Chemical Technology
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Module - 3
Pulp and Paper
Lecture - 3
Recovery of Chemicals

The module 3 of the chemical technology course lecture 1 and lecture 2, we discussed about the introduction to pulp and paper industry. In module 2 we discussed about different pulping and bleaching process, what are the advancement that has taken place in case of bleaching process. Now, we will be discussing in the lecture 3 of this module about the recovery of the chemicals, because the black liquor, which we are generating from the pulping process that has to be the chemicals that has to be recovered and the lignin the organic part, also that has to be utilized for generation of the power or the steam.

So, that is one of the very important section in case of the craft pulping process or in case of the bagasse, because in case of the agro, agro-base raw material will not using the recovery of the chemical. But now because of the environmental problem that has been made mandatory for all the agro-base material either to go for the recovery part or many of the mills as they have shifted to the waste paper.

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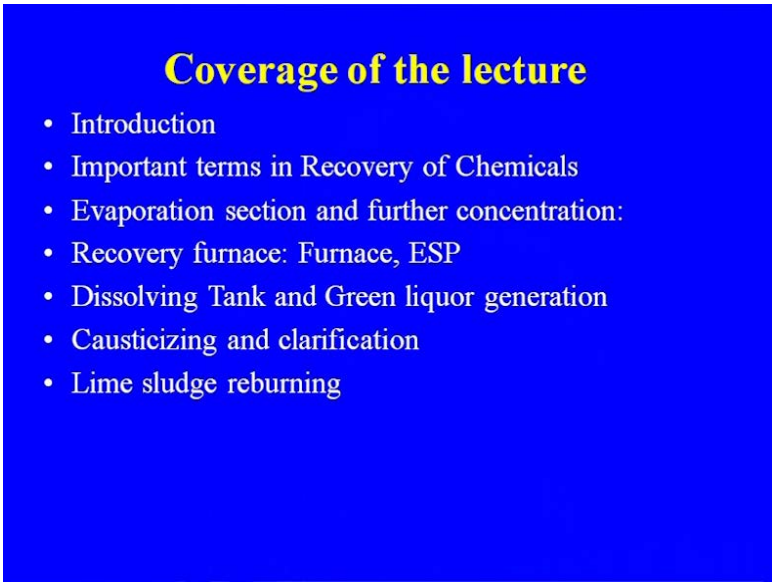

So, the coverage of the lecture that will be introduction, importance of the recovery furnace, what are the various terms used in the recovery of the chemicals, evaporation section and further concentration of the black liquor, which we are getting from the washing section of the pulping process. Because in case of the washing section the concentration of the black liquor varying very widely that is around, if good washing is there that may be around 15 to 16 percent, if the , if the washing is not proper that will be dilute black liquor around 12 to 13 per cent will be getting.

So because as you are firing at a concentrated black liquor and if the concentration is right definitely that will improve the efficiency of the recovery furnace. So, the evaporation and the further concentration of the black liquor that is very important, then we will discuss about the recovery furnace and then because you see the ESP electro static precipitator. That is the integral part of the furnace or any boiler just remove the particular particulate matter, but here in case of the recovery furnace here the importance of the ESP is there because we are separating the sodium sulphate from the flue gas, which we are getting from the furnace.

That sodium sulphate is recovered from the flue gases and it is continuously it is fed to the again recovery furnace. So that sodium sulphate is converted to sodium sulphite, dissolving tank, where we are dissolving this melt, which are getting from the furnace. Then green liquor production is there and that green liquor because green liquor is more sodium carbonate, so that has to be converted in to sodium hydroxide because our requirement is more sodium hydroxide and the sodium sulphide because this is not participating in the sodium carbonate.

So, causticizing section means the causticizing of the green liquor using sodium lime that we are doing like clarification, separation of the lime sludge and the lime sludge reburning. Because, the lime sludge that is the waste and the huge amount of the lime sludge in the form of calcium carbonate that is been produced in case of the pulping processes or any paper mill, which are having the clate pulping in case of the bagasse because now the lime sludge reburning that has been made mandatory.

So, as I told you earlier also that is the chemical recovery system is an integral part of any pulp and paper units and the efficiency of the chemical recovery plays an important role in the overall economics subject because whatever we are losing the chemical that

will have the direct impact on the overall economy. So, the proper running of the furnace that is also very important.

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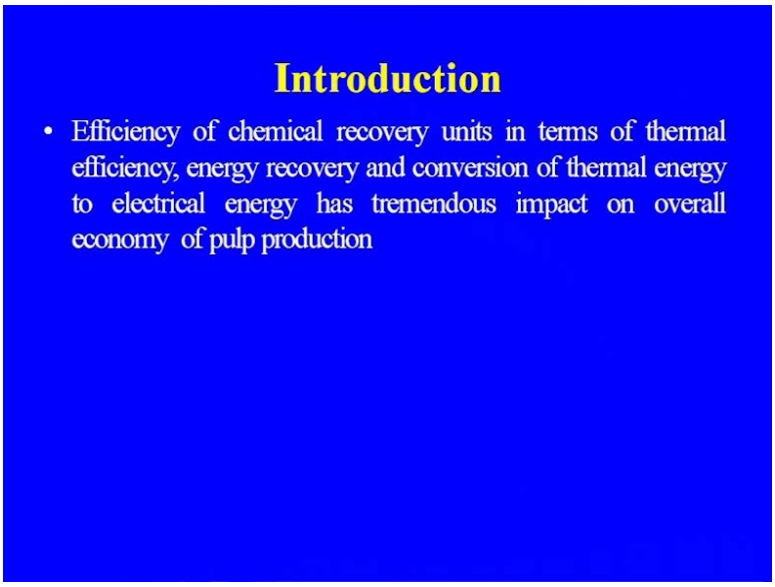

Efficiency of the chemical recovery units in terms of the thermal efficiency, energy recovery, conversion of the thermal energy to electric energy has tremendous impact on the overall economy of the pulp because one of the important you see the in case of the pulping, you are using huge amount of the steam; from where this steam will come? So, most of the paper mill they are having the coal generation, they are having thermal power plant at the same time they are having the recovery furnace from where they are generating this steam and that is steam that is been utilized in the process or it can be also you find the your boiler and that boiler steam and that will go for the generation of the electrical energy.

Although, the earlier agro based mills were not having recovery furnace due to the high silica content of the black liquor and the smaller capacity because one of the as I discussed for the introductive part of the chemical process industry in 1970. That was the era of the industrialization where the many plant concept that came into mini cement plant, mini paper mill, mini fertilizer plant, mini refinery that concept came in same thing was in case of the paper mill. Also, we started using lot of these small agro-based paper mill where the earlier.

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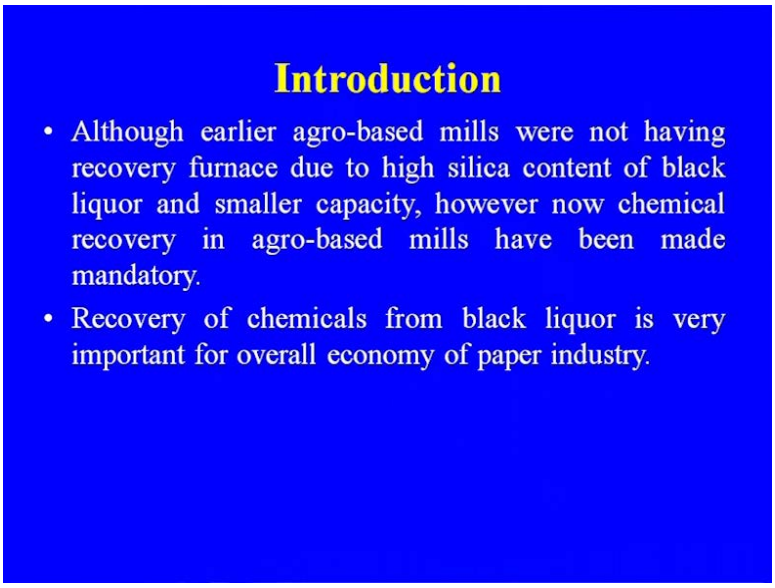

Because it was considered a black liquor recovery of the chemicals on the black liquor that will be not economical, because of the small capacity, because of the more dilution, because of the high silica content. But know that has been made mandatory as per mandatory as per the central position control you will have to go for the, so that there is no excuse for that because some times because the mills they are saying it will be not economical, the infrastructural facility or the because of the poor economics all those things they, all type of the actual excuses that has been given earlier.

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So, recovery of chemicals from black liquor is very important for the overall economy of the paper industry whether it is the agro based or the forest base raw materials. So, these are the various section that is in case of the kraft recovery plant that is the evaporation section, evaporation and the further concentration for that we are having the long tube evaporator 5 to 6 effective evaporator because always you are using the fibrous material that is going along the black liquors, some time choking of the evaporator tubes are also there.

So, one normally one of the bio evaporator there by passing and continuous cleaning of the evaporator tube that is very important otherwise that is also affecting the whole economy. So, direct contact evaporators are also there, but normally the direct contact evaporator that is not recommended when we, if you are interested in the control of the, machine control of the sulphur compounds because here they are coming in direct content of the acid gases.

So, the generation of the marker pens are there. Cascade evaporators we have been cyclones and venture. They are also some of the mills earlier they were having only cyclone and the combine with the venturi scrubber where the both the concentration, separation of the flue gases plus at the same time what about the your sodium sulphite was there, that was the scrubbed from the flue gases.

So, in some of the olden mill they are having the only this combination, this cyclone and the venturi, but now the new breed of the furnaces they are all having the ESP electro static precipitator. So, after the evaporation that is going to recovery furnace from the recovery furnace to dissolving tank and after dissolving that is the causticizing, clarification and the lime sludge reburning.

So, this is a typical flow diagram of kraft recovery system were the after the 3 stage or the 4 stage because now as I told you the concentration of the black liquor that is very important from the recovery point of view. If you are having the more dilution, diluted black liquor then the steam consumption and the kraft recovery especially in evaporation that will variant.

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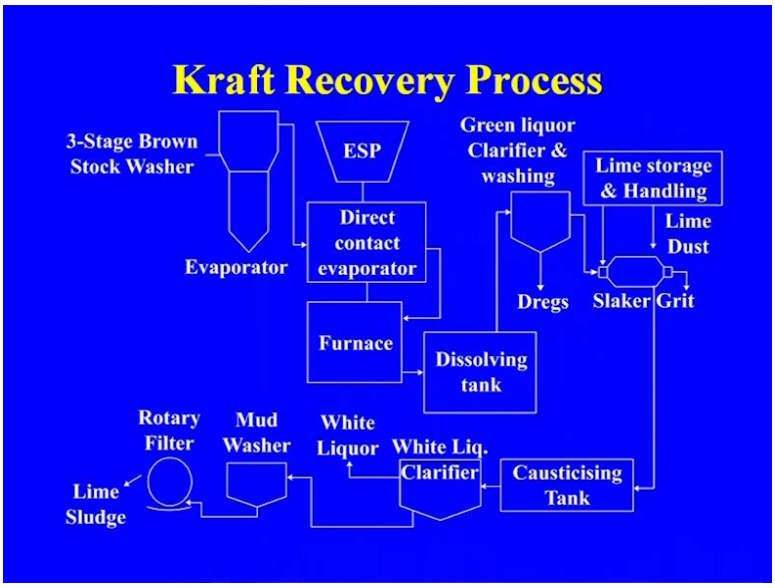

So, in order to have now we are having the 4 stage brown stock washer and from there after the brown stack washer the black liquor actually here the black should be black liquor from the your 3 stage or the 4 stage brown washer that is going through evaporators that as I told you that is normally we having the long tube evaporator in case of the karft recovery process with the backward feed arrangement because you are not the forward feed because it will become highly viscous.

So, in between the after the three effects we are adding the feed. So, that is the backward feed arrangement is there. So, after the, it is going to the direct contact evaporator as the further in some of the mills that has been eliminated from the environmental point of view that the flue gas should not come in the contact with the black liquor, so direct. So, because here you see that furnaces the gases are going in the direction and the heat of the gases that is been utilized for rising the temperature for the evaporation and finally, the product is going to the ESP electro static precipitator or it may be the combination of the cyclone or the venturi scrubber.

But normally as I told you that the most of the modern mills they are having the ESP because the recovery of the sodium sulphate from the flue gas that is very important for the overall economy because that sodium sulphate that we are again reusing. Otherwise you will have to add the makeup sodium sulphate because that sodium sulphate that is converted to sodium sulphite. But during the process lot of this loses of the sulphur

compounds are there, so how to makeup? So, for that sodium sulphite N 2 S O 4 plus carbon in places of carbon that is generating sodium sulphate.

So, this the furnace part and the furnace again it is very complicated, we are having boiler part, we are having the 3 joules are there, dying and the burning. Then the finally, the waste heat relation in the boiler that we are generating, the I will show the diagram of the furnace also. And after that it going to dissolving tank where we are dissolving the white liquor, which you are getting from the causticising section that is going to the dissolving tank, where we are getting the green liquor containing higher percentage of your sodium carbonate.

And this green liquor again it is going to the part separation of the dregs which is there. Dregs that has to be then it is going to finally, because for converting the sodium carbonate to sodium hydroxide we need lime. So, in many of the mills when they are having the lime, if they are producing their own limes because what about the lime sludge earlier because the some of the problems we will discuss later in the other slides about the why the lime sludge reboiling that was not done earlier.

So, slacker where we are adding the lime and after that it is going to causticising tank where the some temperature around 90 degree centigrade to maintaining and causticising the action is taking place. Then it is going to washing of the after the causticising the causticising that is going to the clarifier and after the clarifier because this you are separating the white liquor. We called it a white liquor, again it going to daister. This sludge which we are getting from this it is going to the mud washer and after that is going to the rotary filter. Finally, the lime sludge cake that is separated and the liquor, which you are getting from the rotary filter that is been used recycled here, for the in the mud washer.

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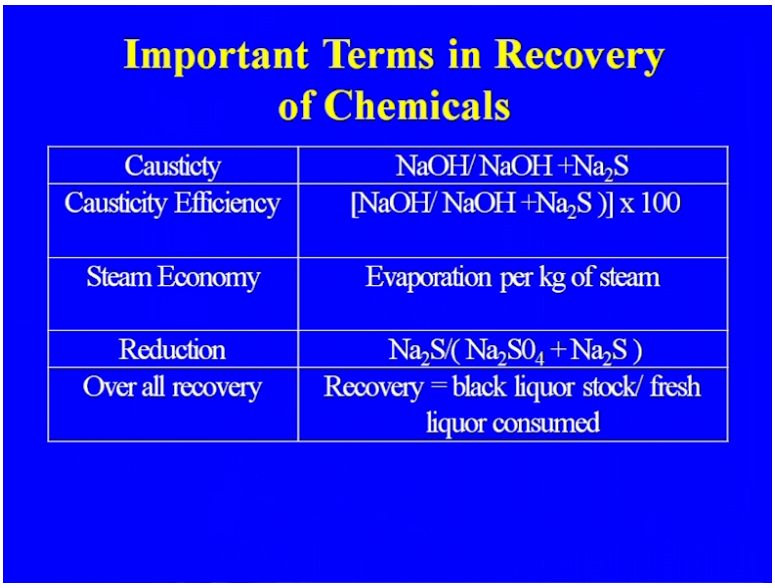

So, these are the term. Already, I discuss about the causticity, causticising efficiency, steam economy that is very important as I knew the evaporation per k g of the steam that is very important in the overall economy of the evaporator reduction N a 2 S divided by N a 2 S O 4 plus N a 2 S over all recovery recover means as the recovery is equal to black liquor stock plus fresh liquor consumed. Because whatever the chemicals that you are recovering that is coming because here the term of N O H and other thing that will be there, so this will be the overall recovery, and that overall recovery that has to be 95 plus if you want to have the better economy.

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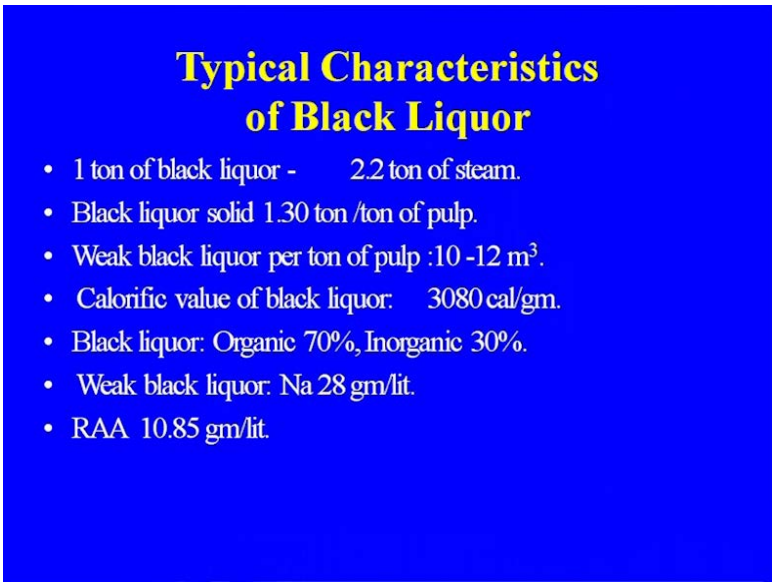

This is the generation of the black liquor. 1 ton of black liquor that will generate 2.2 tons of the steam and as I told you the concentration of the black liquor that may be around it may be 15 to 16 per cent. If you are having the very good washing, if it is less washing not better washing. So, normally that problem is there in case of the agro-base that again I am going to discuss in detail. So, black liquor solids 1.3 tonnes per ton of the pulp, weak black liquor per ton of the pulp 10 to 12 m cube that is actually again it is changing depending upon the efficiency of the washing type of the washers you are having.

If more dilute more black liquor, weak black liquor you will be generating. This is the calorific value as you see the one of the important aspect in case of the why you are going for the recovery because the black liquor that is containing about 70 per cent of organic, 30 per cent of inorganic and the weak black liquor that is sodium content, residual alacrity content. So, these are the some of the characteristics of the black liquor. One more development that is taken place because the emission of the mecrcaptan that is very , if you go to the any kraft pulping mill they will find the smell of the mercaptans there.

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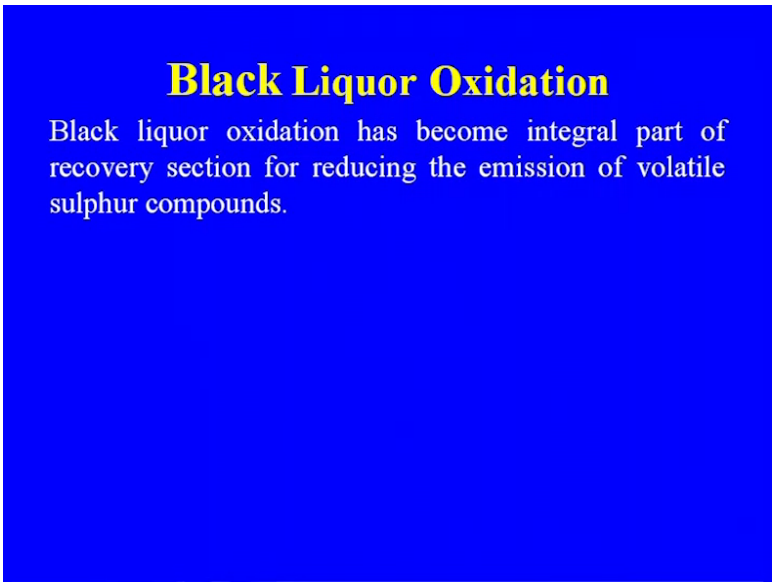

So, black liquor oxidation that has been becomes integral part of the recovery section in most of the mills. Although, Indian condition we are not using earlier for, but now if you want to reduce the emission of the mecrcaptan, then you will have to go after the black liquor oxidation.

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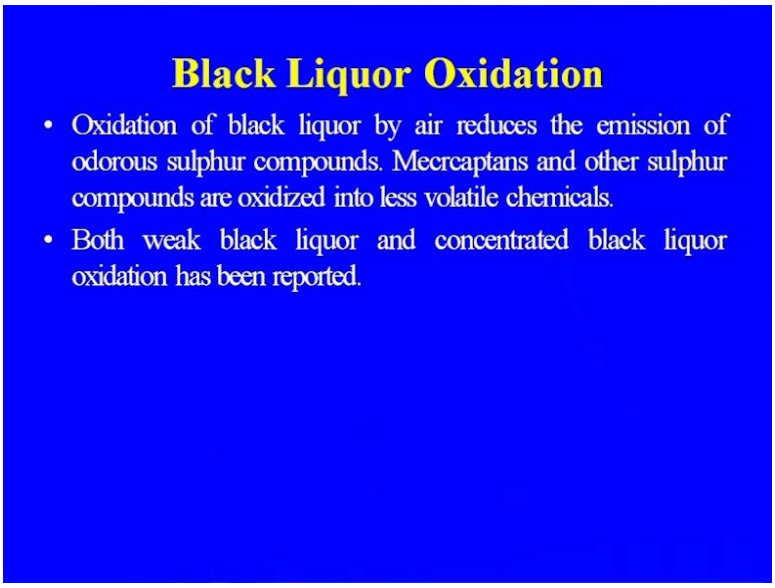

So, oxidation of black liquor by air reduces the emission of odours sulphur compound because before that it is converted to sodium sulphite, sodium thiosulphate. Mecrcaptan and other sulphur compounds are oxidized into less volatile chemicals. Both because they are two types of black liquor oxidizing system that has been the weak black liquor, weak black liquor means before going to the evaporator.

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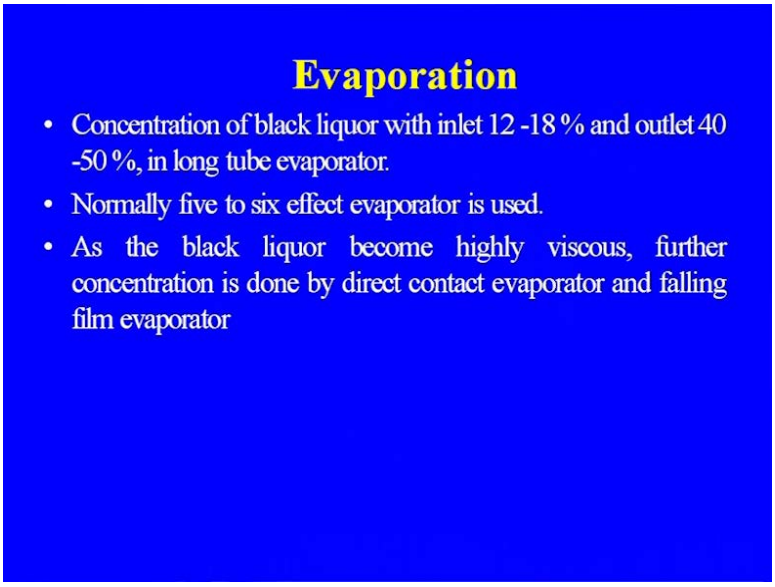

If you are having the black liquor oxidation, then the emission that may be less, but if you are having the concentrated black liquor then definitely it is after the concentration.

So, in both the cases, in both the process but normal weak black liquor that was the earlier very common. This is the evaporation because S W we are getting a weak black liquor, concentration of the weak black liquor that will vary and the outlet that will be around 40 to 50 per cent depending upon the term.

Suppose, in Indian condition were the more bamboo we are using. In case of the bamboo we have been in the hard silica. So, the your range of the concern to final concentration depth maybe less. So, in long TV operator we getting around 45 to 50, 40 to 45 you can say, but if you are having the softer. Definitely you can go for higher concern, normally 5 to 6 evaporator as the evaporator become highly viscous, further concentration is done in the direct contact evaporator.

Another development that has been because just to avoid the direct contact evaporator falling film evaporator by the concentration of black liquor is in the form of the film and the evaporation is taking place and so the concern higher concentration you can. So, the choking problem of the tube for the high viscous that is actually the, we are able to work home combine the following vibrator.

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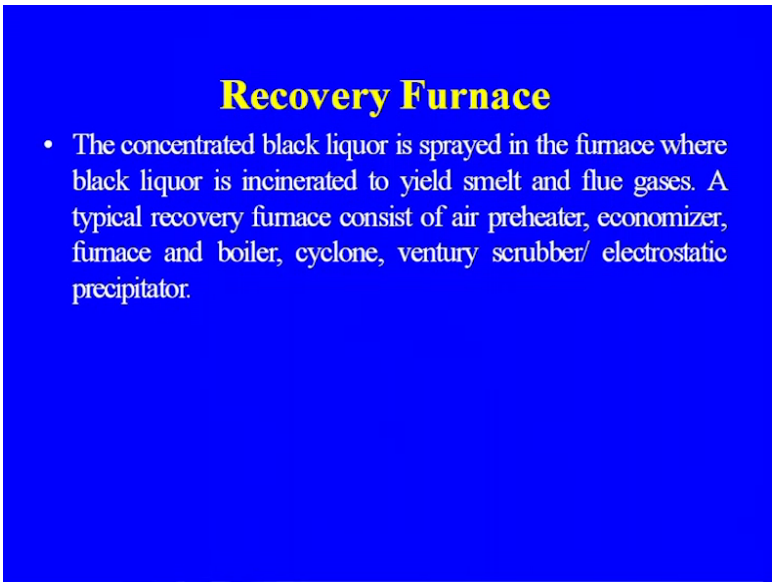

After the evaporation concentrate the concentrated black liquor that is sprayed in the furnace where black liquor is incinerated to yield smelt and flue gases. And this smelt that is containing the various pole chemicals, which is we are recovering in the subsequent stages. So, flue gases a typical recovery furnace these are the some of the part

air preheating because normally inhaling boiler you see preheater, economizer where the flue gases. That will be used for the air preheating, economa, water economizer the waters you going to boiler, furnace, boiler cyclone ventury or electrostatic these are the some of the part of the typical recovery furnace. So, these are the actually the concentrated black liquor when you are spraying in the furnace.

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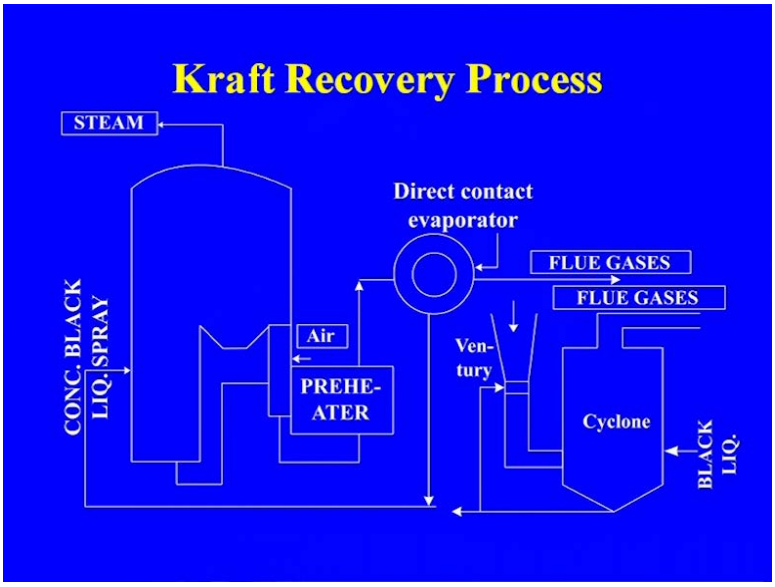

So, these are the some of the stage that are reducing zone in the bottom to burn the organic drying zone, oxidation zone. This is a typical, actually the where the ventury is shown. Then cyclone or it may be even after the cyclone that may, it may go to the ESP also. So, the here black liquor that is being actually the sprayed concentrate black liquor and the burning that is taking place. Here we are taking that is also the preheated steam, water is also preheated in economizer. So, this steam is generated and that steam we are using for the power generation or for the daister where for the cooking we need the steam.

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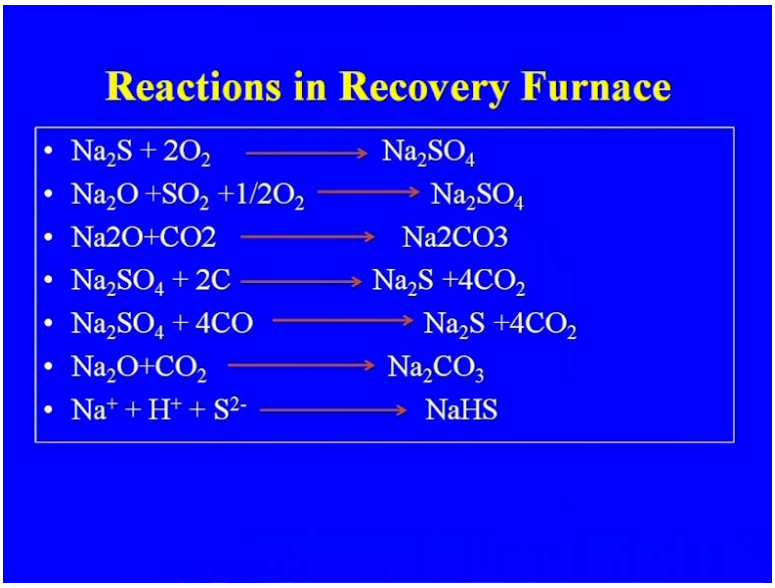

This is the reaction , large number of the reaction that is taking place and if it is the in all the reaction N a 2 C O 3 that is form the percentage of N a 2 C O 3 is that more and at the same time sometimes the sodium sulphate is formed from N a 2 S and that is it, sodium sulphate. Again it is converted to N a 2 S and which is coming along with the N O H and N 2 c 3 in the your green liquor. And so this is the, how the reaction that is taking place and the after the here actually they have continuous loss of the sulphur compound are there. So, what we are doing? We are adding the sodium sulphate which is again converted to sodium sulphate.

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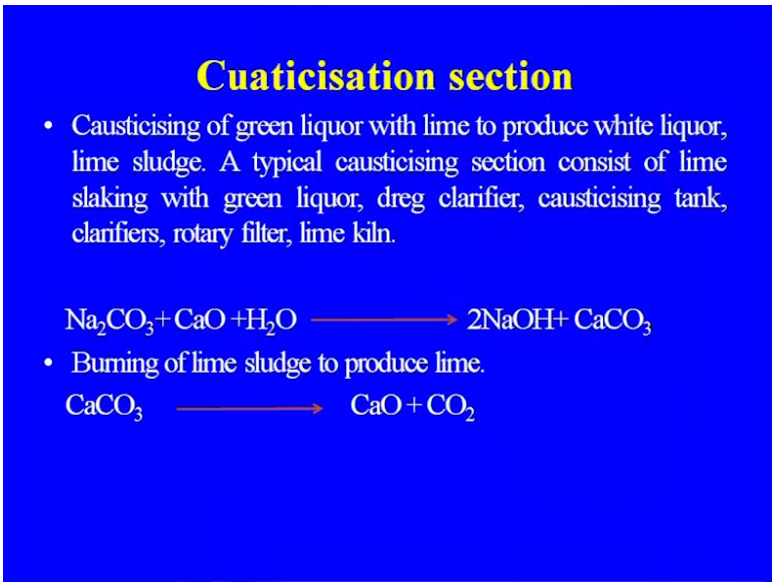

Then dissolving where the smelt that is we dissolve and the green we are getting the green liquor, this is the about the cuasticising section where the cuasticising of green liquor with lime to produce white liquor is there. So, we are producing the white liquor at the same time what is happening with reaction of sodium, sodium carbonate with the C O H, N O H and the C a C O 3 will be calcium carbonated, that is the pure calcium carbonate that we are getting, but you see the one of the problem that was there in case of the because of use of the bamboo or other agro-based raw material.

Silica content is high in case of the lime sludge and so the lime sludge of to produce lime that is reburning of the lime sludge to produce. That is now it has become the mandatory to go for the lime sludge. Because earlier I remember in orient paper mill they used to have this lime kiln for producing the lime. So, after that again some problem was there because of the high silica that was making the coating of the silica and the your calcium, this sludge.

So, the because of the sometime the sodium content of this sludge that was also getting problem. So, all those problems that complicated the reburning and the your available lime which you are, we are getting in the case of the lime that was less and another factor in case of the lime sludge reburning is that we are getting lime at cheaper rate than what we are producing.

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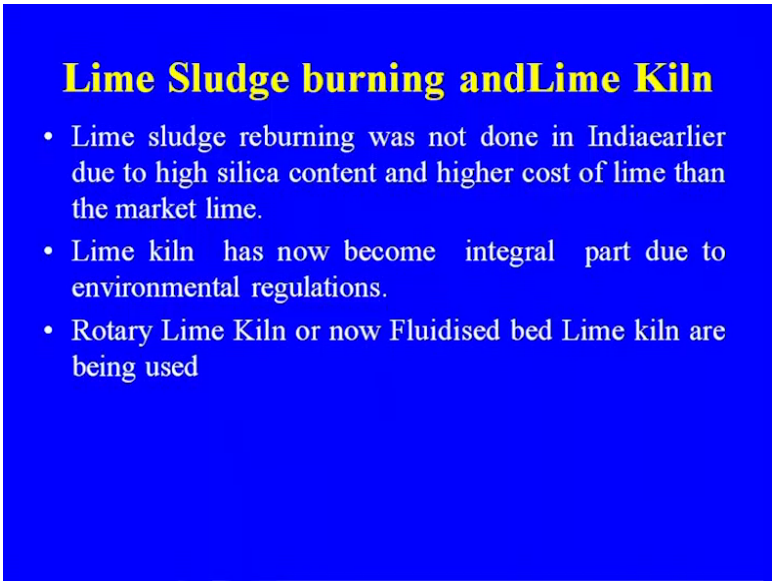

So, lime sludge reburning was not done in the India earlier due to the high silica content and higher cost of lime than the market lime, because once you are getting a thing at lower why to go to produce, but at the same time. If you want to maintain environmental standards, you want to have the less environmental problem, then you will have to compromise with the cost also.

So, that is the how the again some of the mills they started reburning of the lime sludge. They stopped the reburning again because of the environmental pressure. Again they have gone for the lime sludge reburning and now the lime kiln has become integral part. So, for that the either you can have the rotary lime kiln or the fluidised bed lime kilns are now being used.

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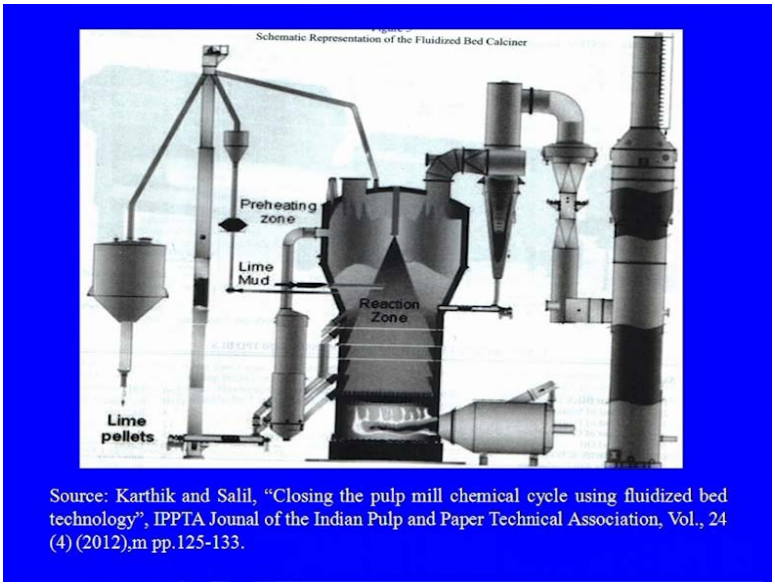

This is the fluidised bed actually the lime kiln that you are having for the preheating the lime mud that is going to the fluidized bed and so this some of the problems, which are inherent in case of the lime kiln that is eliminated here with and finally, we are getting the lime. So, that lime again that can be used and this is the new development that is taking place in case of the lime sludge reburning, otherwise the earlier it was the rotary kiln that was been used.

Recovery of the chemicals from the agro base as I told you the recovery of the chemicals in agro base we are, that has become a that became problematic, because all the black liquor which was generated after pulping people where discharging. As such to the water

stream or to the river stream or the small flow of water was there into the another thing and so the, and because the concentrated agro base mills were there in the western part of UP, in Punjab and Haryana.

So, lot of the problem was there, because the that is giving the brown colour to the water and so even if we put one drop of the black liquor to the one bucket water that will be coloured. So, this was the problem all the colour, all the black liquor even at the same time they were losing also the valuable chemicals which are going along the and the valuable organic. So, that was the actually the problem in case of utilization of the, of the agro base mill.

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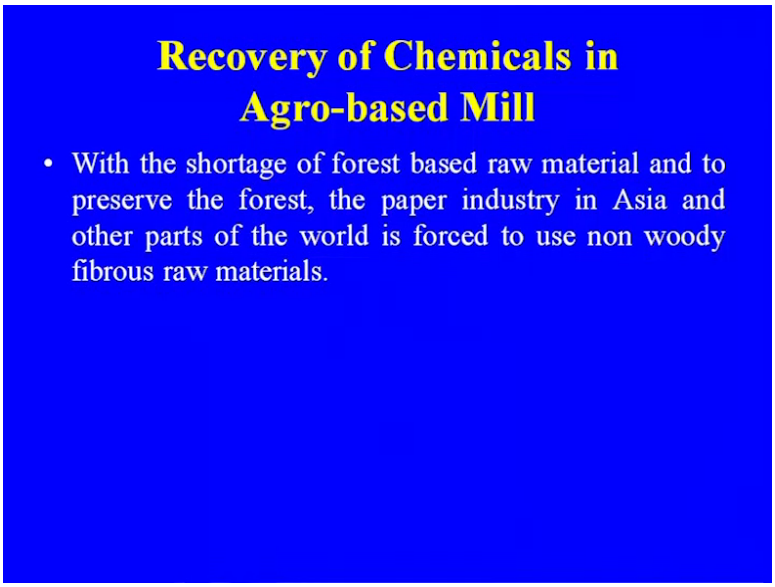

With the shortage of the forest based raw material and preserve the forest, the paper industry in Asia and other part of the world is forced to use non woody fibrous raw material. China, they are using the huge amount of agro based paper mill, but one of the advantage they are having their coal is better and the quality of lime is also better. So, that is one of the advantage they are having, but the agro base mill in India and China well developed in comparison to other part of the Europe.

India is the leading country in using the substantial proportion of the non wood fibre. So, they are also helping in the your sustainable development of the industries, sustainable development of the paper industry with the using of the waste material that is fibrous raw, agro based raw material which are not being used earlier. Either it was burnt or it

was just used for the fodder. So, this is the how the development that has taken place in case of the agro base, but the lime sludge recovery of the chemicals that was problematic in case of the your agro base paper mill because of the high silica content, which is there in case of the your black liquor.

So, that was the problem and as the era of 1970's that was the era of industrialization, after the 50 we got independence and the units came. Then the, our requirement with the increasing population. So, the paper because (( )) all the paper when the large integrated paper mills they use to have the capacity of 100 to 200 in capacity. So, that was the, but just to meet the demand of the growing population number of I need to (( )) economy and just to promote the industrial development number of the mini paper mill came and they started the paper mill using the agro-base mill without any (( )).

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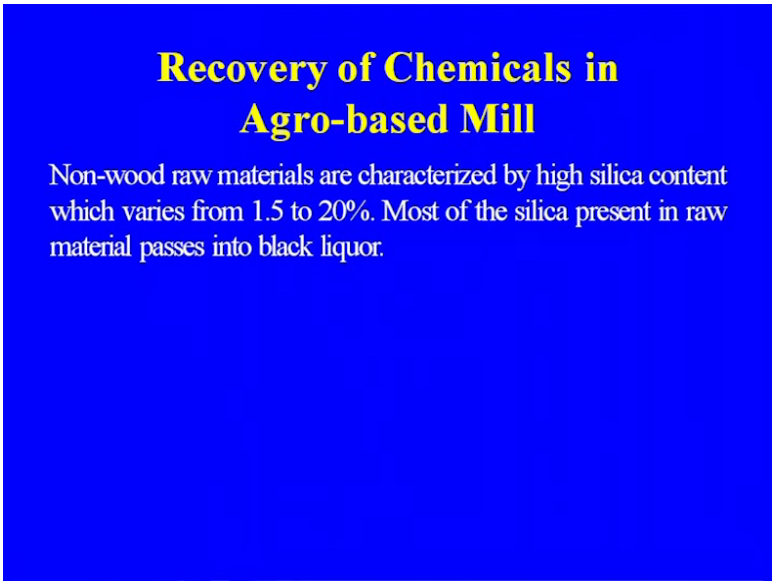

So, this is the non wood raw materials are characterized by high silica content which vary 1.5 to in case of the (( )) started at the maximum, in case of the bamboo also it is, although it is, it is not coming in the agro-base, but bagasse also coming silica, but in case of the weak start that is 4 per cent, so that is, that is the reason why we prefer more weak start for pulping than the you are (( )). Most of the silica present in the raw material passes into black liquor.

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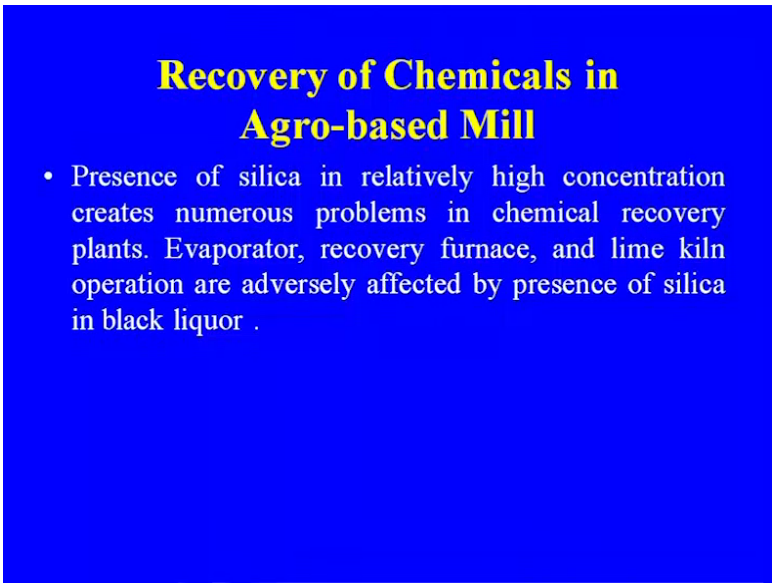

So, the presence of the silica in relatively high concentration creates numerous problem in the chemical recovery as I told you earlier also what is happening. We will have to evaporate, we have to concentrate the black liquor and we will have to go for higher concentration of the weak black liquor that is the requirement to have the better efficiency of the chemical recovery section.

So, how to get? Because here, they are having the property. So, the requirement of more dilution was there in the smaller paper mill for the recover thing black liquor. So, these are the some of the, so evaporator more silica, highly viscous and so the how to concentrate this black liquor. So, additional requirement was there or if you are feeding at a lower concentration. Then definitely whole economy of the furnace that is going to be affected, lime kiln operation that again if the silica is going more, so lime kiln operation that will be adversely effected by presence of the silica.

So, earlier what happened, they work on the just to remove the silica from the bamboo and the black liquor before it going to the evaporation and so they remove this silica by carbonation and that process that has been developed by Centre Pulp and Paper Research Institute, Saharanpur and some of the (( )) is they also did work on the (( )) of the your black liquor.

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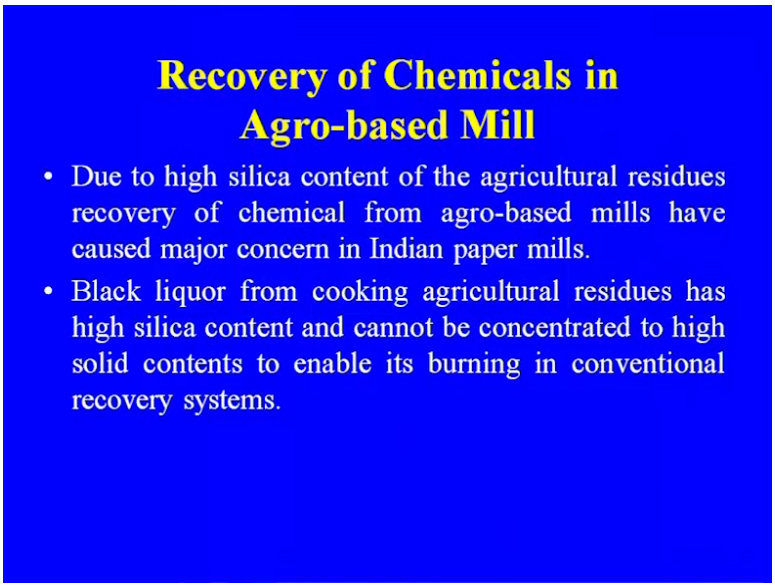

So, this is the actually the problems which I told you due to the high silica content of the agriculture residues, recovery of chemical from agro based mills have caused major concern in Indian paper mills. And so this was the actually one of the reason because the conventional recovery furnace, conventional evaporator they were not sufficient to meet the requirement to have the better economy of the chemicals, which you are getting through the recovery.

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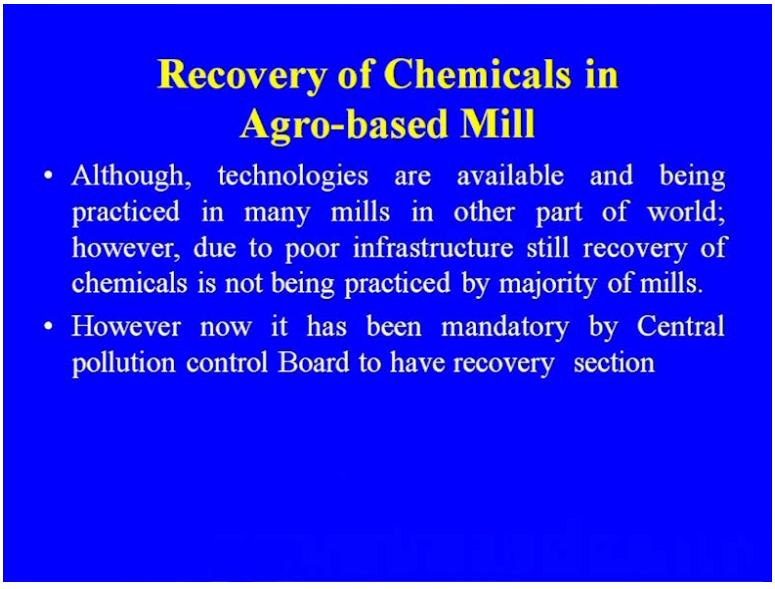

So, black liquor from the cooking agriculture residues has high silica content and cannot be concentrated to high solid content which we are able to achieve in case of the hard route or the soft route or the bamboo that we are having. So, burning that is a problem. Although, the technology are available and being practiced in many mills in other part of the world; however, due to poor infrastructure still recovery of the chemical is not being practiced. Actually, the now the, that is in mandatory so the most of the mills which are not using they have close the mills, they have close using of the agriculture residue, they have shifted to the waste paper based.

So, this is the typical concentration of the, so silica that is very high in case, in the black liquor. These are the actually the typical composition of the black liquor that we are getting. So, because you see here organic and inorganic these are the two important constituents of the black liquor which we are losing earlier. That was going to detain and the organic in the form of the (( )). So, that created, if you see the, if you are having 100 tonnes of the integrated mill based on the bamboo hard wood and the 100 tonnes of the agro based. So, pollution load in case of the, a small paper mill that is used to be around you can say the three times more than the, a integrated (( )).

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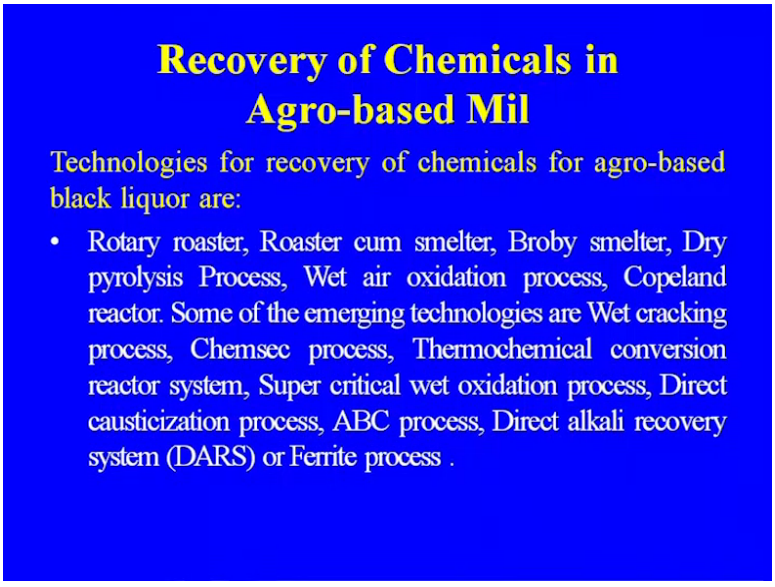

That is why the reason why the, why the recovery of the chemical and new technology and various technology that has been developed. These are the some of the technology that for the recovery of the chemical rotary roaster, roaster cum smelter and because even

that problem was there in case of the bamboo when we started. We are having the high silica content.

So, some of the mills even Andhra, I remember Andhra people, they are having the rotary roaster. Some of the mill they start with rotary roaster for their black liquor and rotary cum, roaster cum smelter that was actually suggested the, these are other type of the coke plant, some of the merging technology in the wet cracking, chemsee process, thermochemical conversion reactor, super critical wet oxidation process, direct cuasticization process, ABC process, direct alkali recovery or the ferrite process.

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Actually, you see the in case of the fluidized bed soda recovery system where the weak black liquor containing high silica content is concentrated to about 45 per cent in multiple effect evaporator, venturi scrubber and cyclone is sprayed in the fluidised bed combustion system. And so the, that can be used in case of the small paper. This is the fluidized bed actually the reactor that is for the feed and this fluidized bed and then the finally, the product you are getting.

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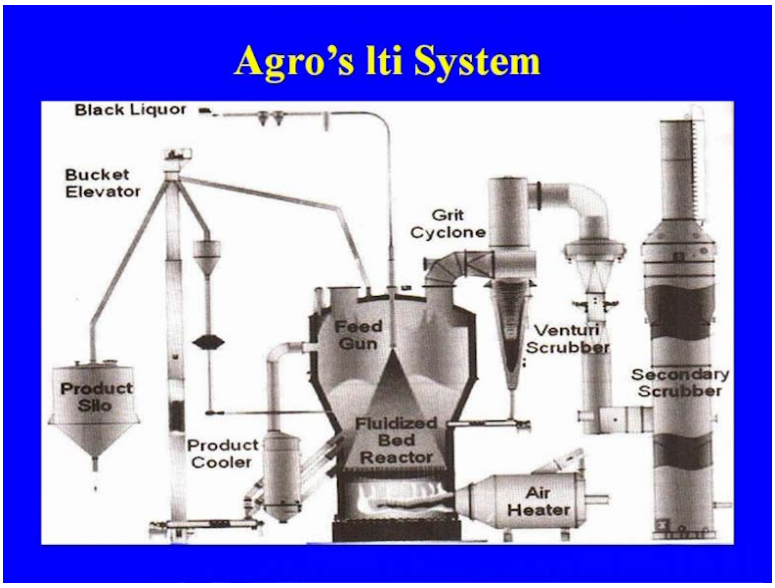

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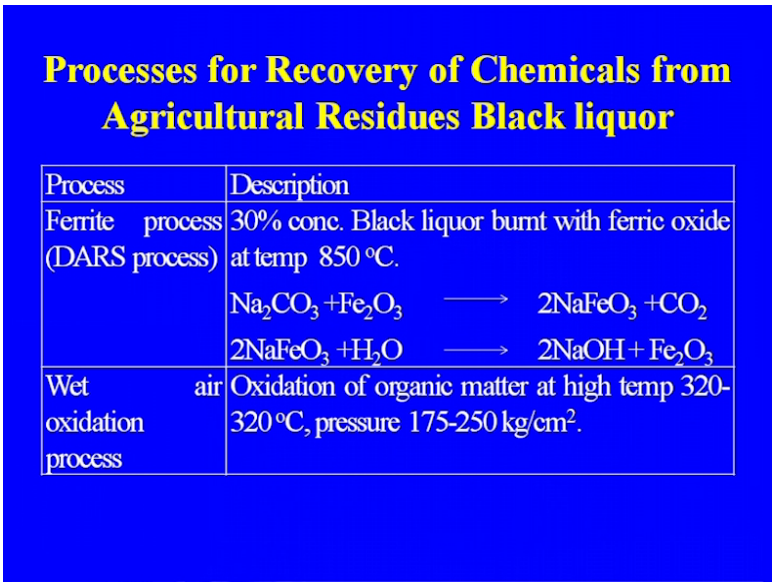

These are the some of the processes that is being used in case of the recovery of the chemicals from the recovery. Ferrite process or DARS process, 30 per cent concentrate black liquor burnt with ferric oxide at temperature, this is the temperature and the sodium ferrite and the sodium ferrite with again react with the water you are getting the (( )) to get back here. So, this was the technology that was suggested and wet air oxidation that is also one of the technology that has been suggested for the oxidation of the organic matter.

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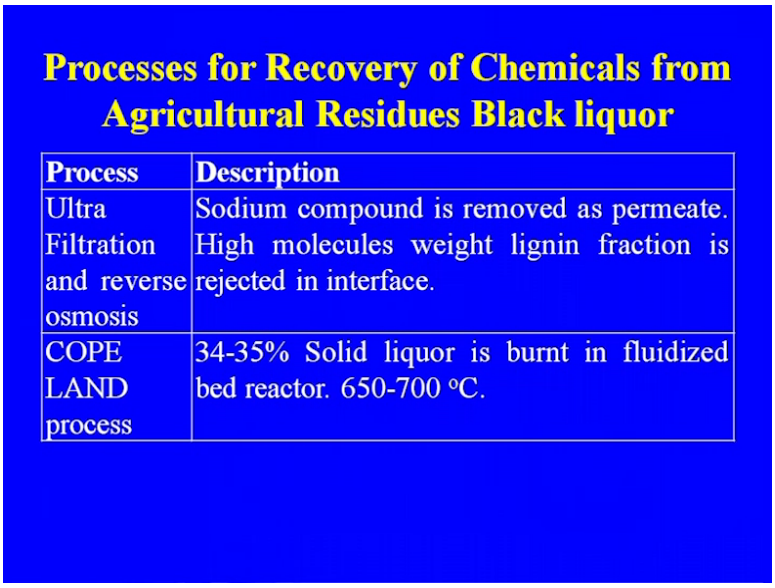

Then the ultra filtration reverse osmosis that has been also tried for the concentration of the black liquor to the higher concentration. But again the same problem was there in case of the membrane process where the chocking of the membrane and the cost of the membrane and that was the actually the initial stage of the implementation; so the lab work and the (( )) lot of the work for the, on the ultra filtration in the reverse. Already, now in the show industry we have gone for the, your membrane process for the which you are getting. But here actually the problem was there, because of the sulphur compound. Cope land process, this is also the fluidizer bed reactor that we are getting.

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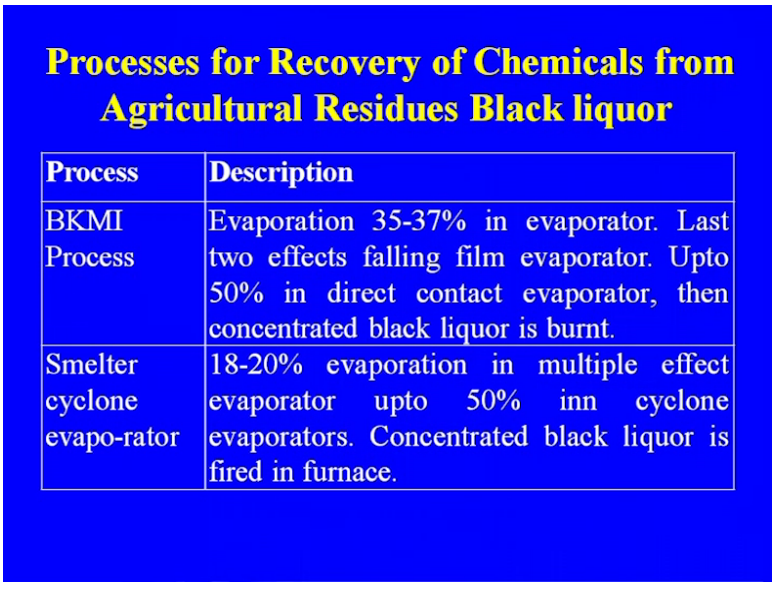

BKMI process, where 35 to 37 percent in the evaporator last two effects falling film, because as I told you the earlier also, even the wood base or the bamboo base or the large integrated film. They have also gone for the additional effect along with the 5 to 6 effect falling film evaporator and because of that, they are able to concentrate to higher concentration, then what it was possible to achieve in the conventional processes. So, this is one of the smelter cyclonic evaporator 18 to 20 percent evaporation of the multiple effect evaporator and 50 percent in the cyclone evaporator.

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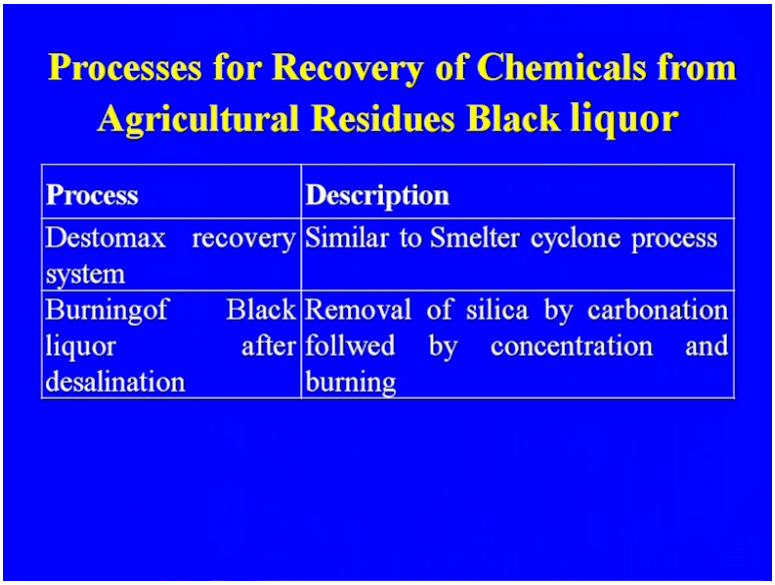

Destomax recovery section, similar to this smelter cyclone burning of the black liquor after desalination; one of this, not salination, but desilication. Actually, the you see the in case of the black liquor, the gasification, which we discussed during the… Now, they have suggested like gasification the black liquor after the removal of the silica that can be also done just to go for the recovery of the. These are the some of the reference that you can go the…

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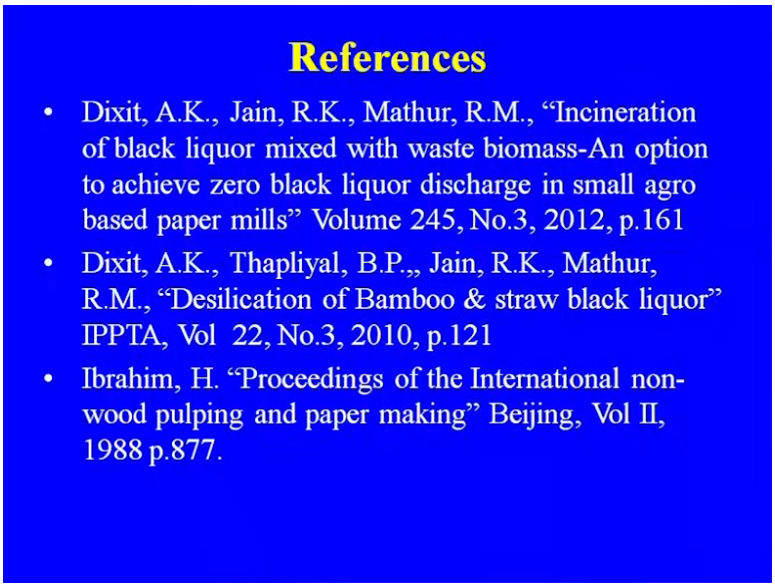

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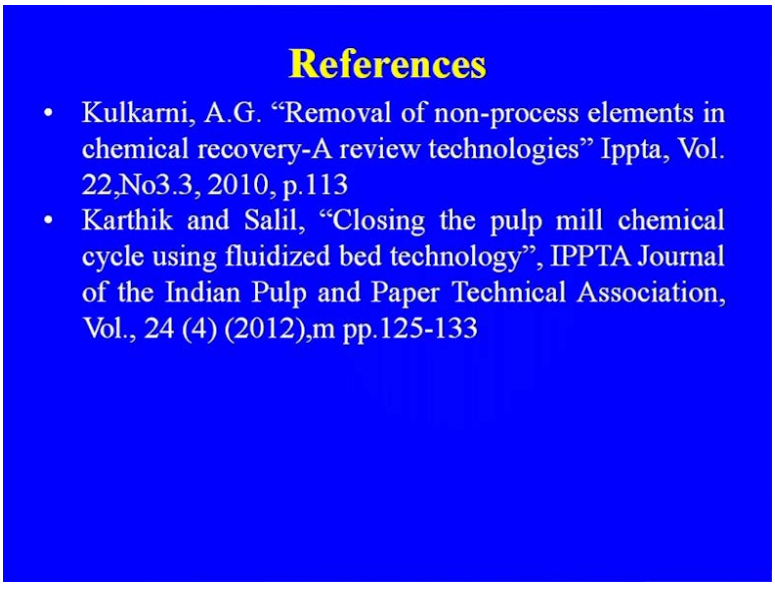

So, we discuss about the recovery of the chemicals from the and so the recovery of the chemicals, because you see the, now the most of the mills which even where having the less recovery means 85 percent recovery. They have just gone for the new recovery furnaces, so that the efficiency that has increased and recovery furnace, how, so that was the one in the development of the recovery furnace. Another development in case of the recovery, section of the recovery of the chemical that has been the introduction of the following film operator, which has been implemented in all the paper mills just to improve the…

And another thing that we can do in case of the, just to have the better efficiency of the recovery of the chemical, that is the better washing to add one more stage so that the we are getting the black liquor which is normally used to be 10 to 12 percent. We can increase to 15 to 16 percent. So, that will help in the again overall economy. Similarly, in case of the agriculture residue, which was considered that is a non-economical, but sometimes you will have to compromise with the cost, with the environment also.

So, just to reduce the environmental load, definitely we will have to go for the black liquor or the recovery of the chemicals. And so that is the reason why now, you see already in the bagasse base means they are having the recovery furnace, they are doing the recovery of the chemicals. Only the problem has been in case of the why it is, why it is, wherever, wherever you are using. So, already some of the mills, many of the mills which have been large mill, larger capacity mills based on the agro-based in India they have gone for the recovery furnace and they are successful.

Although the, any new development is not free of the problem, but they have added and they are recovering the chemicals, but efficiency definitely in case of the agro base recovery furnace in comparison to the your other integrated army based on the hardwood bamboo and the softwood, that is lower. That is the one of the major constituent, and just we will have to think of the improving the efficiency as we have been achieved 95 percent in case of the conventional recovery furnace used for the black liquor base on the hardwood and softwood and the bamboo. So, these are the some of the thing that has to be, but in future all the agro-based paper mill definitely they will, they are now you can say that they are based on the recovery of the chemicals, because now environmental standards are becoming so and so constant that the stringent, that we will have to go for recovery of the…