Basic Environmental Engineering and Pollution Abatement

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Lecture 48

Pollution Control in Petroleum Refinery and Petrochemicals Industry

Hello everyone. Now we will discuss on the topic Industrial Pollution Control in grossly polluting industries part 4 and in this class will focus on the pollution control in petroleum refinery and petrochemicals industry.

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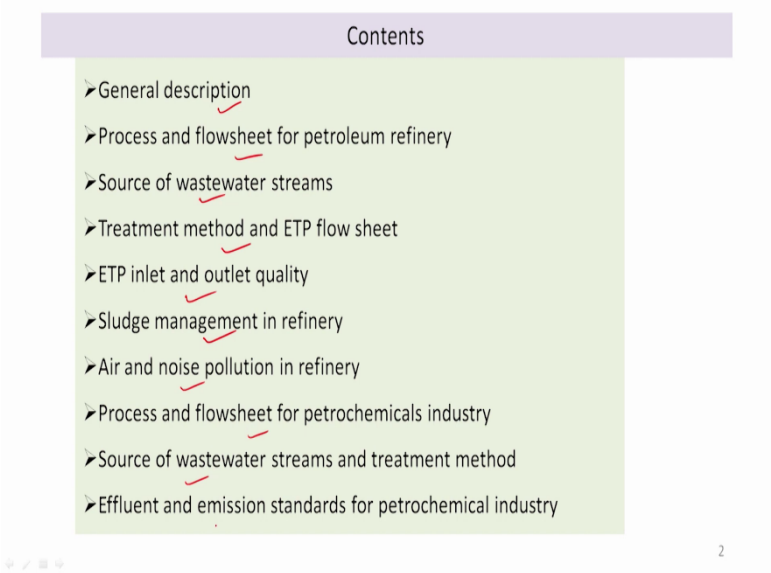

The contents are general description, process and flow sheet for petroleum refinery, source of wastewater streams, treatment method and ETP flow sheet, ETP inlet and outlet quality, sludge management in refinery, air and noise pollution in refinery, process and flow sheet for petrochemicals industry, sources of wastewater streams and treatment method, effluent and emission standards for petrochemical industry.

So, in the petroleum refinery, we know that crude oil is converted into different petroleum products like say LPG, kerosene, diesel, petrol, etc. And crude petroleum is transported from the oil fields to the refinery and then desalting takes place and then atmospheric distillation takes place and we get different products and the bottom products also we get. And then the bottom product is called the atmospheric residue. Atmospheric residue is processed in a vacuum distillation column and some liquid is recovered and the remaining part comes as the bottom product which is called vacuum residue.

So, these are the basic operation that is desalting then atmospheric distillation, vacuum distillation but this is not sufficient, there are many other conversion methods which are applied in refinery complex to meet the market demand of different petroleum products.

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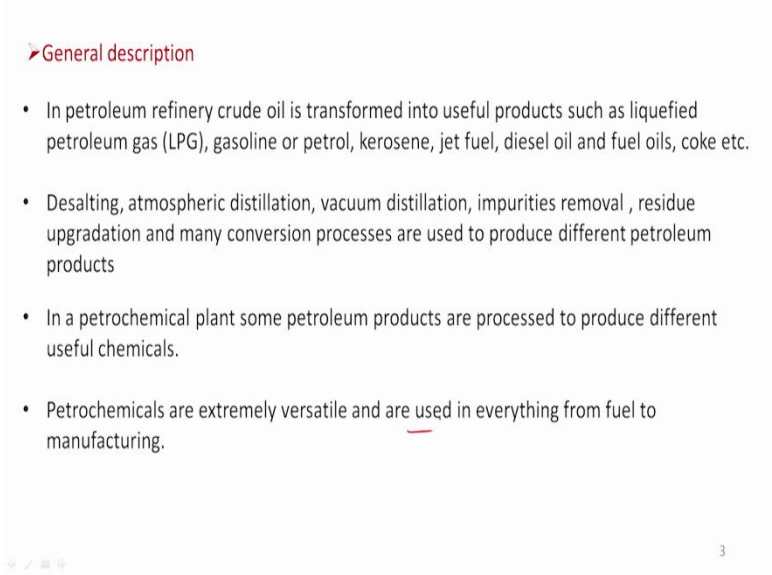

And in petrochemical plant some petroleum products are processed to produce different useful chemicals. And petrochemicals are extremely versatile and are used in everything from fuel to manufacturing different types of compounds are produced from the petrochemicals. Now, we will see the process proceed for petroleum refinery. So, overall refinery process and conversion of intermediate products. So, here we are having a crude oil, after desalting it is coming to atmospheric distillation.

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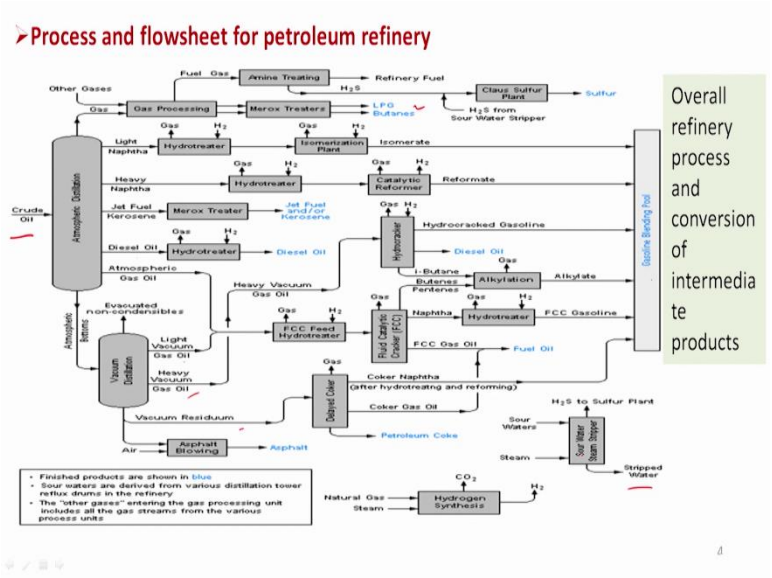

So, this gas which is getting out then we are getting the LPG here and then next product to light naphtha. After gas then it is light naphtha after light naphtha, heavy naphtha, then jet fuel, then diesel, then atmospheric gas oil which is coming here at atmospheric bottom or atmospheric residue it is coming to vacuum distillation. Where vacuum is created, and temperature is also more than this atmospheric distillation. So, here the more complex molecules are broken down and the lighter vacuum gas oil and heavy vacuum gas oil are produced in vapor form and then condensed and it is collected.

And the bottom part we get the vacuum residue then here this vacuum residue is further processed to extract more liquid from it through delayed cooker or through deasphalting process. So, this is the major operations which are involved in the petroleum refinery apart from this we see many intermediate operations are there like light naphtha to hydrotreter then isomerization then it is coming to the gasoline blend and then gasoline pull and then heavy naphtha again hydroteator then catalytic reformer again it is giving us gasoline.

So here we are getting jet fuel so murex treatment it is jet fuel and or kerosene. Here we also get the petroleum part and this gasoline, direct gasoline that is called and diesel oil also we can get as a more heavier part and here you know that hydrogenation hydrotreater so, we can diesel oil we are getting here with improved quality and atmospheric gas oil and the light vacuum gas oil then are going for FCC feed and the cracking takes place hydro crackers and then FCC fluid catalytic cracking then it is going there alkylation and ultimately we are

getting the gasoline and heavy vacuum it is also going to the hydrocracker and hydrocracked gasoline.

So, these are the different network of processes we can say. So, which are responsible to get more gasoline. So, when the market has more gasoline demand. So, these are more gasoline or blend. So, when more demand of gasoline that can be made by this. So, this is the overall process and in this case which we have natural gas steam, it is hydrogen synthesis can takes place by this the vacuum residue also and here in this case, sour water near steam tipper. This is an important that is stripped water the steam and sour water we are sending here. Sour water means there sulphur will be there and ammonia will be there. So, those will be removed off by the stripping of steam. So, then we are getting the stripped water. So, this is one part of wastewater treatment we will discuss in the wastewater treatment in the refinery.

So, this is the overall process flow sheet now, in each and every step there will be the chance of the production of some wastewater or there is chance of the production of gas streams that is the emission of gases due to leaks or any other reason.

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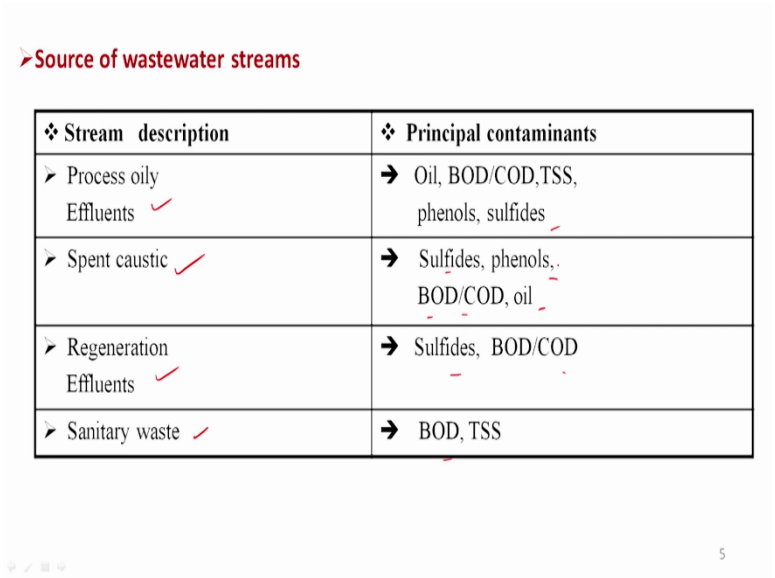

And if we see the different streams of wastewater generated in this refinery those can be classified as process oily effluents or spent caustic, regeneration influents and sanitary waste. So, what is process oil effluents for different processes we may use some water and that wastewater can be generated which will be containing the oil and spent caustic basically it is produced in the sweetening process Meroux process and where scrubbing of the gases is there

with the use of alkaline. So, that is spent caustic we can use and regeneration effluents means when we regenerate the catalysts then also there are some effluents are generated.

So, those are the regeneration effluents and catalyst is widely used in different processes in the refinery. So, regeneration is also widely used and wastewater is also generated to this regeneration. And the sanitary waste is coming from the office, etc. So, if it is different waste streams or having different composition like say process oily effluents will be having oil, BOD, COD, TSS, phenol sulphides and spent caustic will have sulfide, phenols, BOD, COD, oil and regeneration effluent sulfides BOD, COD, and sanitary waste will be having BOD, TSS. So, we see here there is no that very special chemical which needs to be separated except the phenols and some oil also.

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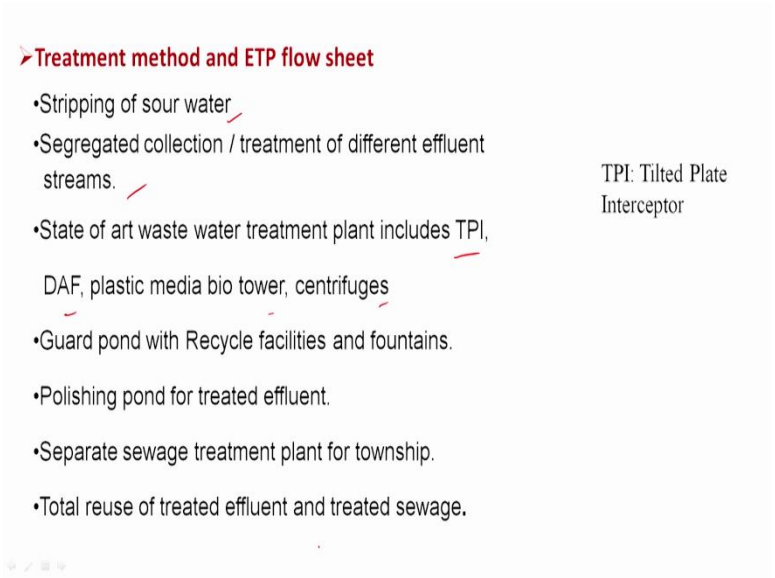

So, the treatment method and ETP flow sheet will see for this. So, one important aspect was that stripping of the sour water. So here in some processes, SO_2 is used. So, in that case, SO_2 is also available in the water. So that SO_2 has to be removed from the water and then the water will be some stripped water.

So stripping of sour water is one important part of the ETP flow sheet and then segregated collection treatment of different effluent streams. As you seen them different streams are generated having different compositions with different compositions with different concentrations as well.

So, the segregated collection and treatment of different effluent can be used. And state of the art wastewater treatment plant includes TPI that is tilted plate interceptor that is used for the removal of oils. And DAF the dissolved air flotation to break the oil water emulsion, and this is used for that purpose. And plastic media to bio tower to improve the performance of the biological reactors and the processes and centrifuges for the de-watering purpose.

Guard pond and recycled facilities and fountains. So, these are also used to maintain the treated wastewater and polishing pond for treated effluent and separate sewage treatment plant for township. So, normally the refinery plants is very big in size and already it has some township. So, that sewage should have a separate sewage treatment plant and total reuse of treated effluent and treated sewage is necessary.

So, ZLD concept is being implemented gradually from glossy polluting industries. So, the complete recycling of waste stream is another aspect which industry should consider seriously nowadays, and main constraints and treatment philosophy for this refinery wastewater.

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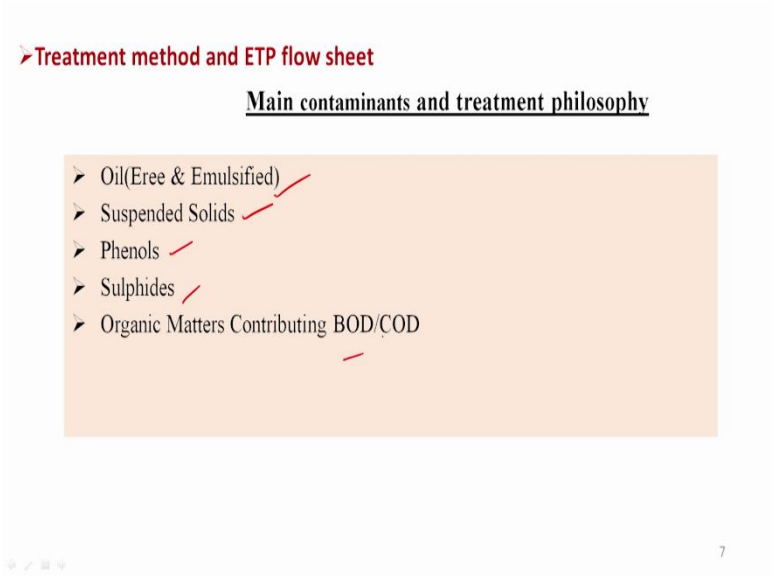

If we consider then because you see here, we have oil separation, suspended solids separation, phenol separation, sulphide separations and organic matter separations. So, these are the basic need for the treatment of wastewater of the refinery.

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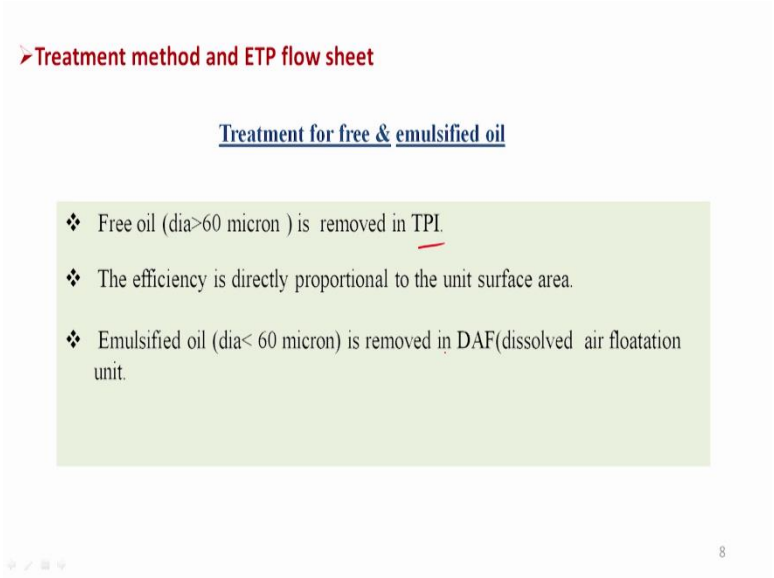

And then how we will do the treatment for free and emulsified oil. So, free oil is removed by TPI, we have already shown that some belt conveyor. So, free oil is removed in TPI and the efficiency is directly proportional to the unit surface area and emulsified oil is removed by dissolved air flotation unit.

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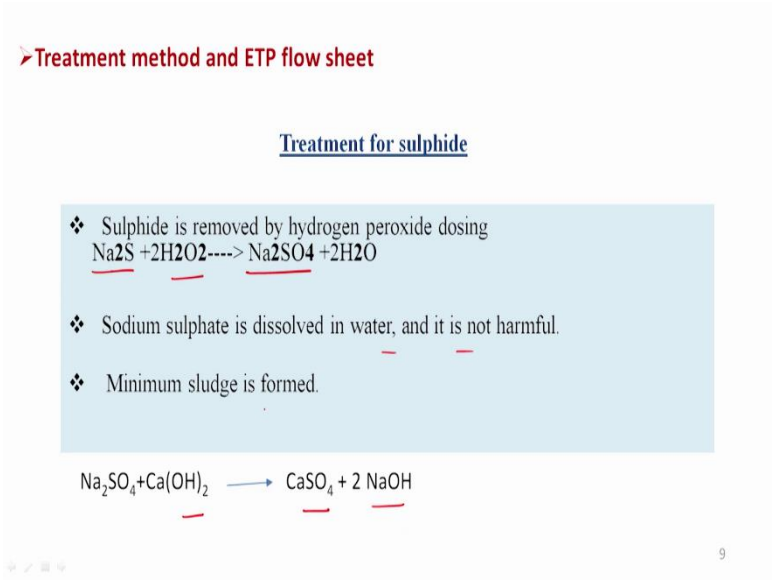

And treatment for sulfide. So, sulphide may be represent as Na_2S in some water stream. So, in that case, if we provide H_2O_2 so that Na_2S can be converted to Na_2SO_4, we have discussed that H_2O_2 as a oxidizing agent and advanced oxidation process we can say.

$Na_2S + H_2O_2 \longrightarrow NA_2SO_4 + 2H_2O$

And sodium sulfate which is produced here that is dissolved in water and is not more harmful, but further this can be removed by adding calcium hydroxide. So, calcium sulfate will be produced 2NaOH.

$Na_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2NaOH$

And as already we have discussed in case of sugar industry that this calcium sulphate can further be removed by using polyelectrolytes. So, minimum sludge is formed that is our objective to produce the less sludge.

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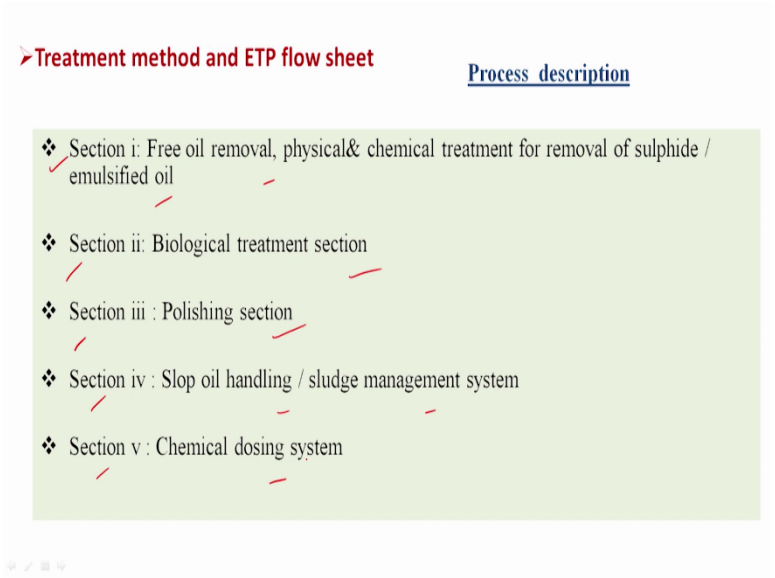

And process description. If we consider then we have section 1, section 2, section 3, section 4 and section 5. The section 1 deals with free oil removal, physical and chemical treatment for removal of sulphide and emulsified oil and section 2 biological treatment and then 3 is polishing treatment that is tertiary treatment and 4 is slop oil handling or sludge management system and 5th section that is chemical dosing system it requires many chemicals and that can be properly managed.

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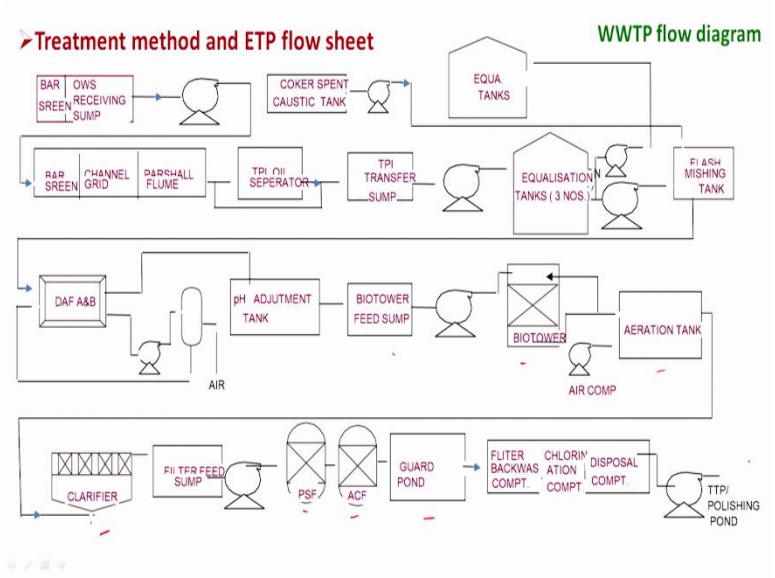

Here we see the wastewater treatment plant flow sheet or flow diagram. So, we have wastewater, then as discussed earlier the bar sreen oil, water separation receiving some after bar sreen it is coming here. So, after bar sreen the water is coming to oily water separation receiving tap sump and then it is sent to box crisp channel grid and your parcel flume and then it is coming to TPI oil separator and after TPI oil separator TPI transfer sump and then equalization tank and then equalization tank to flash mixing tank and flash mixing tank to DAF dissolved air flotation and then from this it is going to pH adjustment and then bio tower so up to this we are having primary treatment and the secondary treatment feed dump and then bio tower then again this bio tower conversion to ensure further degradation.

The aeration tank is also used and then after that it is going to clarifier so sludge will be collected as secondary sludge and then filter it is going to have filter feed sump that will go through the packed bed that is sent filter and activated carbon filter. And then the guard pond this guard pond that is the store of for the storing of this treated water and that will go for further tertiary treatment which has having three compartment that is filter backwash compartment these water is used for the back washing of these two filters.

So then chlorination so chlorination is not done here because this us use recycled for that purpose and then it is chlorinated and it is going to disposal compartment and disposal as per the need if needed, then tertiary treatment is necessary for polishing as a polishing step and then it is used for different application.

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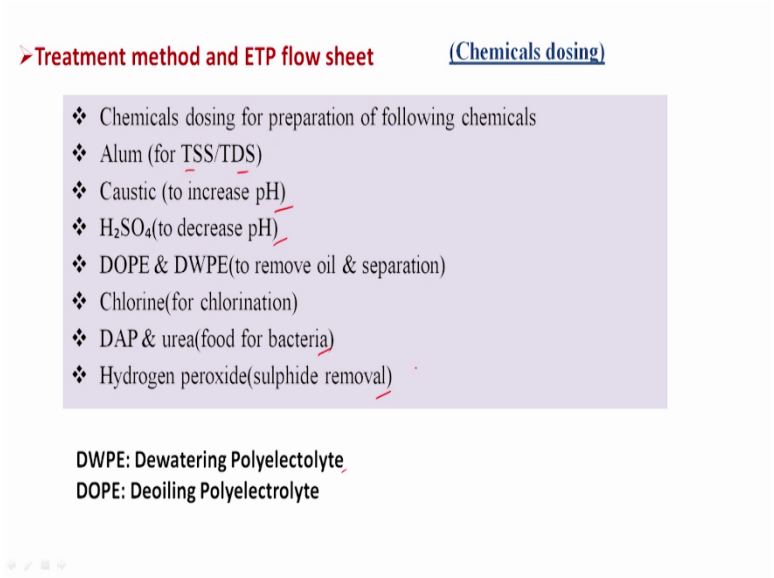

Now, chemical dosing so chemicals dosing for preparation of following chemicals like alum for TSS and TDS caustic to increase pH, H_2SO_4 to decrease pH, DOPE and DWPE that is dewatering polyelectrolytes and deoilling polyelectrolytes to remove oil and separation and chlorine for chlorination, DAP and urea certainly for the growth of the microorganisms for the secondary treatment and hydrogen peroxide sulphide removal. So, these are the different chemicals which are used in the plant. And for sulphur removal calcium hydroxide can also be used like say sugar industry plant, which we have discussed.

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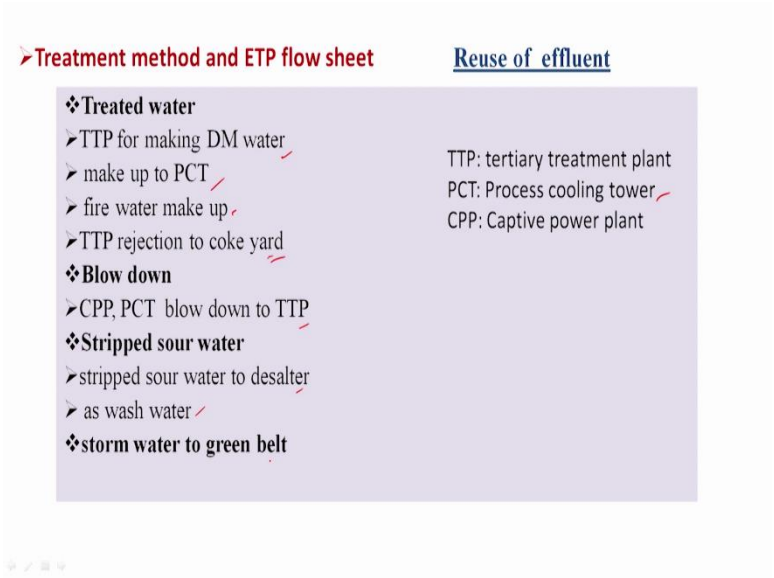

Then here we will see how the treated water can be reused so TTP that is tertiary treatment plant for making DM water. So, this water after going to the tertiary treatment plant it will be sent to the DM water plant and then make up to PCT that PCT is your process cooling tower or fire water makeup or TTP rejection to coke yard.

So, after TTP we will be getting the concentrate, let us say RO reject, so that will go to coke yard. And blow down that from in the CPP that is captive power plant and PCT blowdown will go to tertiary treatment plant. And then stripped sour tower that is stripped sour water to desalter as wash water. So, these are the two applications of the stripped sour water, and storm water to green belt. So, these are the different reuse applications of the effluent.

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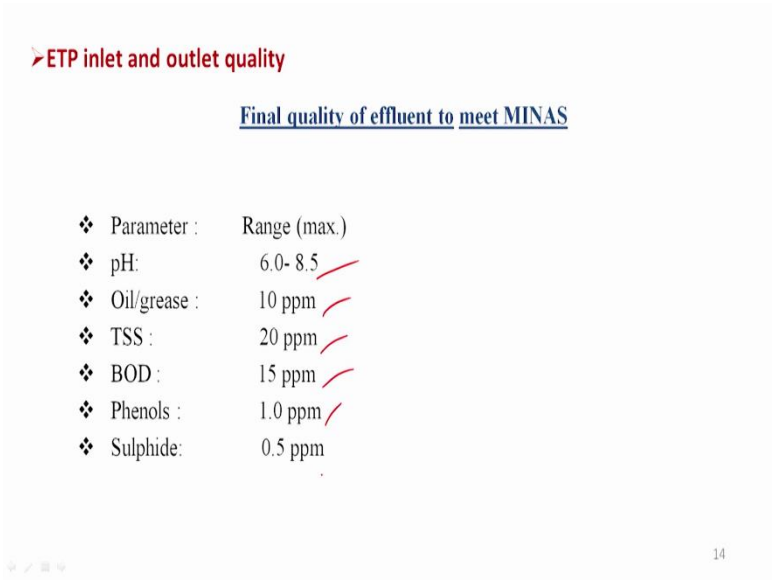

And the final quality of effluent to meet minimum standard So, that is your pH 6 to 8.5, oil and grease 10 ppm, TSS 20 ppm, BOD 15 ppm, Phenols 1 ppm and sulphide 0.5 ppm.

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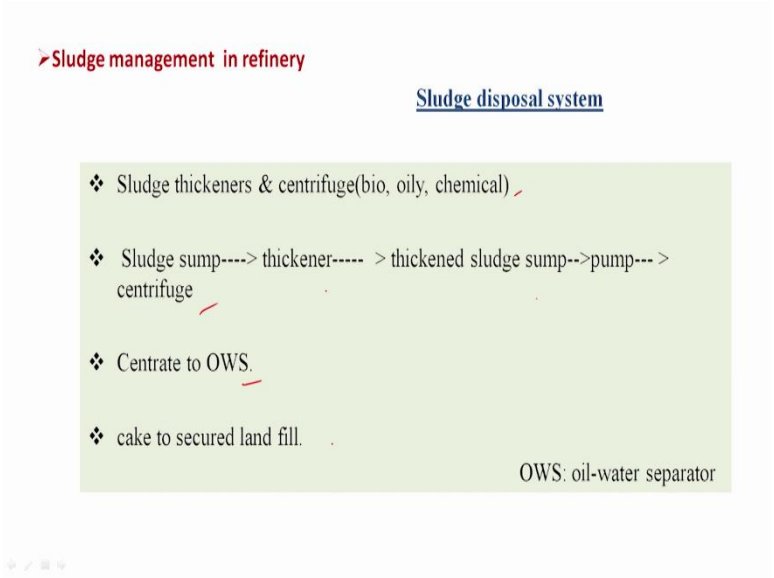

Now we will see the sludge disposal. So, both secondary and primary sludge are generated, so, sludge thickness and centrifuge are used for this purpose. So, sludge sump to thickener to thicken sludge sump then pump then centrifuge This is the sequence of operation and it the concentrate to oil water separator and cake is formed that is sent to the secure landfill.

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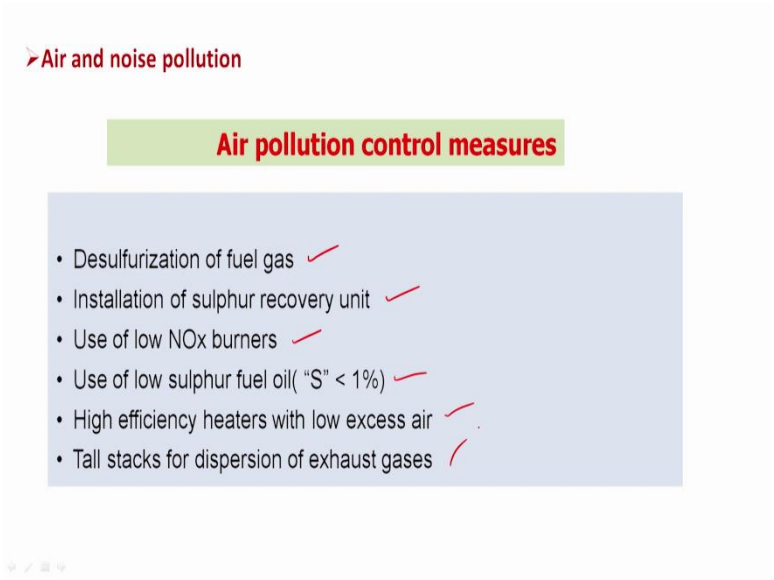

And air pollution in case of refinery if we consider then desulphurization of fuel gas, installation of sulphur recovery unit, use of low NOx burners use of low sulphur fuel, high efficiency heaters with low excess air, and tall stacks for dispersion of exhaust gases. So,

already these are discussed in your earlier classes also, on the basis of these concepts the design of different units. Air pollution control units can be decided and installed.

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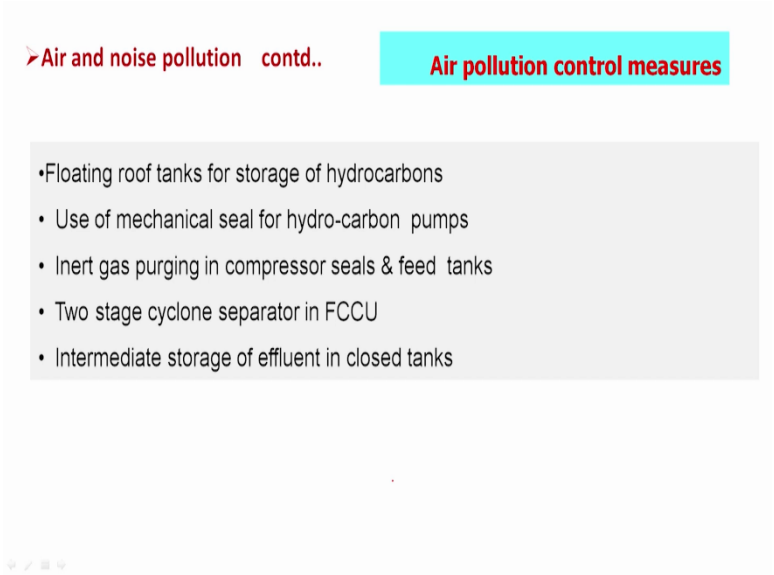

Some other measures for air pollution are floating roof tanks for storage of hydrocarbons. It reduces the leakage and use of mechanical seal for hydro carbon pumps, inert gas purging in compressors seals and feed tanks, two stage cyclone separator in FCCU, intermediate storage of effluent in closed tanks. So all these helps to reduce the air pollution including the leakages.

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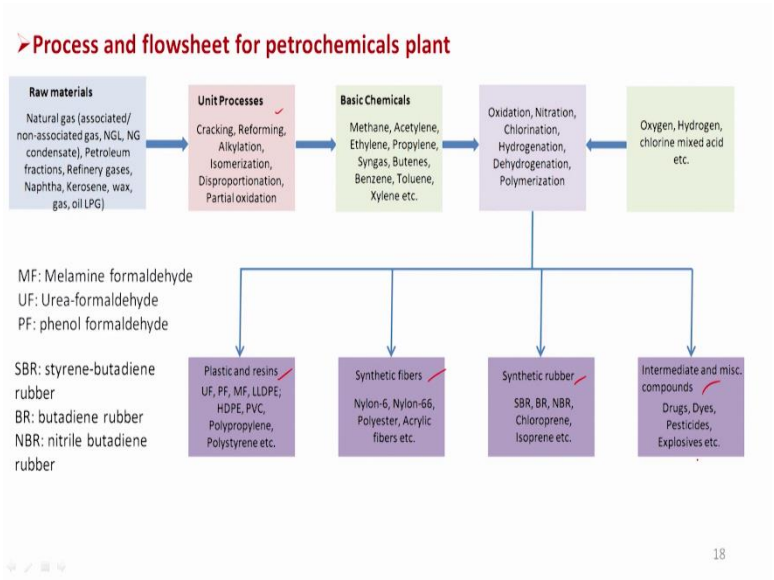

Now we will see the pollution control in petrochemical industries. And the first we will see the process and flow sheet for petrochemical plants. This slide shows us different raw materials used for the petrochemical plants and different unit processes used in it and basic chemicals which are produced from these raw materials.

And these basic chemicals are further reacted with some oxygen, hydrogen chlorine mixed acids and then through oxidation, nitration, chlorination, hydrogenation, de-hydrogenation polymerization, we can get different petrochemical products or different petrochemicals like say plastics and resins, synthetic fibers, synthetic rubber, intermediate and miscellaneous compounds. So we can get different types of compounds.

Let us say for plastic and resin. So you can get UF, PF, MF, LLDPE, HDPE, PVC, polypropylene, polystyrene, etc. where MF is melamine formaldehyde and UF urea formaldehyde resin, PF phenol formaldehyde resin, and synthetic fibers include nylon 6, nylon 66, polyester, acrylic fiber, etc. And synthetic rubber SBR, BR, NBR, chloroprene, isoprene. So SBR is styrene butadiene rubber, BR butadiene rubber, NBR nitrile butadiene rubber.

Similarly, in this case I have intermediate and miscellaneous component drugs, dyes, pesticides, explosives, etc. So many different types of chemicals and petrochemicals we can get in this petrochemical plants. So, there will be different units, different types of operations, and from each unit an operation there will be a chance of pollution generation. Now, we will be seeing here.

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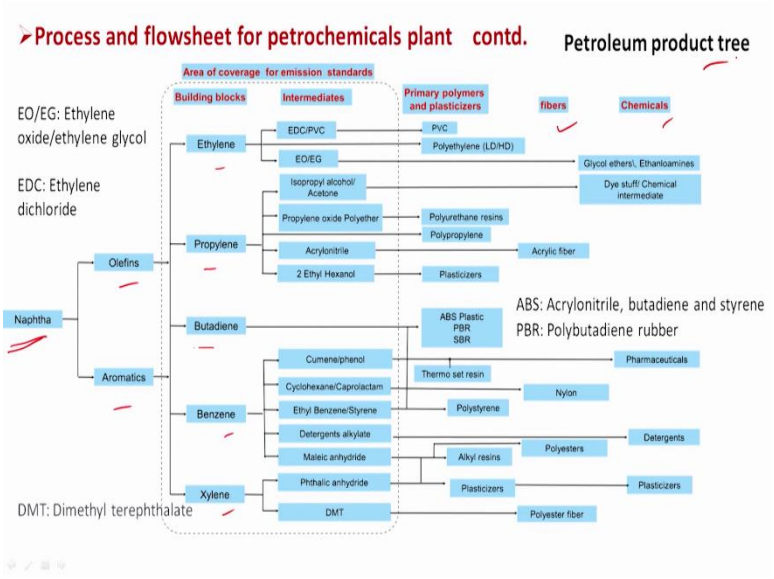

So, whatever may be the products in most of the petrochemical plants, the naphtha it is considered a basic raw material and which contains olefins and aromatics and from these after naphtha cracking will get ethylene and propylene and butadiene these are building blocks and these are olefin types of compounds and aromatic compounds are also there that is benzene and xylene. So, these are the building blocks and these are converted to different intermediates and primary polymers and plasticizers then maybe fibers or maybe chemicals.

So, ethylene we can get EDC, PVC, EO, EG, where EO and EG is ethylene oxide, ethylene glycol, EDC is your ethylene dichloride and PVC polyvinyl chloride. So, there we can get PVC, polyethylene LDHD low density high density or here we can get glycol ethers, ethanolamine, etc.

Similarly, for propylene we can get isopropyl alcohol, acetone and then propylene oxide, polyether, acrylonitrile, 2 ethyl hexanol again from these we can get dyestuff and chemical intermediates here we can get polyurethane resins, here we can get directly polypropylene and we can get acrylic fiber and here we can get plasticizers.

Similarly, from butadiene we can get ABS you can get PBR, you can get SBR, for ABS use acrylonitrile butadiene and styrene and PBR is your polybutadiene rubber. So, here we are getting rubber also and from benzene and xylene we can get different intermediates from benzene we can get cumin phenol or phenol and then cyclohexane, caprolactam, ethyl benzene styrene or styrene, detergents acrylic, malic anhydride and which are converted into

different products as mentioned here that is a pharmaceuticals, thermoset resins, nylon, polystyrene, detergents, alkyl resins and polyesters.

Similarly, from the xylene we can get phthalic anhydride, DMT and then that is DMT dimethyl terethalite and then plasticizers and we can get polyester fiber. So, these are the different products we can get from naphtha. So this is the petroleum product tree which are generated in the petrochemical complex.

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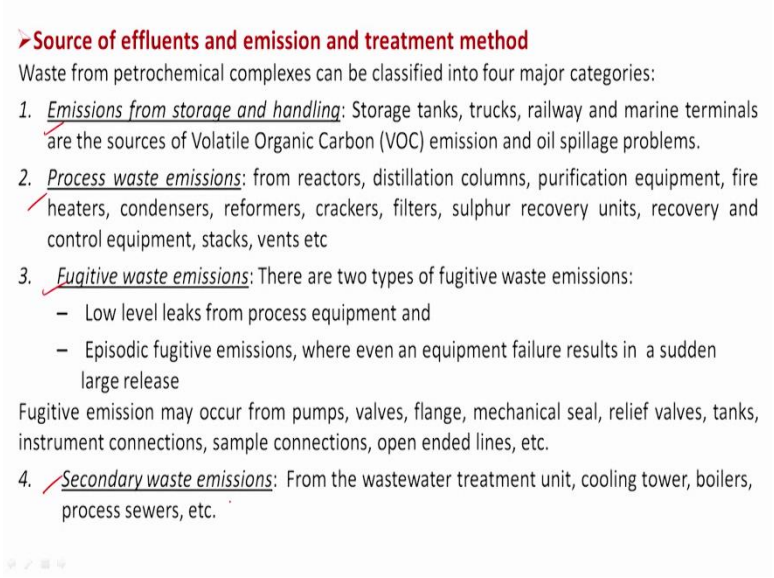

Now we will see the different source of emission and wastewater generation. So, important sources are emissions from storage and handling, then process waste emissions, fugitive waste emission and secondary waste emissions. Suddenly thus emission from storage and handling. The storage tank tracks railway and marine terminals are the sources of volatile organic carbon emission and oils spillage problems, process waste emissions from reactors, distillation columns, purification equipment, fire, heaters,, condensers, deformers, crackers, filters, sulphur recovery unit, recovery and control equipment, stacks and vents etc.

So here heaters furnace those are extensively used in this refinery and petrochemicals unit. Fugitive waste emission there are two types of fugitive waste that is low level leaks from process equipment and episodic fugitive emissions where even an equipment failure results in a sudden large release.

And this fugitive emission may occur from palm, valves, flange, mechanical seal, relief valves, tanks, instrument connections, sample connections, open ended lines etc. and

secondary waste emissions from the wastewater treatment unit, cooling tower, boilers, process sewers, etc.

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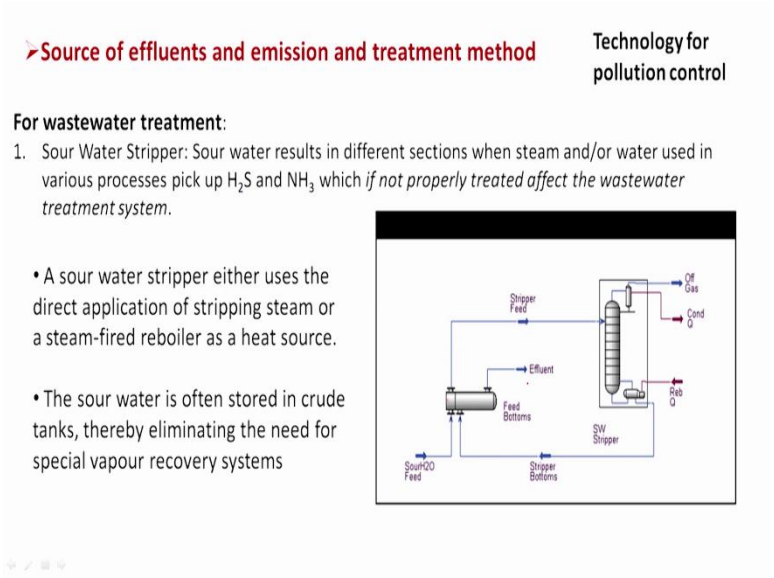

Now, there are some technologies for pollution control for wastewater treatment. So, the sour water how this can be treated. So, sour water results in different section when steam and or what are used in various processes pick up H_2S and NH_3 which is not properly treated affect that wastewater treatment system. So, this is a sour water treatment plant. The sour water stripper either uses the direct application of tripping steam or steam fired re-boiler as a heat source the sour water is often stored in crude tanks, thereby eliminating the need for special vapor recovery systems.

So, here sour water it is coming and then it is going to the feed to the stripping section and then gas off sulfur H_2S gas is going out and ammonia is also going out and then we have stripped water. So, that is used as the effluent. So, that is why we are able to remove the sulphur now, by the stripping.

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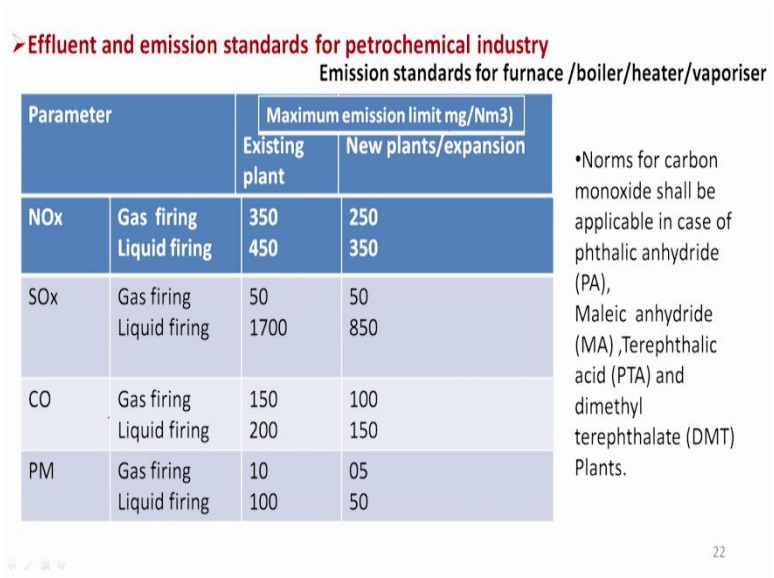

Now, emission standards for furnace, boiler, heater and vaporizer, as you mentioned that there are a large number of these types of equipment used in this petrochemical industry. And here NOx, SOx, CO, PM it is given for gas firing and liquid firing case. Gas firing and liquid firings are different cases for the release of these pollutants for existing plant and for new plants and expansions. So, this is mg/Nm^3 these are the limits it is given see that for new and expanded plants, there is significant changes in the standard values.

So, that is why it is targeted to reduce the pollution as well. And in some cases, we may have phthalic anhydride, malic anhydride and terethalic acid and dimethyl terethalate. So, in that case norms for carbon monoxide shall be implemented.

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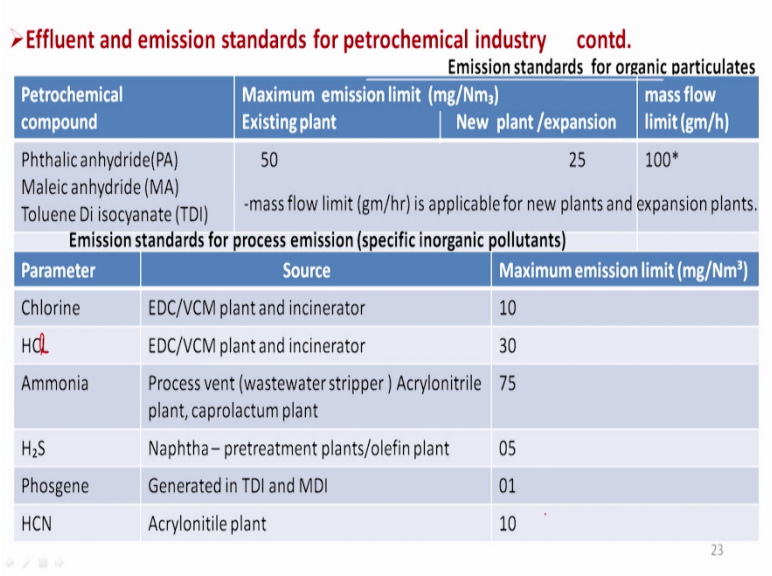

And emission standards for organic particulates like phthalic anhydride, maleic anhydride and this so 50 existing limit and then new 25 and mass flow limit is 100. Emission standards for process emissions specific inorganic pollutants also it is given this is the emission standard for process emissions. So, like chlorine, HCl and then ammonia H_2S, phosgene, HCN. So, these are the different sources and this is the maximum emission limits.

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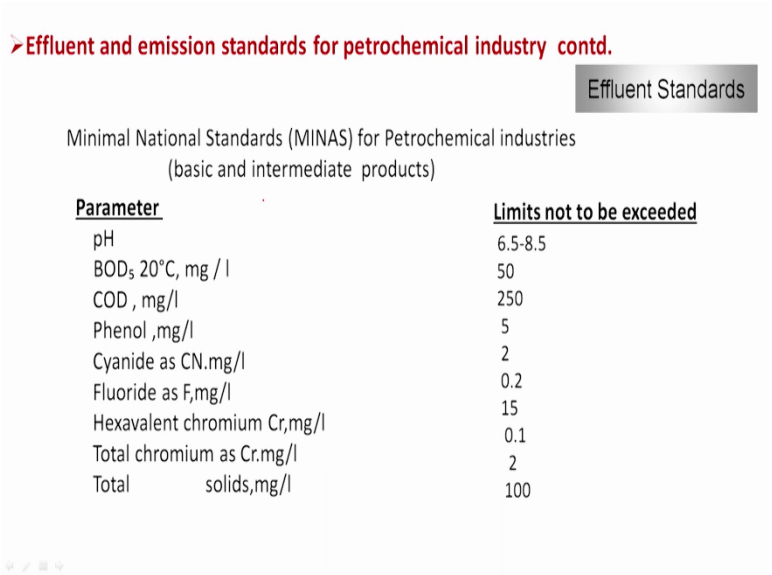

And this is the effluent standard for wastewater. So, pH is 6.5 to 8.5, BOD5 50 mg/l, COD 250 mg/l. Phenol 5 mg/l, cyanide 2 mg/l, fluoride 0.2 mg/l, Hexavalent chromium 15 and this is the standard of effluent and this slide shows the minimum national standards for

petrochemical industries that is for effluent that is wastewater. So, we have discussed different aspects of the pollution control of petroleum refinery and petrochemicals industry up to this in this class. Thank you very much for your patience.