Physico-Chemical Processes for Wastewater Treatment
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Lecture 58
Wastewater Treatment in Petroleum Refining Industry

Good day everyone and welcome to these lectures on Physico-Chemical Processes for Wastewater Treatment. So, in the last few lectures, we are studying the case studies with respect to wastewater generation and their treatment in different types of industries. So, already we have studied the treatment strategies which are there in the sugar industry distilleries as well as in the fertilizer industry. So, today we will be discussing the wastewater generation and treatment strategies with respect to petroleum refining industry.

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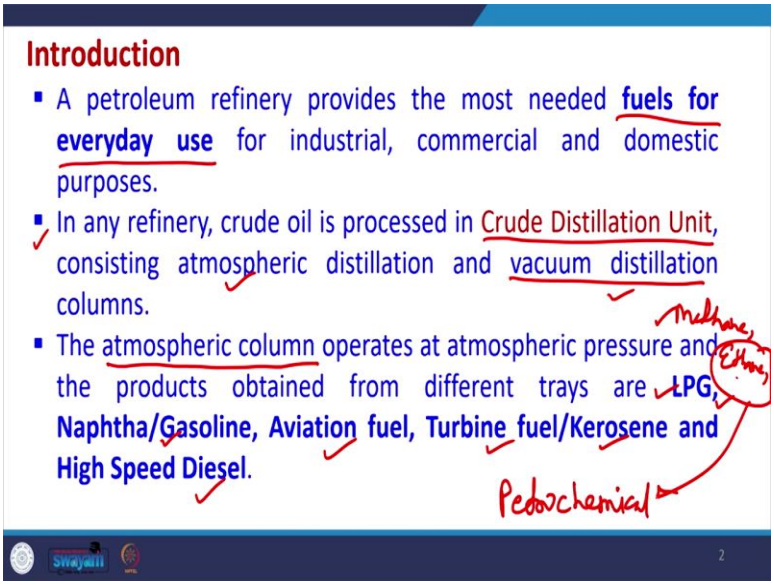

Now, any country requires lot of fuels for everyday use, and these fuels are used in industrial application, a lot of commercial application including the railways, buses, etc, and also a lot of for domestic purposes as well. Now, without the fuel, any economic and not survive, so, the backbone of any economy nowadays is the crude oil and its various products, which are obtained after its treatment or its conversion or processing in the refineries.

So, refineries provide the different types of fuels for everyday use, also, they provide lot of chemicals, which are further used in the petrochemical plant, and that petrochemical complexes

convert those chemicals into lot of products with which we use in our daily uses. So, all these include like clothes, a lot of plastics so, all those materials are obtained from crude oil only. So, after crude oil, the petroleum refinery converts these things into various types of products. So, the in short, the petroleum refinery is the basic backbone on which whole of the country survives or grows and without that the growth of any country is not possible nowadays.

So, now in any refinery, the crude oil is processed in the crude distillation unit consisting of 2 distillation columns basically, one is called as mass varied distillation column and another is called vacuum distillation column. So, in these distillation columns, the crude is processed and we get lot of products. So, the first column is called the atmospheric column, which operates at atmospheric pressure and the products which are obtained include from if we considered from the top.

So, they will include methane and then lot of ethane, ethene depending upon various types of products so, ethane, LPG, Naphtha or Gasoline, Aviation fuels, Turbine fuels or Kerosene and High Speed Diesel. So, these are the basic products which are obtained from the atmospheric column itself. Now, we can see the methane natural gas, so, all these are backbone.

Now, ethane, propane and butane so, propane and butane will go into the LPG but ethane and ethene and other things are propane propylene. So, these actually form the backbone of petrochemical industries. So, that is why many of the companies have petroleum complexes along with the refining unit very close by so that they can convert these chemicals into petrochemicals which are further used for getting lot of products.

In addition, this LPG is used in the domestic fuel all of us use, gasoline is used for all running all the petrol related vehicles, then aviation fuel is the backbone of the aviation industry and it is being used for use as a fuel in the airplanes etc then we have kerosene, which is an aviation fuel are very similar.

So, then we have high speed diesel etc which is used for heavy vehicles and it is used as a fuel in these heavy vehicles. So, we can understand everything obtained from this atmospheric distillation column they are they are the major fuels which are used in running any other country.

And so, that is why any country or including India have lot of dough, we do not have the crude oil is still we have a large number of petroleum refineries and that are very, very essential.

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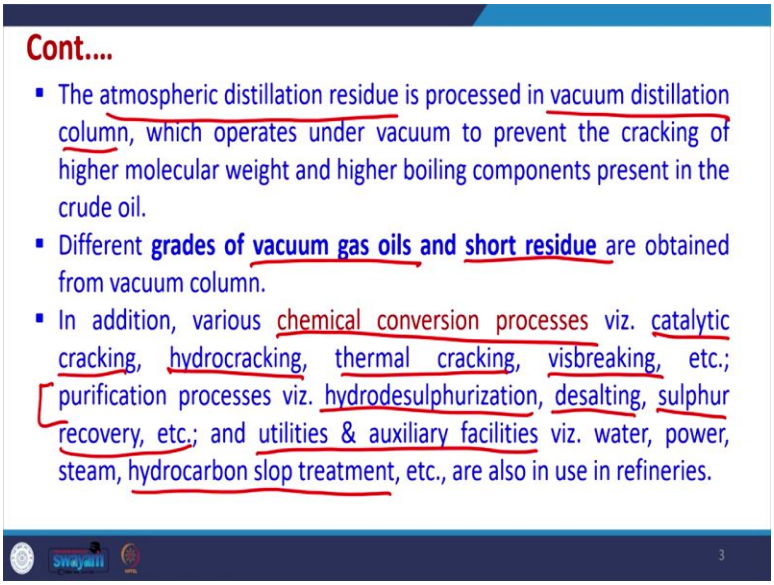

Now, the atmospheric distillation residue which is left it is further processed in the vacuum distillation column and it operates under vacuum certainly to prevent the cracking of higher molecular weight and higher boiling components present in the crude oil residue after the atmospheric distillation.

So, different grades of vacuum gases and short residues are obtained from the vacuum column. So, after vacuum column also we get lot of products including like bitumen, which is used for road making, lot of varnishes paints and their backbone chemicals are obtained after these units. So, all these both atmospheric distillation unit and vacuum distillation unit are very very important.

In addition, after getting lot of these products, lot of chemical conversion processes are used in the petroleum refinery for converting one chemical into another also for separating out lot of undesirable things from these products and these may include like sulphur, so sulphur has to be separated. So, we know BS6 BS5 norms. So, all those things have to be performed beforehand in the refinery itself.

So, we use a lot of chemical conversion processes, which are like Chem catalytic cracking, hydrocracking, thermal cracking, visbreaking etc. In addition, we use a lot of purification process like hydrodesulphurization for removal of sulphur from petrol, (dv), diesel, ATF and various types of gases then deserting unit sulphur after removing the sulphur the sulphur recovery has to be done, because we cannot leave it into the atmosphere.

Similarly, we have lot of utilities and auxiliary facilities also in any refinery because lot of water, power, steam and other types of utilities are required. And also, we have hydrocarbon slop treatment facilities, wastewater treatment facilities so, everything is present in the refinery. So, refineries are highly complex refineries along with petrochemical industry if it is close by they are more complex.

And now the now the concepts here are coming where the petroleum refinery, petrochemical complex and in fact fertilizer industry all need to be very close by because naphtha can be used in the fertilizer industry. So, there are lot of things which can be introduced. So, that is why these complexes will become huge in nature very soon.

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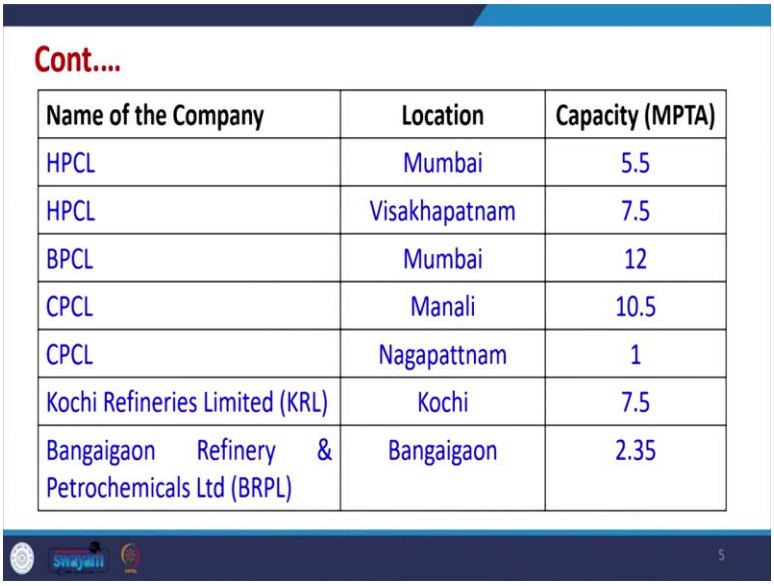

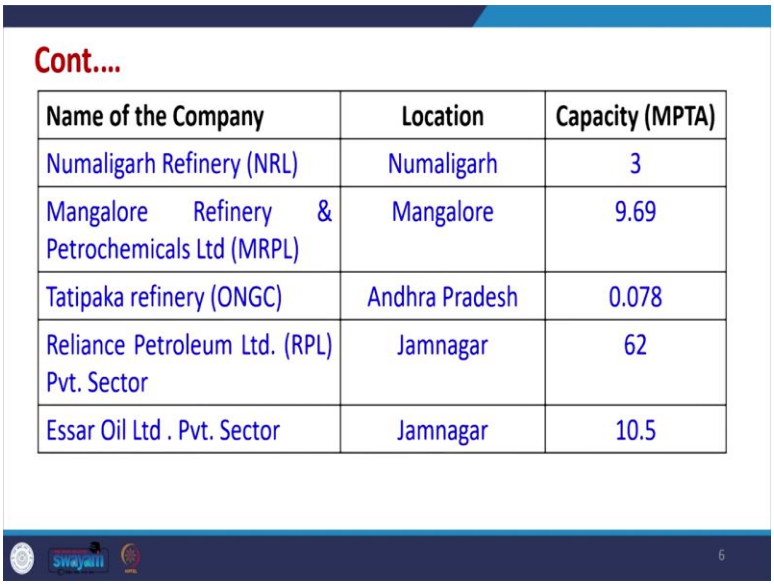

Now, a number of oil refineries in India are present as told earlier. So, IOCL, HPCL, BPCL, CPCL, Kochi Refineries Limited, BRPL which is like Bongaigaon Refinery& Petrochemicals Limited, then Numaligarh Refinery so and then Mangalore Refinery& Petrochemicals Limited, ONGC, Reliance Petrochemical so, it is the biggest one of the, then Essar Oil, Bharat Oman Refinery. So, number of refineries are situated in India and all of them are processing crude oils, which are actually obtained from different parts of the globe.

So, as such their characteristics are entirely different and they may contain different amount of metals, inorganics, undesirable impurities in different concentrations. So, thus the streams which are generated in these refineries also have lot of difference in characteristics and the amount of water which is generated or amount of air pollution which is generated is also different. Now, coming into wastewater management in different refineries.

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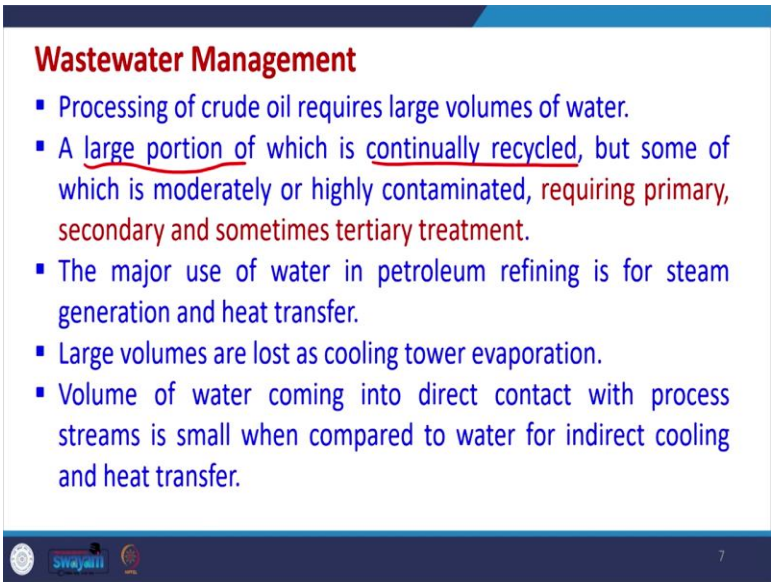

Now, the processing of crude oil requires a large volume of water for further uses in different section, these large portion of water is continuously recycled, but some of which is moderately or it may become highly contaminated with undesirable pollutants and thus it will require primary secondary or tertiary treatment, the major use of water in the petroleum refineries for stream generation and for heat transfer, the large volumes of such water or larged as cooling tower evaporation section. Now, volume of water coming into direct contact with processes steams is generally small when compared to water which is being used for indirect cooling or for heat transfer. So, actual direct contact is very very less in the refinery, but still large quantity of wastewater may get generated.

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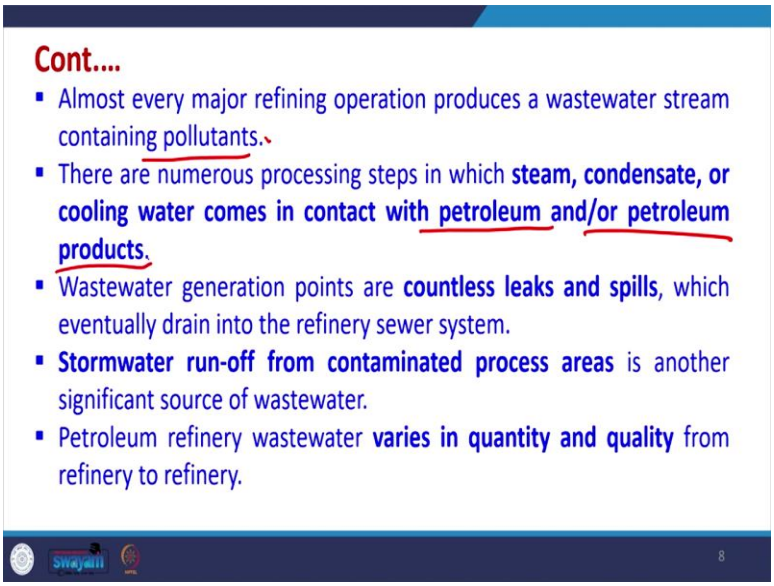

Almost every major refining operation produces a wastewater stream containing some undesirable pollutants. And this is because that there are numerous processing steps in the petroleum refinery where steam condensate or cooling water will come in contact with petroleum or petroleum products. So, it is possible that it may come in context so, these will go into the water. Now, wastewater generation points are enormous a large number of leaks and spills are possible and from which these contexts are there and eventually this water will rain into the refinery sewer system or refinery water collection system wastewater collection system.

Also, the stormwater runoff from contaminated process areas will contain significant source of wastewater because these petroleum and petroleum products will get mixed up with this a storm water. So, that is possible though the petroleum refinery wastewater will vary in quantity as well as quality from refinery to refinery and because these refineries are highly complex depending upon that what type of product what type of crude oil they are processing, what type of product they are desiring. So, they may have different intermediate processes. So, that varies from refinery to refinery so that is why the petroleum refining the wastewater also varies in quantity and quality.

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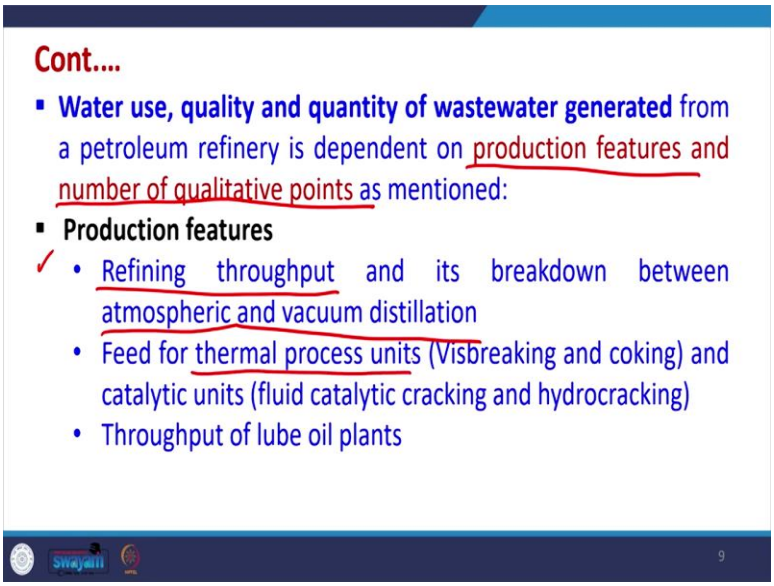

Now, the water use quality and quantity of wastewater generated from a petroleum refinery is dependent upon the production features of that particular refinery and the number of qualitative points which are discussed here. So, a number of qualitative points may be there which upon which the quality and quantity will be dependent the production features may include Refining throughput that what is the capacity of that refinery and its breakdown between that how much is being processed in the atmospheric and vacuum distillation unit also the how much is being processed in the thermal process units these includes visbreaking and coking and also in the catalytic units like FCC and hydrocracking. So, and also the throughput of the lube oil plants which is there in the refinery. So, these production features are very important.

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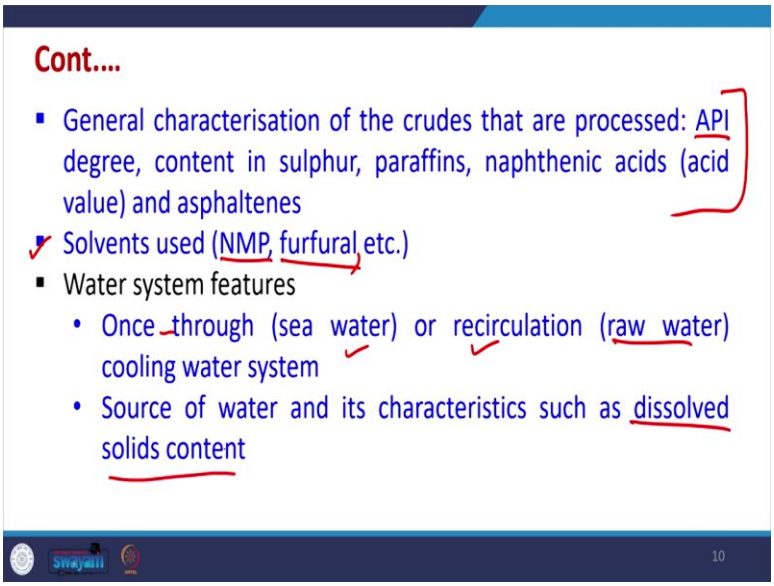

General characteristics of the crudes that are being processed like what is its API gravity, what is the sulphur content paraffinic and naphthanic acid content in the water (and all) in the crude and also what is the asphaltene content of the crude. So, all these the crude oil characteristics, they also differentiate. In the plant itself we may be there in the refinery, a lot of solvents are used. So, what type of solvent whether it is NMP, furfural any other solvent which is being used are depending upon the quantity and quality of a type of solvent, the wastewater characteristics also may vary.

Now, the water system features may include that what type of water it is being used in the refinery whether it is once through like seawater or raw water it is being re-circulated through cooling water system. So, depending upon this the water quality or wastewater quality may vary. The source of water needs characteristics such as dissolved solid content is another important aspect with respect to wastewater generation and its characteristic.

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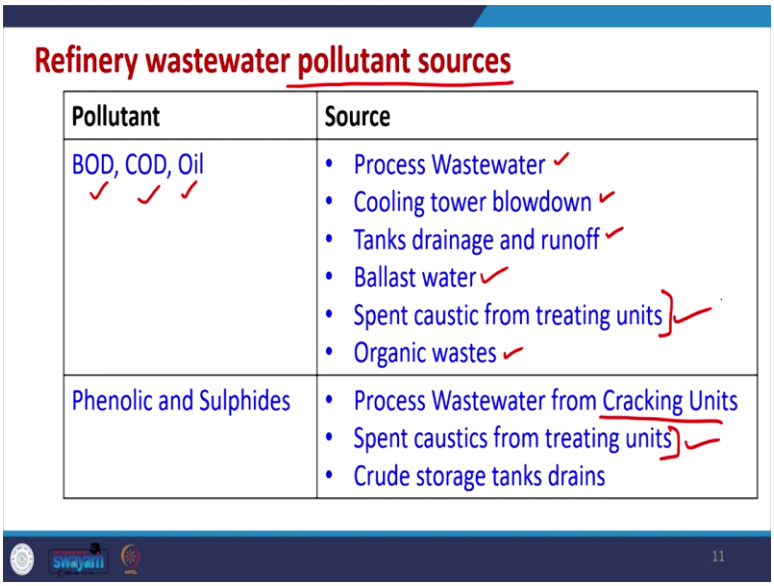

Now, there are different types of different in the wastewater which is generated in the refinery, the pollutants, which are coming their sources may be different. So, this is being discussed here in these slides. So, from what are the sources of BOD, COD and Oil. So, this is very important, water quality parameter. So, from where it is coming, so, the chances are that it may come from the process wastewater, cooling tower blow-down, they may be drainage and runoff from the tanks section, then the ballast water maybe there, spent caustic from the different treating units that is one problematic area, then lot of organic waste may go into the water. So, that will constitute BOD, COD and Oil.

Now, a lot of phenolics and sulphides are present in the petroleum refinery wastewater and these resources are from process wastewater from the cracking unit. So, they are phenolic and sulphides are present, also spent caustic from the treating unit this is very problematic section of the petroleum refinery. So, where a lot of different types of pollutants are getting generated, then the crude storage tank drain from their also phenolics and sulphides may come.

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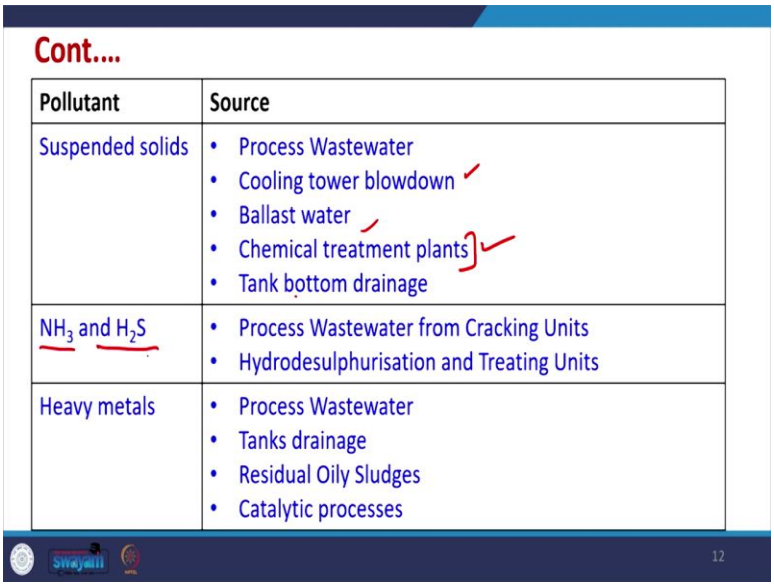

Similarly, suspended solid from process wastewater, cooling, tower blow-down, ballast water chemical treatment plant so, from there suspended solids then the tank bottom drainage if it is there, ammonia and H2S because this is possible ammonia and H2S so, process wastewater from cracking unit and also from hydrodesulphurization units this ammonia and H2S may come, heavy metals may come from Process Wastewater, Tanks Drainage, Residual Oily Sludges, Catalytic Processes. So, all these all these water quality parameters or pollutants may be present in the refinery wastewater.

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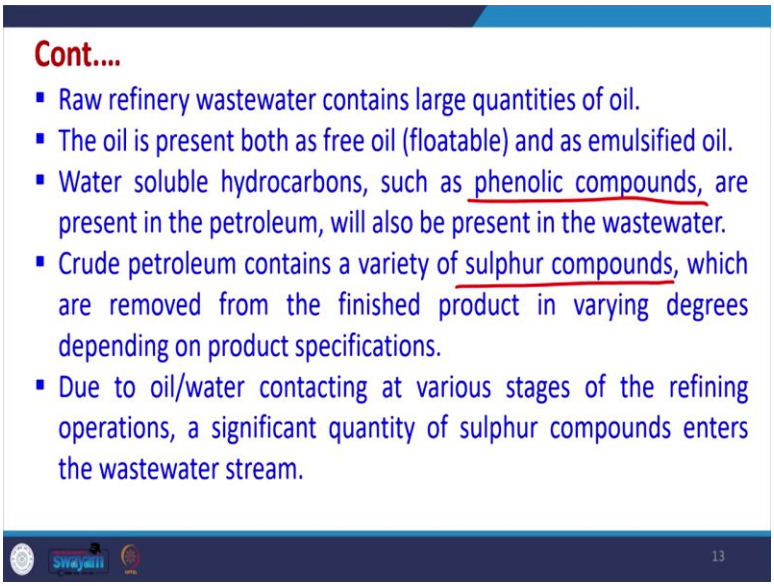

So, the raw refinery wastewater contains a large quantity of oil, the oil is present both as free oil which is floatable or as as emulsified, in comparison to fertilizer industry the amount of emulsified oil is much higher as compared to in the fertilizer industry in the petroleum refinery. Now, the water-soluble hydrocarbons such as phenolic compounds are present in the petroleum and so, thus they are present in the wastewater also. The crude oil petroleum contains a large variety of sulphur compounds. So, these may be present. So, these may be a simple thiophenic compounds or aromatic thiophenic compounds which are difficult to remove.

So, and they have to be removed from the finished product in varying degrees depending upon the product specification, nowadays the specifications with respect to petrol diesel are very similar so, that means, these compounds have to be removed from petroleum fuels such as petrol or diesel before using them in the vehicles and because of removal, so some quantity of that may go into the water also due to oil water contacting at various stages of the refinery operations a significant quantity of sulphur compound may enter into the wastewater streams, now this is also possible.

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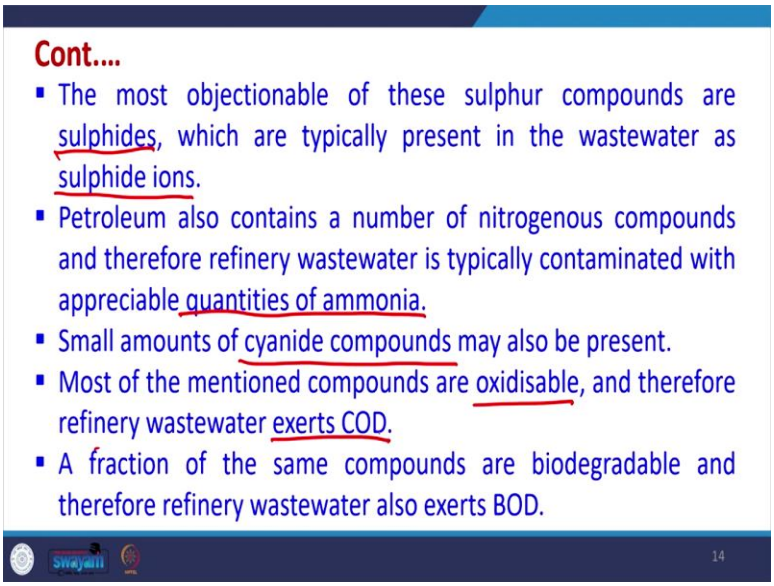

Now, the most objectionable are the sulphur compounds are like sulphides which are typically present in the wastewater as sulfide ion and they have to be removed, petroleum also contains a lot of nitrogenous compounds. So, therefore refinery wastewater is typically contaminated with appreciable or large quantity of ammonia also and that has to be removed, which is similar to that in the fertilizer industry.

Similarly, a small amount of cyanide compounds may be also be present and which is totally not desirable. Now, that these type of nitrile or cyanide compounds, are acetonitrile, acrylonitrile, all of them may be present in the water and these presence of these compounds make the water highly toxic. So, they must be removed from the refinery wastewater. So, most of the mentioned compounds which have been mentioned now, they are oxidizable and therefore, refinery the wastewater exerts lot of COD. So, this COD has to be decreased within the specified norms. The fraction of the same compounds are biodegradable and therefore, refinery wastewater exerts BOD also, but large amount of COD.

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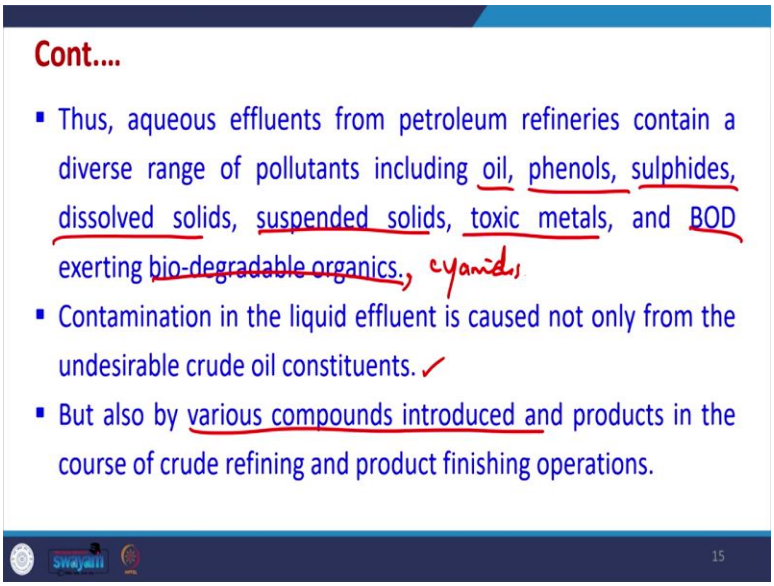

The aqueous effluent from petroleum refineries contain a diverse range of pollutants. These may include oil, phenols, sulphides, dissolved solids, suspended solids, a lot of toxic metals be BOD exerting biodegradable organics and also cyanides. So, there are different possibilities which are present. So, cyanides may also be present. Contamination in the liquid effluent is caused not only from the undesirable crude constituents, but also from various other compounds introduced and the products which are being made. So, from there also lot of compounds are coming into the wastewater.

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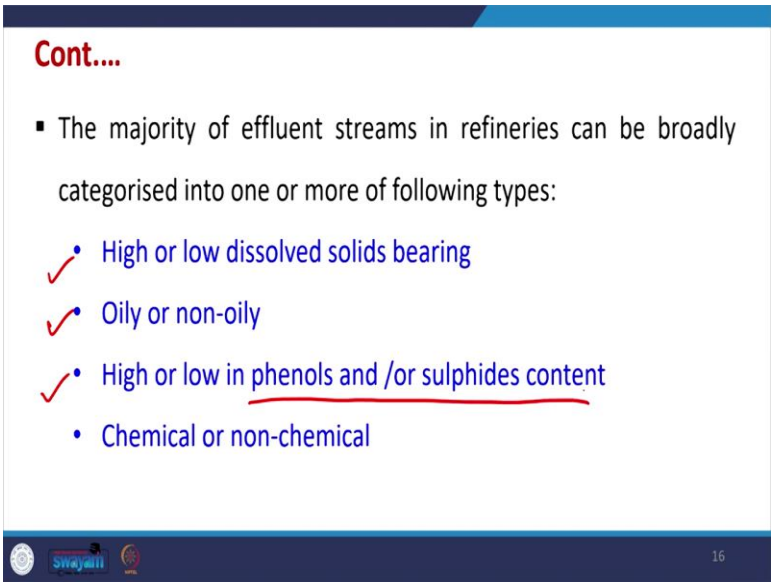

So, we need to treat such wastewater. So, the majority of effluent streams in refineries can be categorized into 4 of these types like high or low dissolved solids containing effluent then Oily or non-oily effluents, high or low in phenols or sulphide content, then chemical and non chemical type of compounds may also be present in the water.

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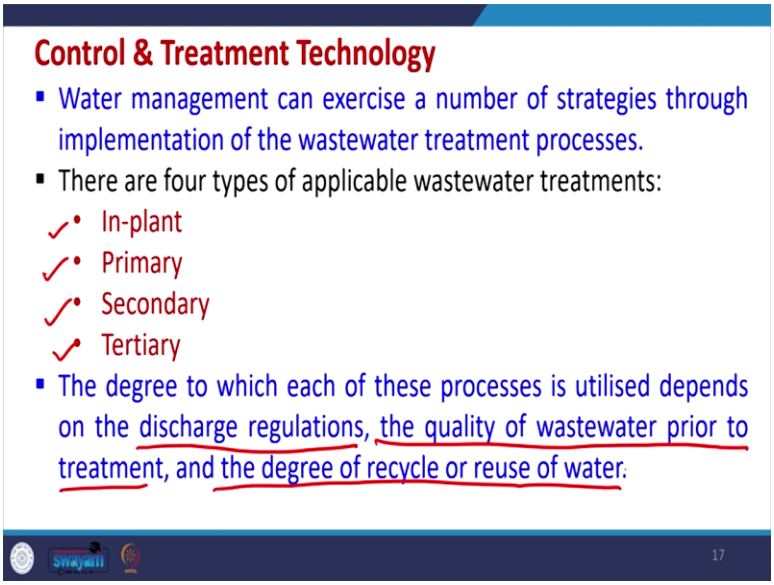

So, what are the different control and treatment strategies which have been adopted in the refineries for treatment of refinery wastewater depending upon its characteristics. So, this is

there. So, the water management exercise a number of strategies through the implementation of wastewater treatment in the refineries.

So, this may be included like in-plant treatment some within the plant then after collection, we may primary treatment, secondary treatment, tertiary treatment and the degree to which each of these processes are being used depends upon the discharge regulations already restrict the quantity of wastewater prior to treatment which is getting generated and the degree of recyclability or reuse of the water that we are doing in the refinery itself.

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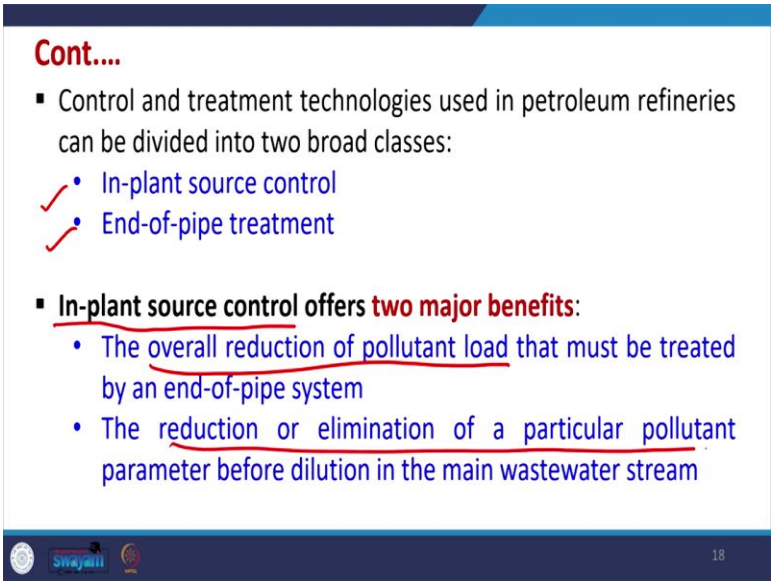

Now, there are 2 strategies one is called in-plant source control and another is end of pipe treatment. So, in-plant source control if we are able to do it has offers 2 major benefits, the overall reduction of pollutant load that must be treated by the end of pipe system will get reduced. So, if you are able to do the in-plant source control, actually the amount of water that has to be treated further will be reduced. So, overall reduction in the pollutant load happens and this is highly beneficial for the effluent treatment plant etc. Also, if we are performing this the reduction or elimination of a particular pollutant parameter can be done before dilution in the main wastewater stream.

So, if any high quantity of any pollutant is coming from only a single source, so, if we can perform treatment there itself that means, we can remove that pollutant. Now, if we are not doing

this, that pollutant will get mixed with other types of other large quantity of wastewater from different section. So, it will be very difficult to remove such pollutant. So, this is possible via using the in-plant source control strategy. So, this is there.

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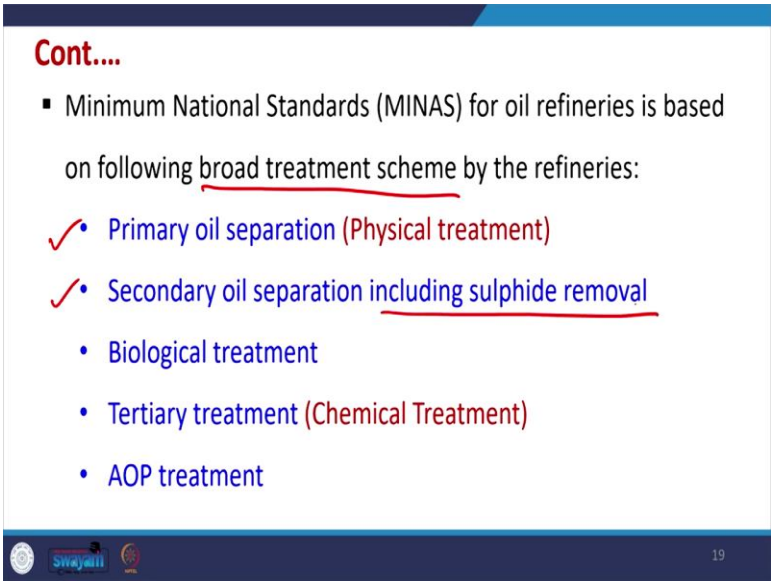

Now, there are certain MINAS standards for oil refineries have been given as for other industries and they are based upon following broad treatment schemes by the refineries. So, we may have primary oil separation method, then secondary oil separation including sulfide removal, then we have biological treatment, tertiary treatment and then advanced oxidation processes may also be applied for that treatment. So, any of all these options may be used for the treatment depending upon the amount of wastewater being generated and the characteristics of the wastewater being generated.

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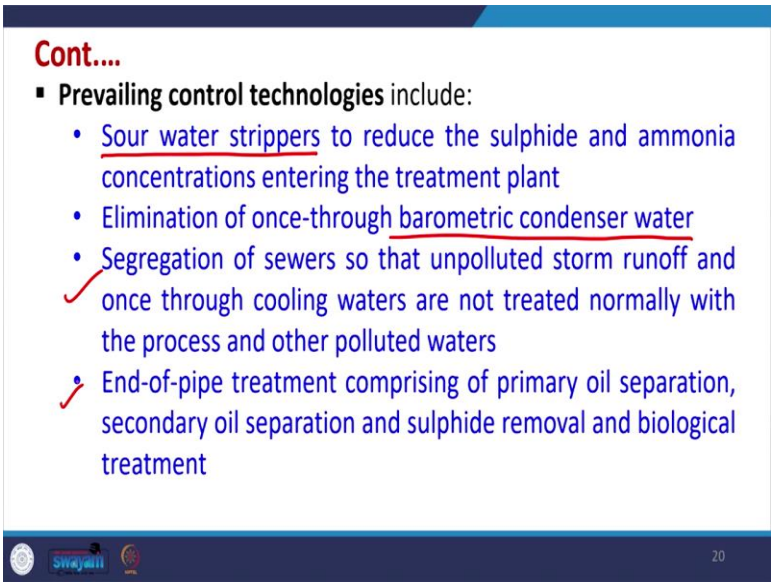

Now, the control strategies, what are the different prevailing control strategies? So, the sour water stripper is used to reduce the sulfide and ammonia concentrations entering the treatment plant. So, this is there. So, if it is done so, it is elimination of once-through barometric condenser water. So, this is done this eliminates this now segregation of severs, so that the unpolluted storm runoff and once through cooling waters are not treated normally with the process and other polluted.

So, we should have a segregation of different water streams within the treatment strategy so that we can control the amount of wastewater generated and the characteristics of the wastewater being generated. The end of treatment may comprise a primary oil separation, secondary oil separation already we have discussed we will discuss them more in detail.

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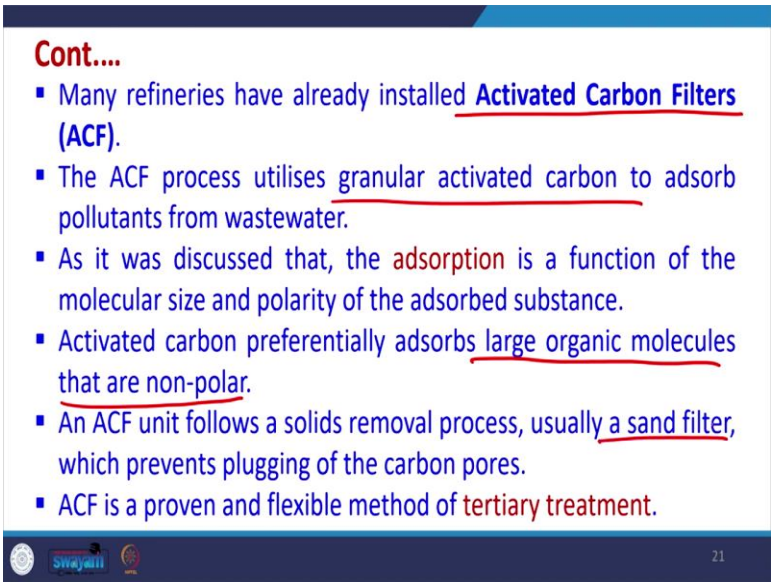

Now, many refineries have already installed this activated carbon filters, this is called ACF. So, ACF process uses lot of granular activated carbon to absorb the pollutant from the wastewater. And, the adsorption is a function of molecular size and polarity of the adsorbed substance. So, the activated carbon with adsorbed large organic molecules that are non-polar. So, ACF unit is followed by a follows a solid remover process, usually a sand filter. So, we will be discussing this in next few slides, which prevents plugging up the carbon so (is car) sand filter may be used before ACF unit and ACF has been proven a flexible method for tertiary treatment.

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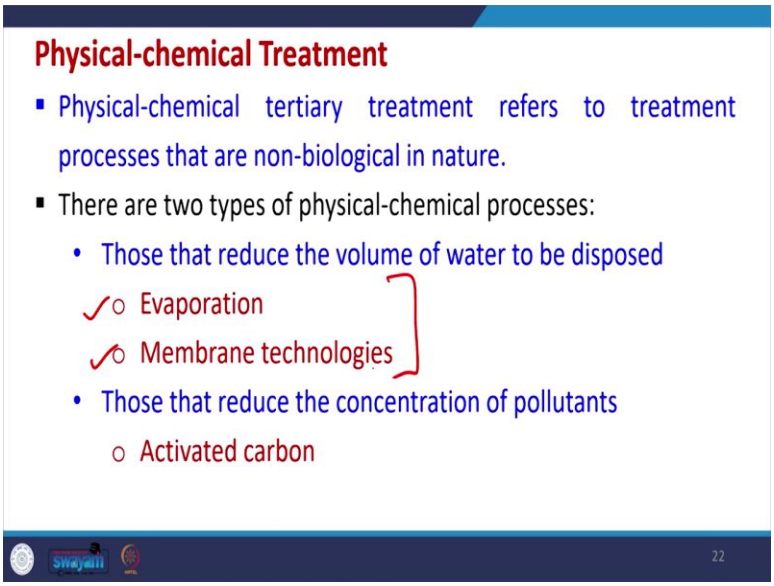

Now, what are the different physico-chemical treatment in the refineries. So, there are 2 types of physic-chemical processes and those that reduce the volume of water to be disposed. So, these may be evaporation technologies and membrane because the water which is obtained the treated water which is obtained after this will be much lesser as compared to the water which goes into this system. So, these are but these are energy intensive units. Then there is another type of physico-chemical process that reduces the concentration of pollutants, but the amount of water generated is virtually same. So, this is activated carbon filters etc. So, that is there.

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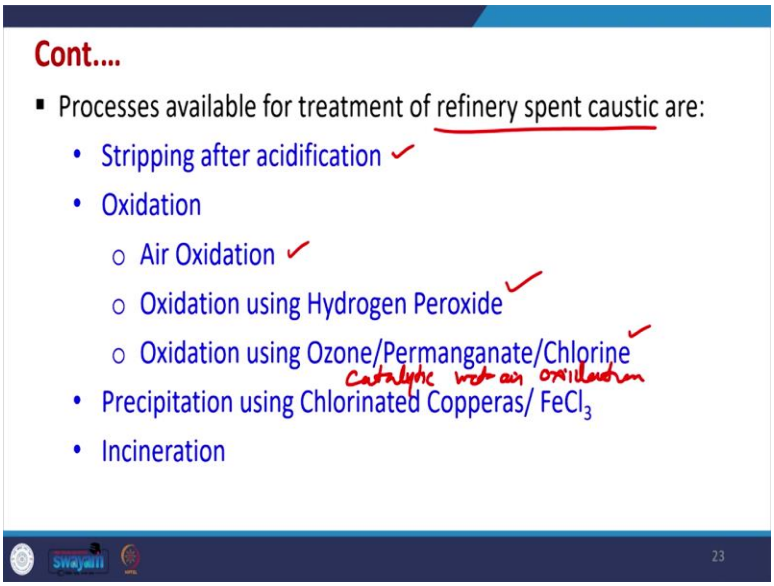

Now, the processes available for refinery spent caustic treatment because this is one of the challenging extremes within the refinery. So, this is stripping. So, we can go for acidification followed by stripping then oxidation using any of this technique or any other techniques. So, this includes air oxidation, oxidation with hydrogen peroxide or oxidation with ozone permanganate chlorine or catalytic wet air oxidation has also been is being tested or is being some places so, that is called catalytic wet air oxidation.

So, this technique is also being used in many places. Precipitation using Chlorinated Copperas or FeCl3 that is possible and then Incineration. So, this is the strategy which is adopted for spent caustic treatment, which is there in the... Now, some of the typical refinery wastewater treatment strategies are discussed here.

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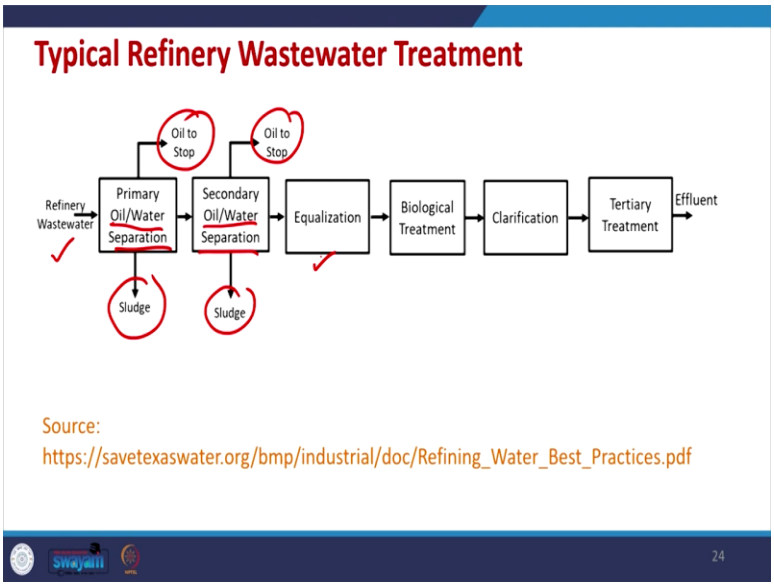

So, here we can see that refinery wastewater is coming. So, we may have primary oil water separation unit, which will remove the oil from the water then we may have secondary oil water separation unit against large and oil to oil will be separated out so, oil will be going to the top after that we have equalization basin followed by biological treatment clarification tertiary treatment and AOPs etc. So, this is there.

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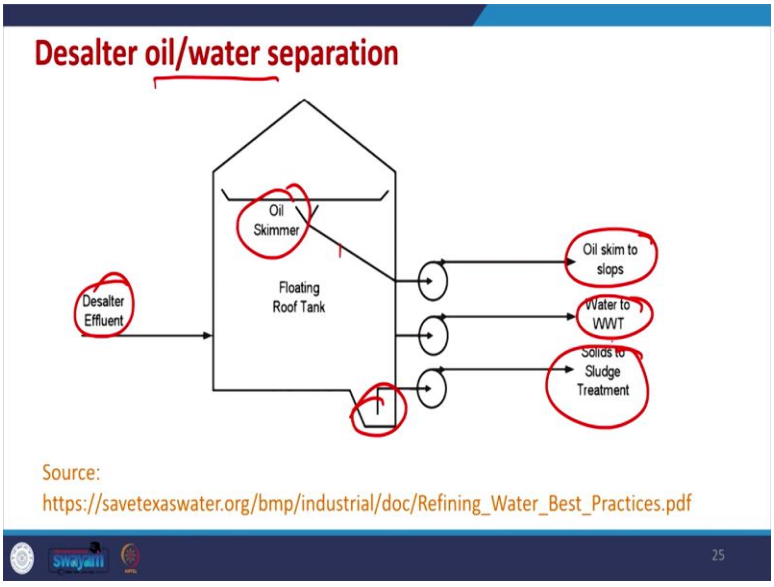

Now, some of the basic operations are discussed here. So, we may have a desalter effluent. So, before going into the oil water separation unit, so, this is there. So, we have oil Skimmer is at the top and (the) this is a floating roof which is there so, which is actually helps in separating oil from the water. So, oil skims, they go to the slops, then the water which is treated it goes for further treatment and the sludge which is getting generated here that goes for sludge treatment further so, this is the desalter oil water separation unit.

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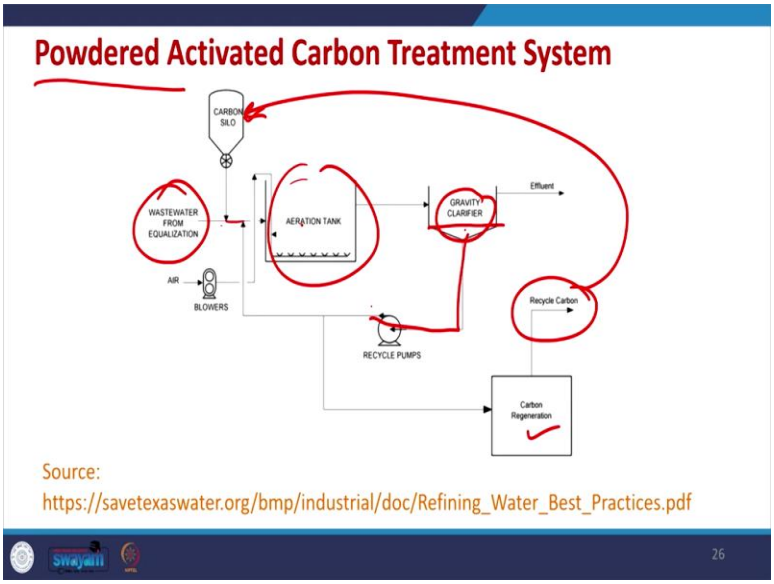

Then, we can have a powdered activated carbon treatment system within the refinery premises. So, wastewater after the equalization base in here and carbon from, so we have this is powdered activated carbon we may have a granular activated carbon bed we may have powdered activated carbon bed so, we have powdered activated carbon bed is used and in this particular unit, so we have this is getting mixed here.

Now, along with that air is also being blown and here the separation of pollutant or absorption of pollutant happens along with some oxidation also. And after that we have a gravity clarifier from which this powdered activated carbon goes and it goes further carbon regeneration depending upon the requirement and this recycled carbon is further used here. So, this is possible and depending upon the requirement it will go back into the aeration unit. So, this is called powdered activated carbon treatment system.

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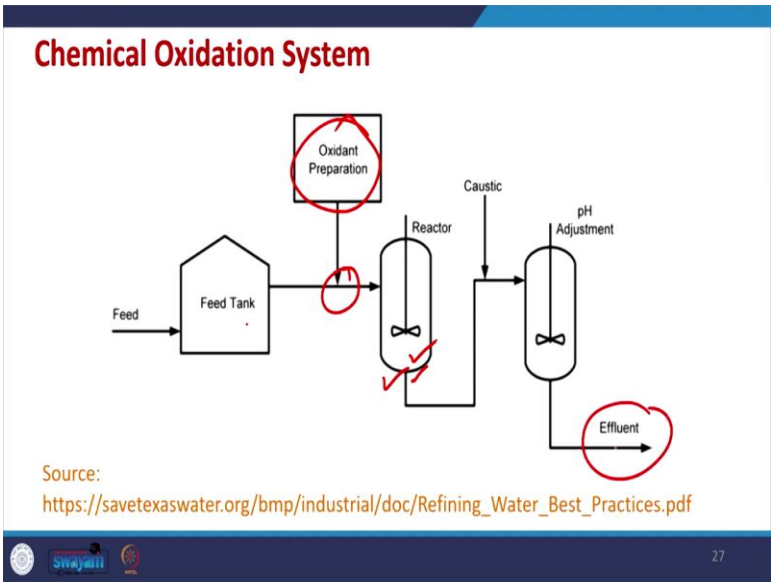

Now, then then there can be a chemical oxidation system as well. So, feed from the feed tank it is going into this reactor. So, oxidant which is already prepared that may be added to this feed and hear the treatment oxidation happens in the reactor the temperature pressure etc will depend and also if we are using catalysts or not. So, this will also be dependent upon the requirement. Now, after that some pH adjustment is done using the caustic and find the effluent maybe treated further or maybe discharged as per the things.

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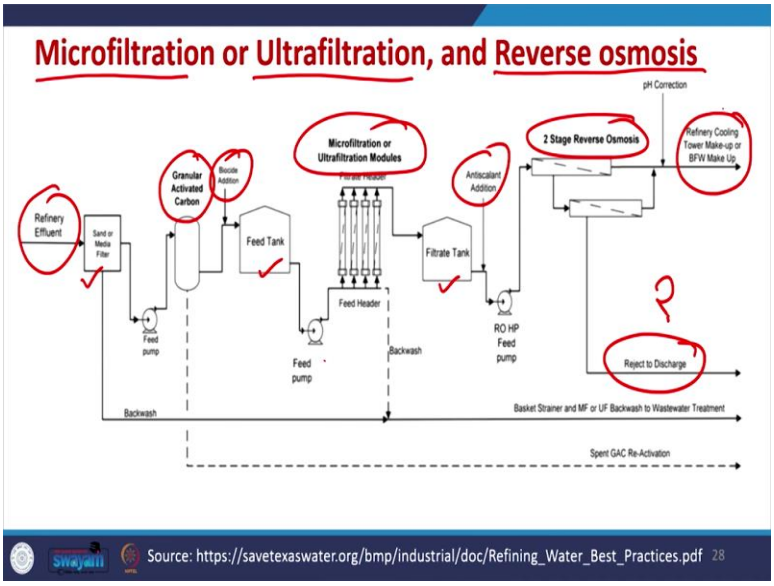

Now, effluent can also be treated in the micro filtration or ultra filtration and reverse osmosis unit in the petroleum refinery. So, the refinery effluent is first pass through sand or media filter. So, this is there and after that it is passed through the granular activated carbon. So, remember this is different than the powder activated carbon.

So, here many of the pollutants will get adsorbed after that it goes into the feed tank and from the feed tank it goes into the microfiltration or ultrafiltration modules so, this will depend upon the requirement how many modules are there, whether it is microfiltration or ultrafiltration. After that the filtrate is coming and some additional chemicals may be used depending upon the requirement after that it goes into the 2 stage or 3 stage or single-stage reverse osmosis unit and from there we get reject which is to be discharged or managed. This is the treatment of reject is one of the key areas and challenging area in the refinery wastewater treatment.

After that the pH correction is done and the refinery, this water which is treated water it goes to the cooling tower makeup or boiling section makeup. So, this will depending upon the characteristics it may go to any place. So, this is another treatment strategy which can be adopted in the petroleum refinery.

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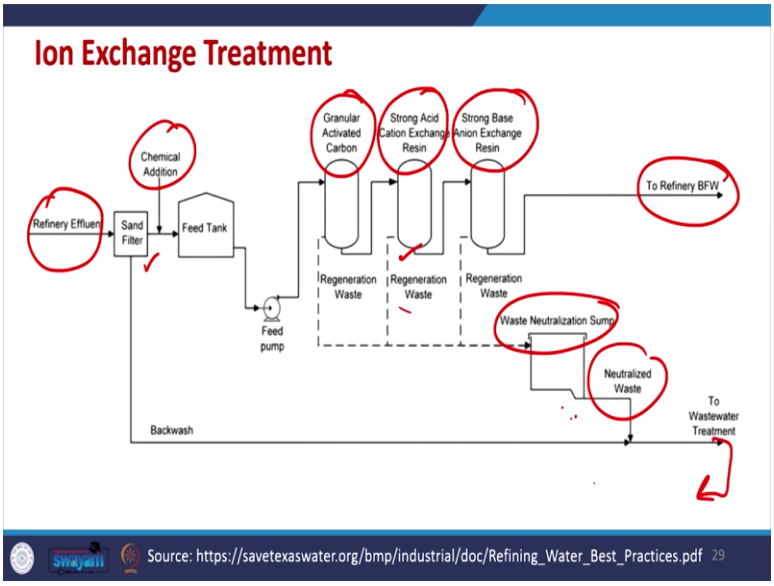

Then, we may have an Ion Exchange Treatment unit also. So, here the refinery effluent is coming, it goes into the sand filter as earlier after that some chemical addition is been done and it

goes into the granular activated carbon followed by cation strong acid cation exchange resin this column is there and then after that base anion exchange resin.

So, it made there and after that it may be reused in the refinery. And sometimes we may have regeneration waste, because a number of such beds will be there it is not only single has been shown. So, each of the bed maybe three forth depending upon the requirement, the amount of water to be treated. So, how many are in operation during a treatment because for all these types of beds, their regeneration is also important.

So, we always have a multiple beds in parallel, where the operation may go on. So, after that further neutralize waste, because the waste from here where regenerated waste or during neutralization or regeneration waste which is coming it will go into this waste neutralization sump and after neutralization it, it will be recycled back and treated again so, this is there.

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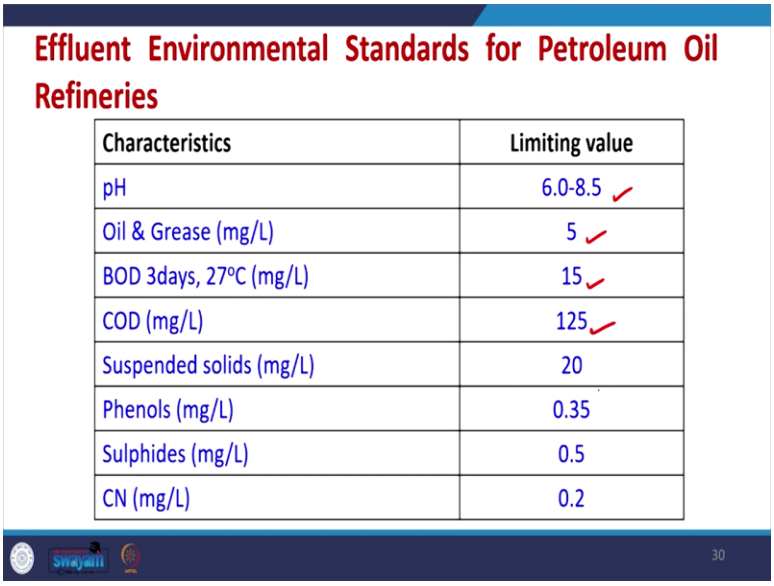

After treatment, certain norms have been set for the petroleum oil refineries and these are continuously changing. So, the norms are like here. So, like pH has to be between 6 to 8.5, Oil and Grease 5 milligram per liter or less, BOD 3 days 15 milligram per liter or less COD 125. So, these are changing these are typical values only just for information.

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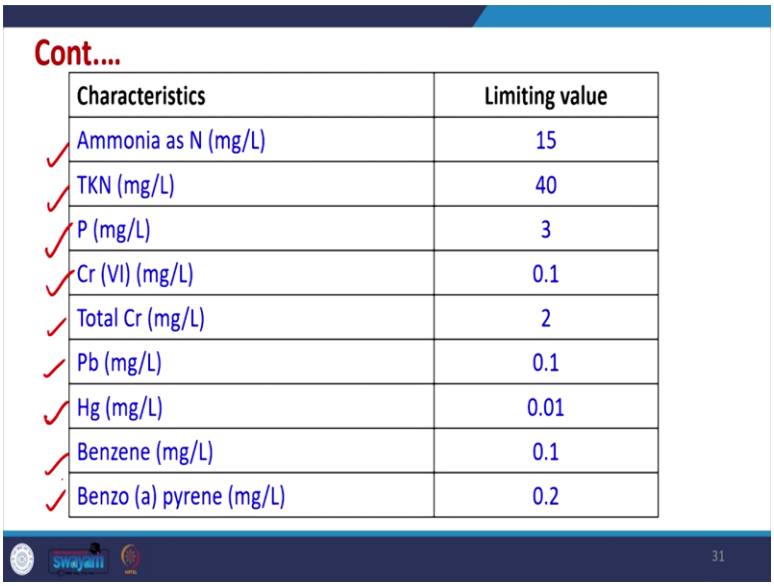

So, all after treatment of wastewater has to comply these environmental standards norm which are listed here including ammonia, TKN, P, chromium 6, Total chromium, lead, Mercury, Benzene, Benzo Pyrene.

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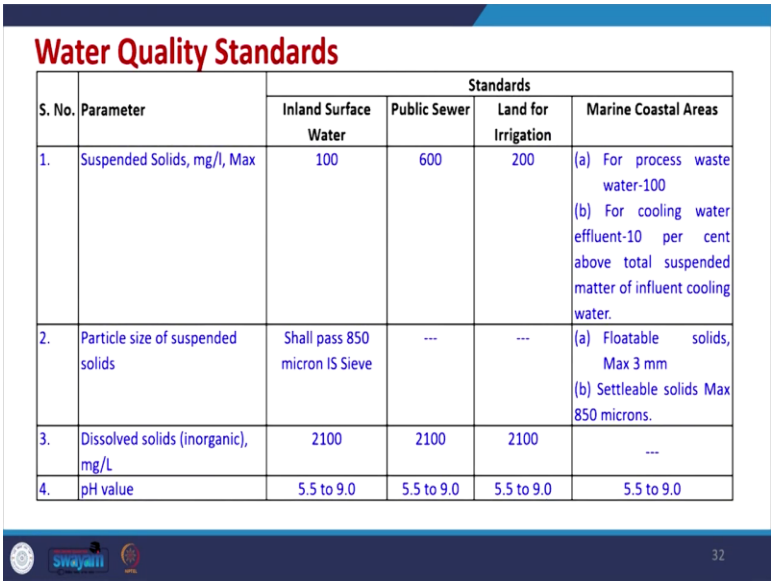

There are a large number of parameters have to be checked and they have to be followed after that treatment.

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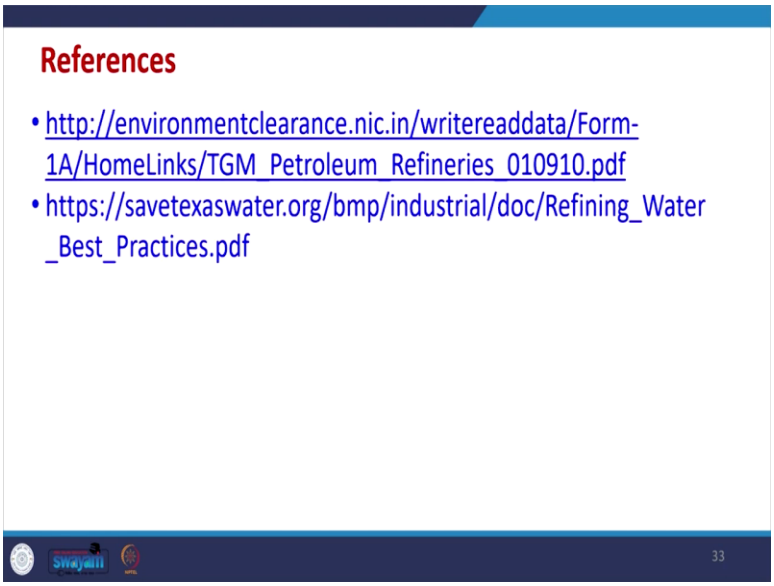

So, these are the various types of references which have been used in the (present) making of the present slide. So, we have we have learned that refinery refinery is highly complex in nature and lot of different types of wastewater are getting generated their characteristics and their quantity will vary depending upon the crude oil being processed, what is the characteristics of the crude oil, what type of product is being made in that particular refinery, what are the production strategies and what are the treatment strategies which are there. So, after wastewater generation these wastewater has to be treated and we can adopt a number of strategies for treatment of such wastewater and we tried to learn a little bit about that treatment. So, with this we will end today's lecture. Thank you very much.