quite a huge volume of water is needed in this process that is another problem.

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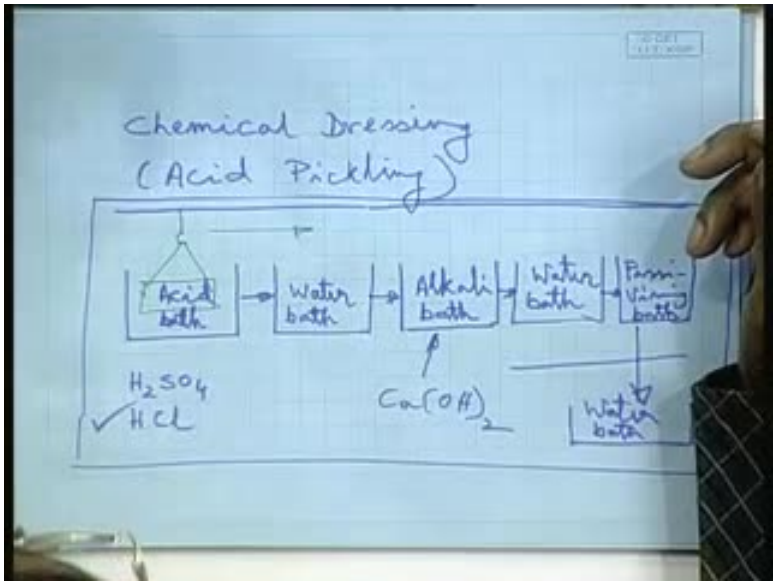

So, these are the two basic problems and finally, as we have mentioned that if the process is automated by way of hanging it from an overhead crane, you go on moving it one after another bath. You will dip the thing but, this whole thing is enclosed in a sort of a chamber, not only a chamber, a shop that means a huge hall; so that hall will be full of this acidic fumes as well as alkaline fumes.

So that will affect that overhead structure, the crane and all that means the overall corrosion possibility of the equipment inside the hall increases, that means the life of this crane and other equipment also has needs to be taken in to account in the entire process, so that is another problem here. Well, those are the so called disadvantages.

What would be the merits of this process? There should be some merits also automated well, it is automated definitely and if we compare with the other process because when we talk about merit it always works out in comparison.

Here obviously, there is no noise pollution it is a quite a silent process, so there is no noise hazard as such. Second, there is no question of work hardening; that problem, we faced in case of shot blasting, that means the surface was getting work hardened that is not happening, there is no question of work hardening taking place here.

Next advantage could be that there is no question of deformation of thinner plates. There in shot blasting, we have seen that the thinner plates rather it is difficult to do shot blasting operation on thinner plate materials, rather it is not advisable event times. But in case of acid pickling, whether it is a 2 millimeter sheet or 20 millimeter plate it does not make much difference only thing obviously, you will have to control all the process parameters properly. So there you do not run the risk of damaging the plate, deforming the plate or corroding the plate.

So those are the advantages point of this acid pickling or the chemical dressing. Finally, since the surface it is protected by passivizing, so they are also depending on how this operation has been done. One gets a highly passive surface that means it gives a necessary protection till the construction is over and your painting, further protection by where painting is provided.

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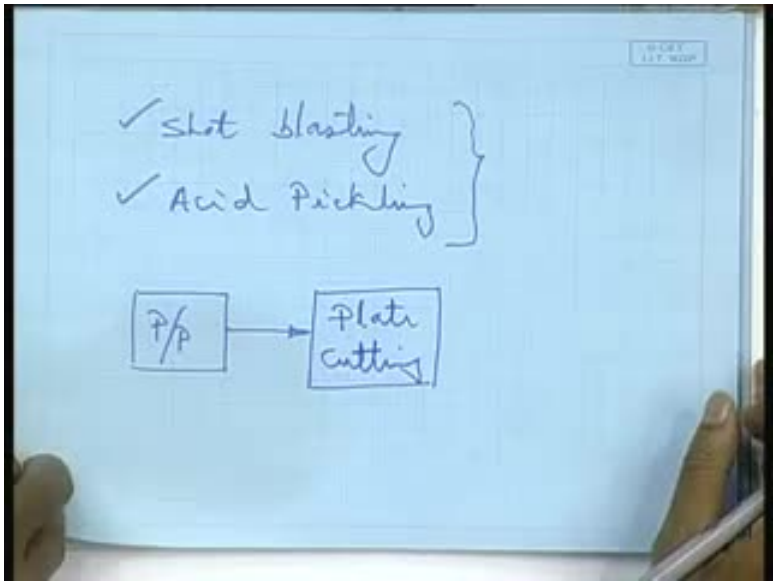

So that is how we see that among all these processes your shot blasting and chemical pickling these are the two process which works out to be effective shot blasting and well it can be termed as acid pickling.

These are the two processes of removing mill scale from the steel material. For removing mill scale from the steel material, mix these two most effective methods of this depending on, at different places you have either shot blasting or acid pickling. Generally, both not necessarily is used. We have seen it as both plus and minus, both of them, so it depends on the one can say on the shipyards choice to have one of them. Obviously, one distinct advantage of acid pickling is it is irrespective of plate thickness it can work; that is a distinct disadvantage of shot blasting method. Also in acid pickling, you do not run the risk of work hardening and eventual surface cracking because, surface crack those cracks will be airline cracks.

Very minute cracks only on the surface as such there benign, as such they do not create any problem but, if the same material is subjected to subsequent fatigue loading then, those benign cracks may become the locations for further crack generation and subsequent crack propagation. So that is how those cracks are differently not benign in that sense because that plate material being used for ship building purpose for ships or offshore platforms it is quite normal and natural that they will be subjected to fatigue loading.

Fatigue loading as you know is nothing but, reversal of stress; so in the service condition it will be subjected. So that way, that is one aspect which has to be thoroughly taken care of while doing shot blasting operation, which is not there in case of acid pickling obviously.

Again, disadvantage as you see that it is a somewhat more hazardous from the point though we are saying that we need not to have any person inside the hall but, in reality that level of mechanization at times becomes difficult; a person has to go in operate the crane, look after the things, so he will be continuously exposed to that acid fume in the hall which is definitely not very healthy.

So that problem is there, requirement of water is very high, that is another disadvantage in this. Finally, disposal of the waste is generated from the process disposal of the waste that is also another problematic. So, it is in fact difficult to pin pointedly say that which one is superior to the other taking whole factors in to consideration. So that is why we see that depending on shipyard choice, depending on availability of other supporting materials, water, etcetera one can have a choice for acid pickling or can have a choice for shot blasting.

Best would have been provided having both, and then one could have derived the advantages of both from this. Well, so that is what is your we come to an end of that activity of plate preparation. So, this was plate preparation and next we will move over to what would be the next operation, logical operation Plate cutting. So, we will come to the plate cutting operation and plate cutting well, just we will take it up in the next class; however, little introduction to this plate cutting.

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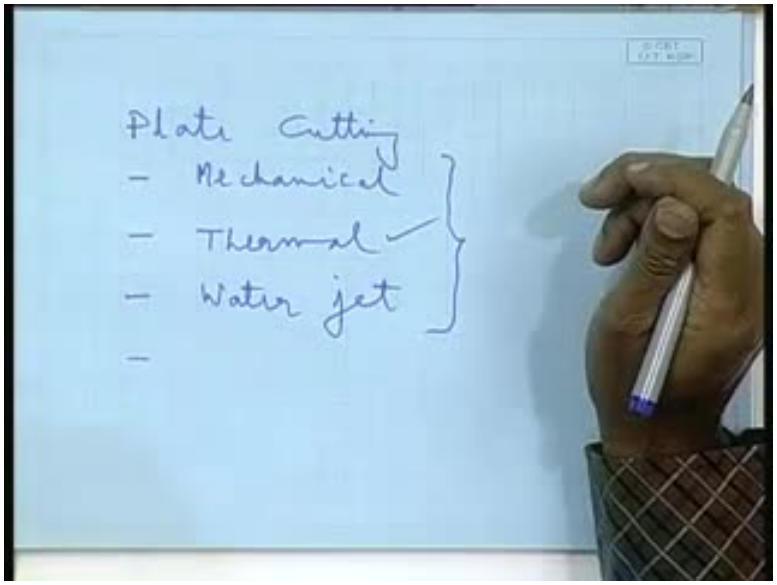

What all types of methods can be used? One is obviously a mechanical cutting, this is a mechanical cutting here, remind you, we are talking about cutting steel plates, aluminum plates such material and of the dimension of 10 meter long plates. So, mechanical cutting obviously it is not question of cutting using an axe or a power saw definitely it is not there; mechanical cutting means by shearing we will talk about that.

Then there can be a case of thermal cutting, by thermal cutting it can be oxidized, it can be plasma, it can be laser that using a heat source, using heat energy we do the thermal cutting. Is there any other method of cutting you have heard about? These are the two very common or rather obvious, chemical not really in this case; another is maybe you have not heard about, which is referred to as water jet cutting.

Water jet that means you use a jet of water, very high energy water jet which will cut through this steel plate. You can imagine the energy there, as you know what are jets are used to disperse crowd, is not it? One takes a shower that is also a water jet but, it is so pleasant to take a shower but, increase the energy of that you would not stand below that. Further, you increase it will pierce through your head, so that is what water jet cutting.

So, thick steel plates can be cut with a jet of water; not thin, thick steel plates. So these are the three basic methods of which obviously most widely used this is the thermal cutting but, if they may come when water jet also will be equally used.

Only difficulties of water jet using these days is its still quite expensive process though the raw material only water but, it is expensive. Well, probably lot of water; there is another thing, lot water is needed. It is there, the entire thing is there but, still it has not - it is being used, it has lot of advantages certainly, so we continue in the next class.