Basic Environmental Engineering and Pollution Abatement
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Lecture 49
Industrial Pollution Control in GPI 4
(Pollution Control in Pulp and Paper, Fertilizer and Copper Smelter Industry)

Hello everyone. Now, we will discuss on the topic Industrial Pollution Control in Grossly Polluting Industries part 5 and we will focus on pollution control in Pulp and Paper, fertilizer and copper smelter industry.

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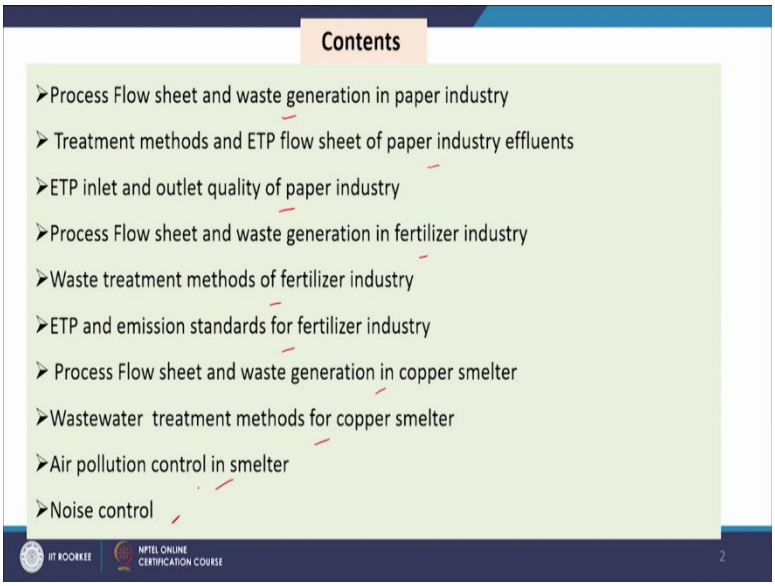

The contents are process flow sheet and waste generation in paper industry, treatment methods and ETP flow sheet of paper industry effluence, ETP inlet and outlet quality of paper industry, process flow sheet and waste generation in fertilizer industry, waste treatment methods of fertilizer industry, ETP and emission standards for fertilizer industry, process flow sheet and waste generation in copper smelter, wastewater treatment methods for copper smelter, air pollution controlling smelter and noise control.

Already we have discussed in detail about the production of different waste streams in different types of industries like sugar distillery, petrochemicals and petroleum refinery, etc. and tannery also. Here we will be discussing on paper and pulp. And then we will discuss fertilizer and copper smelter industry. And basically, already we have known that the wastewater generation takes place through different processes in industries and the composition varies in the wastewater generated through different processes.

So, at first we will identify the different processes through which the wastewater or emissions are being generated. Then for the treatment, we have discussed the general philosophy for the treatment and different methods used for the removal of different types of pollutants. So, those general concepts will be applicable for all the cases, just we will be highlighting some special treatment which are needed in the specific industry type.

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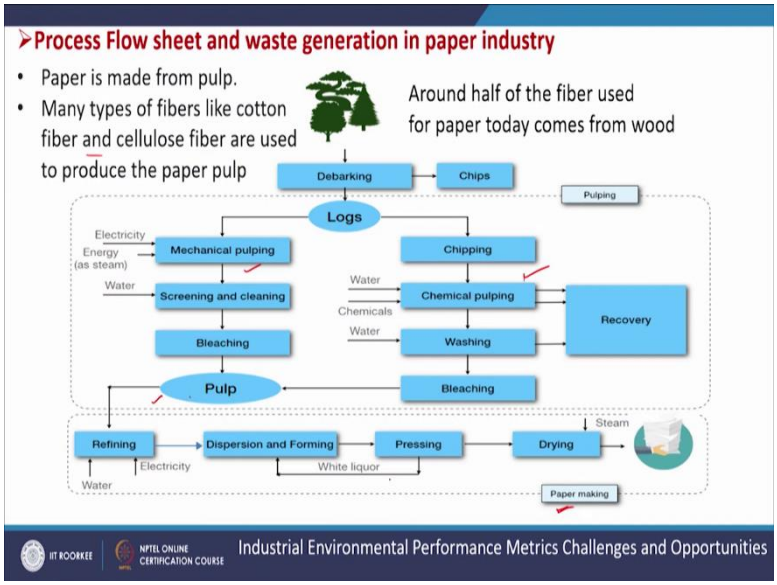

So, now, let us see first on paper and pulp industry. So, this is the flow sheet which gives the paper production. So, you see the paper making takes place basically through these two steps, one is pulping pulp production, then pulp to paper. And this pulp production is basically done from different types of fibers or many types of fibers like cotton fiber and cellulose fiber used to produce the paper pulp.

And it has been found that around 50 % of the pulp is produced from the wood. So woody biomass if we take so after debarking will get logs and that can be processed through different steps like say, this is mechanical pulping or chemical pulping, then we will be getting in both the cases, pulp and then pulp will be further refined and processed. And then we will be getting the paper.

So, if we see the different processes involved let us say in case of mechanical pulping, skinning and cleaning then bleaching and here for chemical pulping chipping, chemical pulping washing and bleaching. So bleaching is one important step and another is chemical pulping. So this one treatment with alkali that is also one important step for the paper production. And here we will see that water is required for all the processes for both

mechanical pulping and chemical pulping and then wastewater will be generated and then that here also for paper making water is reused so waste water will also be generated.

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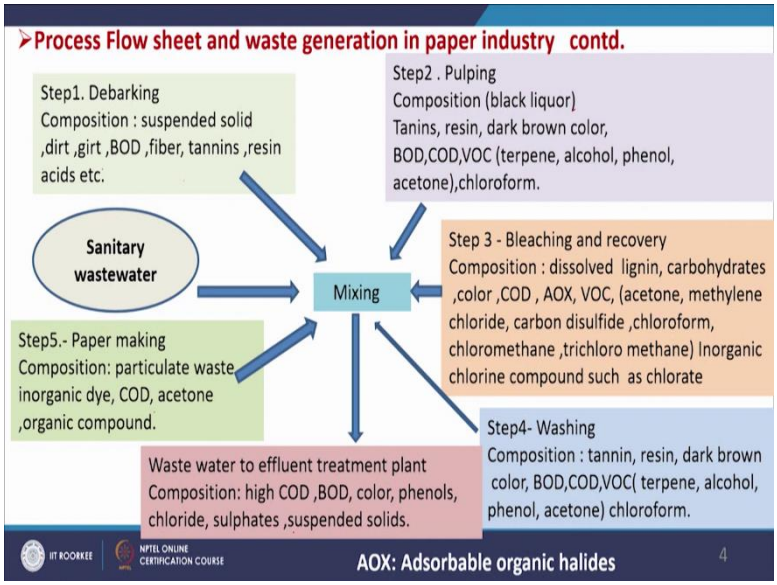

So, we will be seeing the composition of different types of wastewater and we will also see how we can treat it. So, main is your debarking first step so then the composition of the wastewater coming out from its suspended solid dirt, grit, BOD, fiber, tannins, resin and acids.

If we take the overall wastewater generated in pulping. So then composition we get the black liquor, then tannins, resin, dark brown colour, which has and then BOD, COD and VOC volatile organic compounds that is terpene, alcohol, phenol, acetone and chloroform during pulping process during bleaching and recovery.

So, then composition is dissolved lignin, carbohydrates, colours, COD, AOX, AOX nothing but absorbable organic halides and VOC. So, inorganic chlorine compound such as chlorate are also present in case of bleaching and recovery waste waters which is generated from this section and then washing section that also waste water is generated that content tannin, resin, dark brown, colour, BOD, COD, VOC and chloroform and from paper making waste water particularly contains particulate waste, inorganic dye, COD, acetone, organic compound.

Apart from these sanitary wastewaters is also generated in offices and the residential area and in the factory premise the all-water streams either can be separated and segregated and treated and combined and mixed, then further treated or these can be mixed. And then waste water to

effluent treatment plant composition that contains then high COD, BOD, colour, phenols, chloride sulphates, suspended solids. So, this will be the composition of this.

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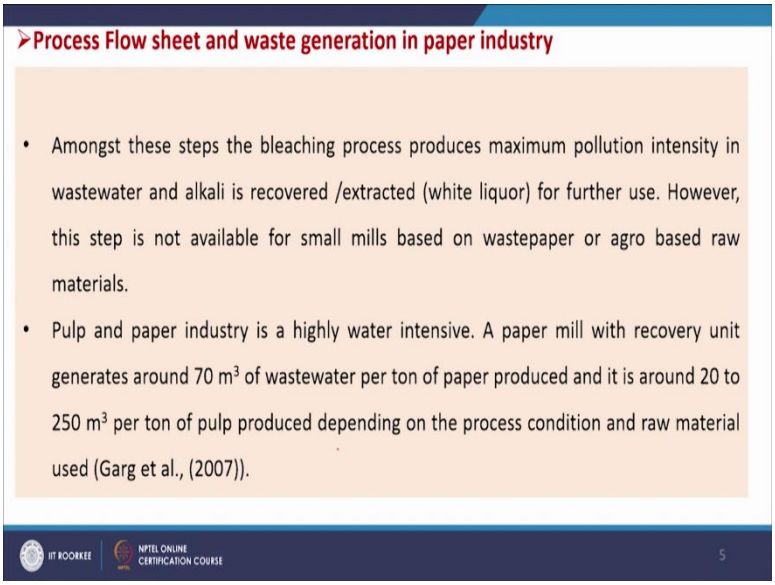

And now, if we compare the different steps through which the wastewater is generated, then you will see that bleaching process is very important where maximum pollution is generated. So, amongst these steps, the bleaching process produces maximum pollution intensity in wastewater and alkali is recovered, extracted. So, the black liquor to white liquor we get and the white liquor used for further application.

However, this step is not available for small mills based on wastepaper or agro based raw materials. So, depending upon the type of mills, the nature of the wastewater or the composition of the pollutants in the wastewater will also be varied. The pulp and paper industry is highly water intensive, a paper mill with recovery unit generates around 70 m^3 of wastewater per ton of paper produced and it is around 22 to 250-m^3/ton of pulp produced depending on the process condition and raw material used.

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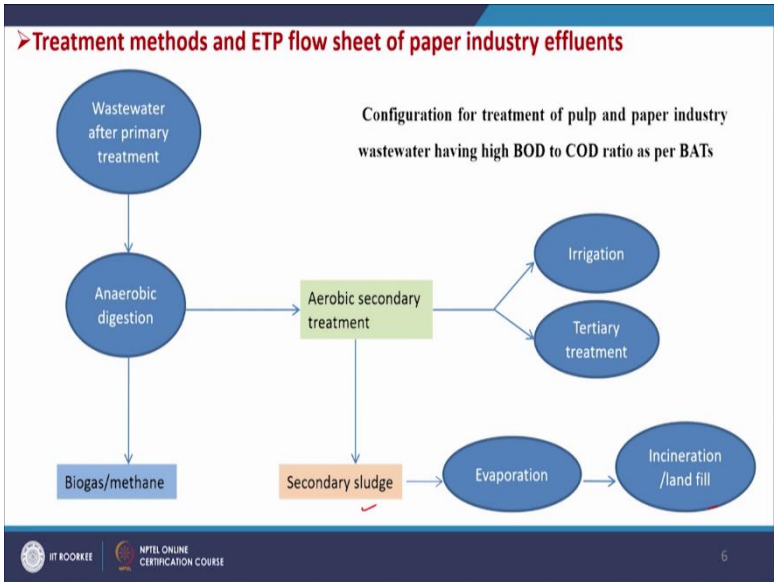

Now, you see the best available technologies, how the wastewater can be treated which are generated in this paper and pulp industry. So here wastewater certainly the primary treatment will be there. Then we will be having anaerobic digestion because COD, BOD is high. So, biogas containing methane can be produced and the slurry which is available, so that can be treated further through aerobic treatment.

The secondary treatment and after secondary treatment we will be getting secondary sludge that can be further evaporated and incinerated or used in landfill. And the water which we are getting from the aerobic secondary treatment that can be further treated through tertiary treatment or can be used for irrigation purpose. So, this is the configuration for treatment of pulp and paper industry waste water having high BOD, COD ratio as per waste available techniques.

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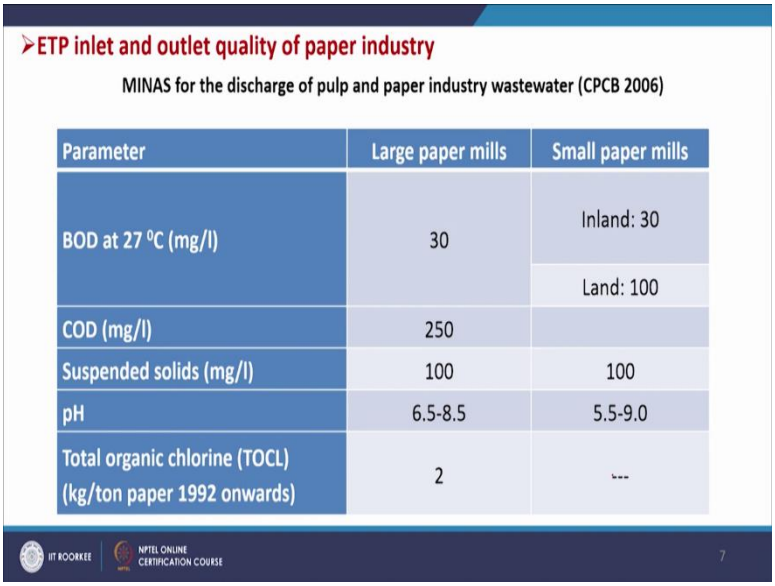

And as per MINAS, minimum standards for the discharge of pulp and paper industry waste water is provided here that is BOD at 27 ^{o}C for large paper mills it is 30. So, small paper mill 30 and land 100. And COD is 250 and suspended solids is 100 and pH 6.5 to 8.5. And here are 5.5 to 9 and total organic chlorine that is your 2 but in this case for small paper mills this is not applicable.

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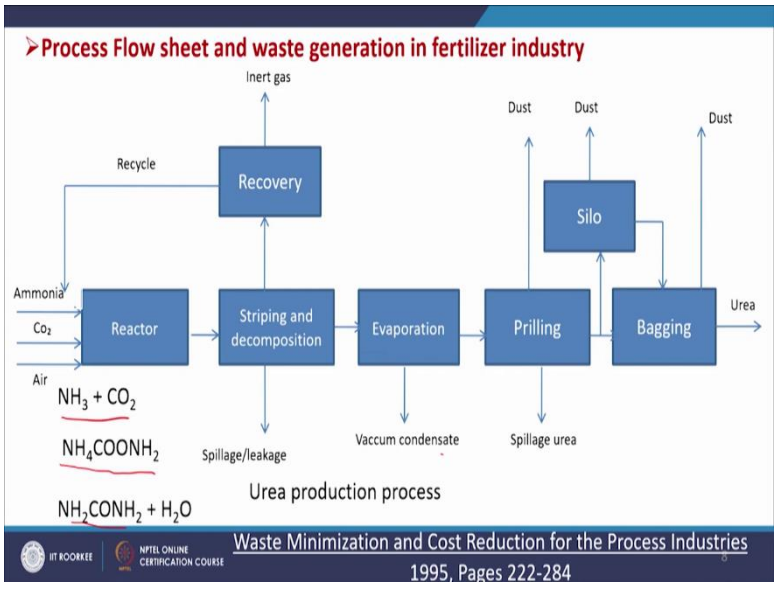

Now we will see the wastewater generation and pollution generation, emission generations in fertilizer industry. So, we know that there are basically three types of fertilizers, one is nitrogenous, another is phosphatic fertilizer and another is your mixed fertilizer that is NPK. So, here we will see the flow sheet for urea production. So, urea nitrogenous fertilizer, which

is produced from the reaction of ammonia and carbon dioxide, ammonia and carbon dioxide reacts an intermediate product NH_4COONH_2 that is further converted to NH_2CONH_2 that is urea.

So, these two gas phase it is coming in the reactor, so a liquid phase it is produced and in stripping and decomposition in this unit the unconverted ammonia and CO_2 is recycled back and inert gases goes up and then we get the spillage leakage here. So, that is the source of pollution then it goes to evaporation then after evaporation the prilling section and again as the spillage urea. Here, we can get vacuum condensate and then this prilling it is going to silo and bagging and for all loads units the dust comes out. So, these are the source of emissions and these are the source of wastewater in urea production plant.

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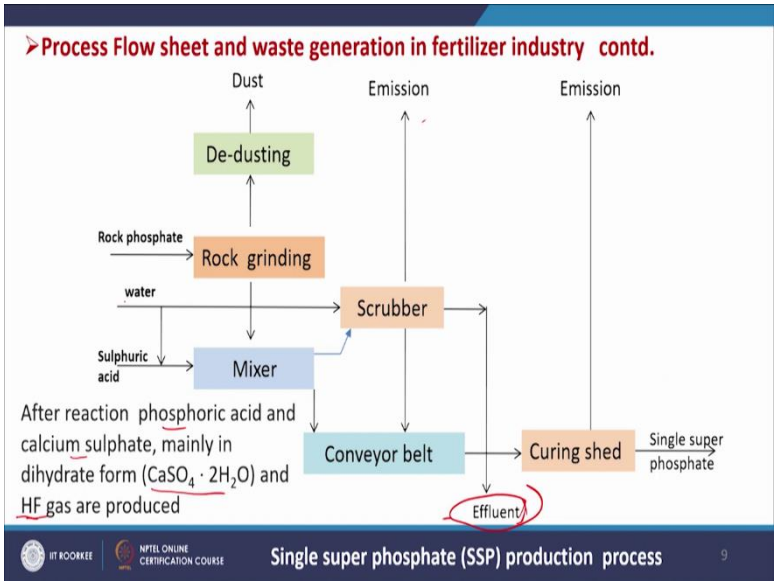

Now, we will see the process of single super phosphate production. So, SSP production, in this case rock phosphate is grinded and reacted with sulphuric acid in the mixture where this rock phosphate is converted to calcium sulphate and phosphoric acid. And mainly this calcium sulphate is in the form of $CaSO_4 \cdot 2H_2O$ and HF gas, hydrofluoric acid is also produced.

So, we see here we have rock grinding so when it is grinded. So de-dusting. So dust comes into the environment and here this fine powder of the rock phosphate is entering into the mixer where sulphuric acid and water is added and after mixing these reaction takes place the solid phase is coming here to the conveyor belt and it is going to for curing shed.

So that pre phosphoric acid which is available here the phosphoric acid concentration reduces with time and ultimately the single super phosphate is produced after certain curing time, where phosphoric acid concentration becomes below certain permissible limit. And from the mixer one gas stream goes out and this gas contains dust particles and also this HF that is hydrofluoric acid.

So, this dust and HF goes through a scrubber and water is sprayed and then with the spray system the HF gas is taken into the liquid and the treated gas goes out as emission and particulates and the HF comes into the water part that is effluent. And this needs treatment or this can be recycled here by replacing this water. And if it is done, then this HF which is generated and available in this water that can also react with this some amount of this rock phosphate and the acid requirement can be reduced to some extent.

So that way, one way it can be managed otherwise, it has to be treated for the removal of fluoride and other materials present in it. So, this is the flow sheet of SSP or single super phosphate production. And we see the sources of emission and the wastewater generation.

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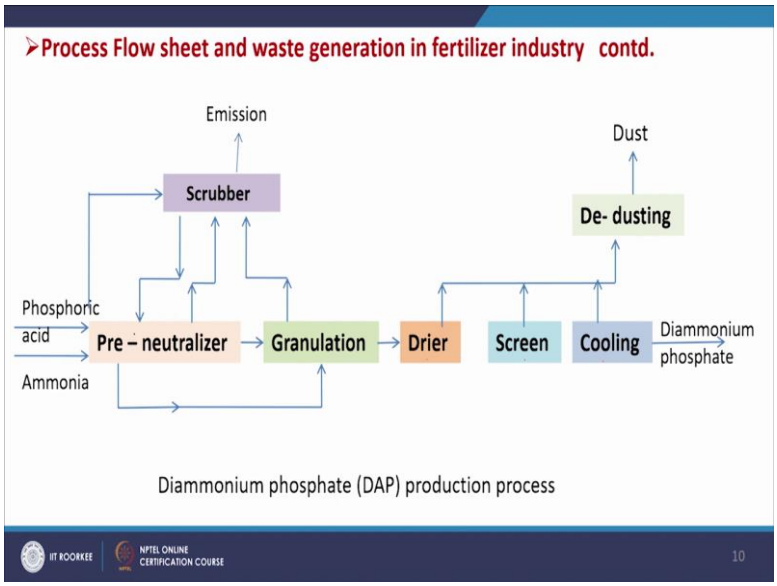

Next we will see DAP diammonium phosphate, another important fertilizer which contains both phosphorus and nitrogen. So, in that case, phosphoric acid and ammonia reacts in the pre neutralizers and then it is granulation and then dryer, then screen and cooling, then we get diammonium phosphate this is the granules.

So in these all operations, there is the dust productions and after de-dusting dust is going. So if proper environmental care is not taking that means particulates separation units are not installed then the environment will be affected. And here also this gas that is going that is after scrubbing we are getting the free gas and we the remaining part is recycled here. So this is a process for the DAP production.

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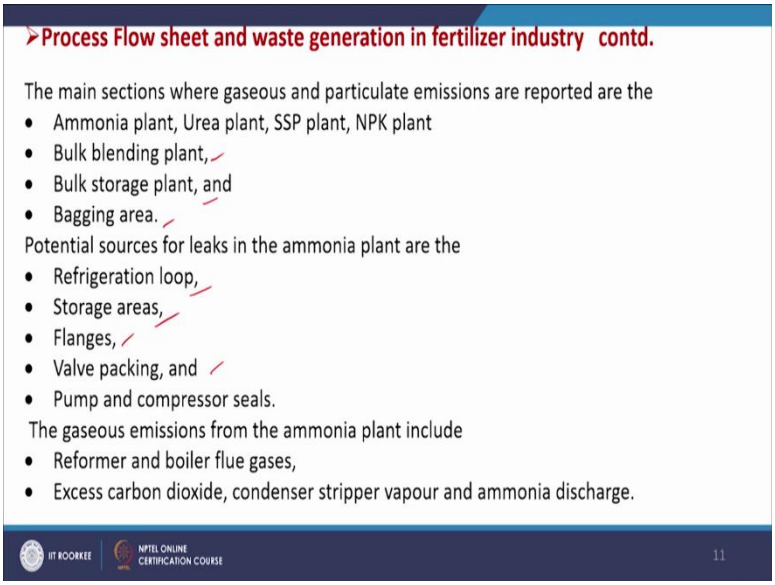

In case of NPK fertilizer. So this is a mixture so nitrogenous and phosphatic fertilizers with potassium are mixed in a reactor and then the granules are formed. So, here also different particulates emission takes place. So, now, we will see the main sections where gaseous and particulate emissions are reported.

So, these are ammonia plant, urea plant, SSP plant and NPK plant and bulk blending plant, bulk storage plant and bagging area. So, main sections are gaseous and particulate emissions take place. And potential sources for leaks in ammonia plant are the refrigeration loop, stories areas, flanges, valve packing and pump and compressor seals.

So, these are some important potential sources of leaking. And the gaseous emissions from the ammonia plant include reformer and boiler flue gases, excess carbon dioxide, condenser stripper, vapour and ammonia discharge. So, ammonia is the raw material and, in many fertilizers, ammonia is produced in suite or ammonia is stored and it is purchased from outside sources. So, these are the different sources of emission in the fertilizer industry.

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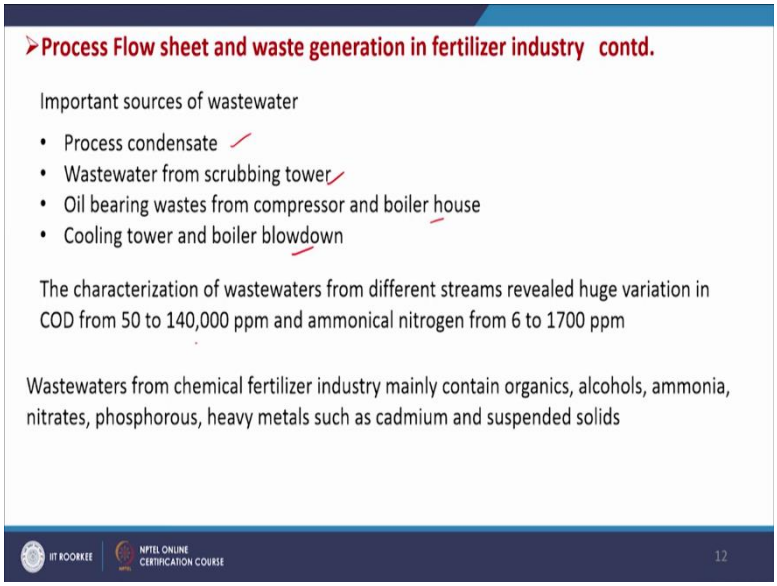

Now, we will see the important sources of wastewater. So, process condense we have seen in urea production and then wastewater from scrubbing tower, oil bearing waste from compressor and boiler house and cooling water and boiler blowdown. So, these are major source of wastewater generation. The characterization of wastewaters from different streams reveal huge variation in COD from 50 to 140,000 ppm and ammonical nitrogen from 6 to 1700 ppm.

So, wastewaters from chemical fertilizer industry mainly contain organic alcohols, ammonia, nitrates, phosphorus, heavy metals such as cadmium, and suspended solids. So, what we see here special type of pollutants which are present in nitrogenous fertilizer that is nitrogen and free ammonia, and for phosphating that is HF. So, we need to take special treatment for the removal of these pollutants, other concepts which you have discussed for the removal of other organic compounds and particulates etc. those will be applied in the similar way.

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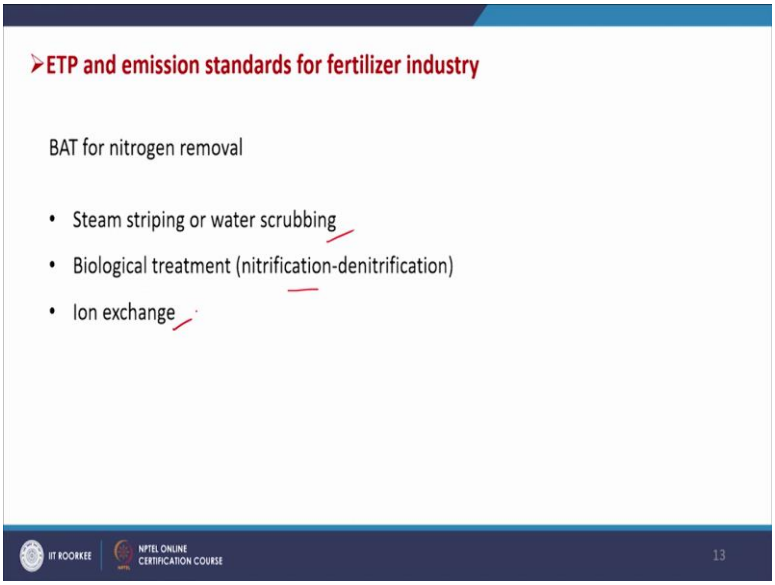

And for nitrogen removal the best available techniques are steam stripping, or water scrubbing and biological treatment nitrification-denitrification, we have discussed in case of sequential batch reactor how the nitrification-denitrification takes place also and ion exchange. So, these are the different methods that are considered at best available technique for the nitrogen removal.

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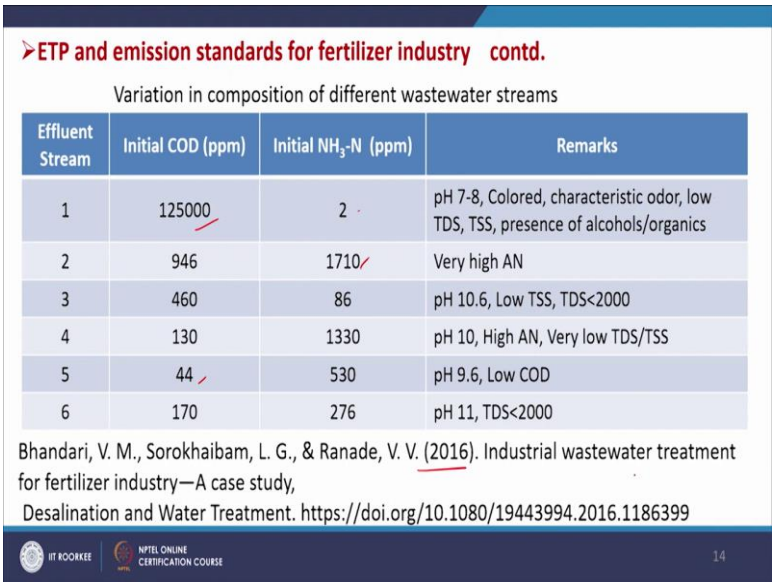

And HF removal already we have discussed that this water stream can be recycled and used in place of water. So, that some sulphuric acid productions will also be reduced or it can be diluted before discharging and making the concentration below the permissible limit. So, now we will see the variation in composition of different waste water streams.

So, here in 2016 report, they have collected different samples from fertilizer industry, but they have not mentioned what is the actual source and it is written that the initial COD concentration is varying widely from 44 to 125000 ppm and initial ammoniacal nitrogen also varies from a wide range 2 to 1710 ppm. And in these different streams they have seen that the compositions are also different and in different concentration as shown here.

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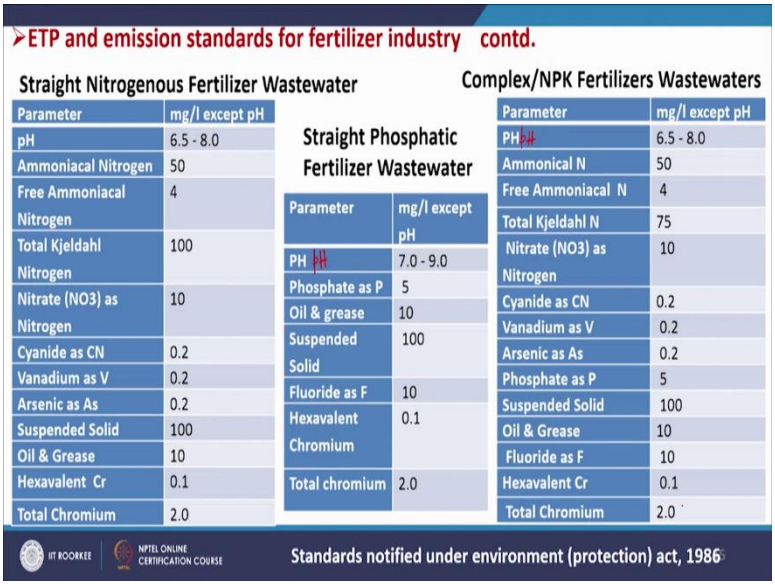

Now, we will discuss on the emission standards. So, straight nitrogenous fertilizer wastewater the standard is like pH should be 6.5 to 8.0, ammoniacal nitrogen 50, and free ammoniacal nitrogen 4, total kjeldahl nitrogen 100 mg/l, nitrate as nitrogen 10, cyanide as CN 0.2, vanadium as V 0.2, arsenic as As 0.2, suspended solids 100, oil and grease 10, hexavalent Chromium 0.1 and total chromium 2.

So, this is for all these units except pH in mg/l and for straight prosthetic fertilizer the pH 7 to 9, phosphate phosphorus 5, oil and grease 10, suspended solid 100, fluoride as F 10, hexavalent chromium 0.1 and total chromium 2.

Similarly, for NPK fertilizers, pH 6.5 to 8, ammonical nitrogen 50, free ammoniacal nitrogen 4, total kjeldahl nitrogen 75, Nitrate as nitrogen 10, cyanide as CN 0.2, vanadium as V 0.2, arsenic as As 0.2, phosphates as phosphorus 5, suspended solids 100, oil and grease 10, fluoride as F 10, hexavalent chromium 0.1, and total chromium 2.0

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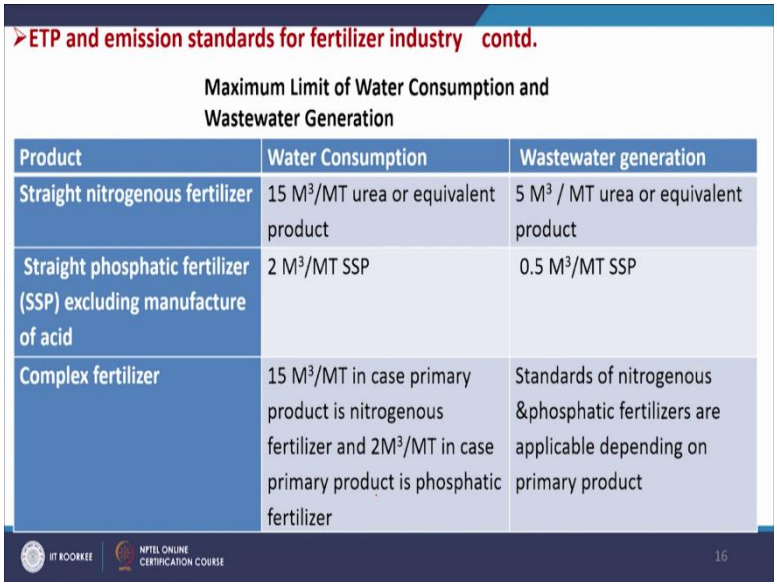

And maximum limits of water consumption and wastewater generation are also provided by the CPCB that is straight nitrogen fertilizer 15 m^3/MT urea or equivalent product that is water consumption and wastewater generation is 5 m^3/MT urea of equivalent product it is recommended and straight phosphatic fertilizer for SSP excluding manufacture of acid that is 2 m^3/MT SSP and wastewater generation 0.5 m^3/MT SSP.

And complex fertilizer that is 15 m^3/MT in case of primary product is nitrogenous fertilizer and 2 m^3/MT in case of primary product is phosphatic fertilizer and standards of nitrogenous and phosphatic fertilizers are applicable depending on primary product.

So, knowing this the variations in the compositions and applying the philosophy of the treatment of wastewater and knowledge we have earned on the basis of the discussions in the last few classes. Now, we can decide a suitable scheme for the treatment of wastewater of these type of industries. Now, we will see for copper smelter.

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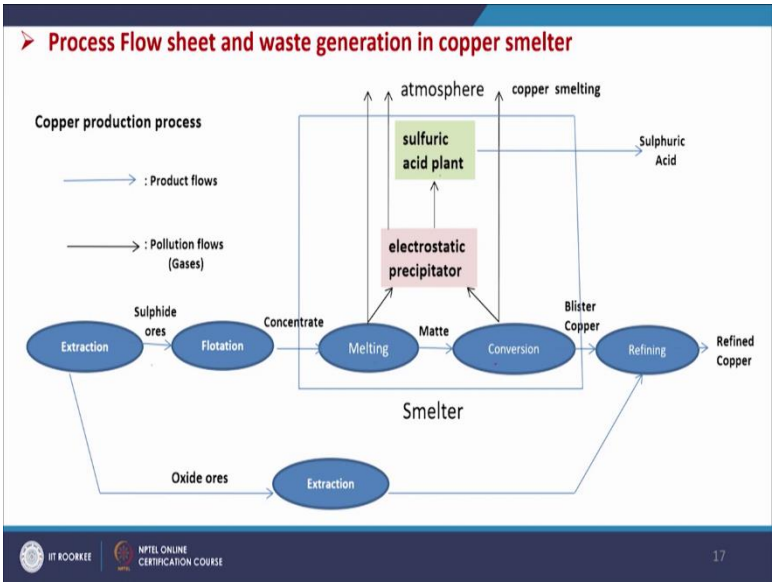

So, we know that from copper ores we get the copper and this copper may be present in ores that is oxide ores or sulphide ores. So, it is oxide ores then metal is extracted from it through hydro metallurgical processes and then if it is sulphide ores then flotation that is separated and through flotation separation or concentration takes place, then it is melted and conversion takes place and then refining it comes. So, there are two routes through which the copper is refined basically.

So, in this operation heating is required. So, as it is hydrometallurgical extraction, so, there will be some solvent. So, in this process, different solvents are mixed in different ratio to make it specific gravity varying from one solvent to other solvent and if the specific gravity of the ore is higher than the solvent, so, it will be settled and if it is lower than this, so, that will be floating so, that a float and sink test can be done also for the separation of the ores. So, that way in this type of operations in smelting operation, we require a large number of solvents and during this operation, the vaporization of the solvent can take place and vapours or VOC can be produced.

So, that will be the one of the important source of emissions in smelting industry. And when sulphide ores are there we see from smelting and conversion process we can get any sulphur containing gases like H_2SO_2, and then these will be converted to that can be converted to sulphuric acid after sulphur recovery. So, that sulphuric acid plant will also emit some acid mist and some particulates matters can also be emitted through this route. So, these are the

atmospheric emissions which can take place and some wastewaters are also generated throughout the process.

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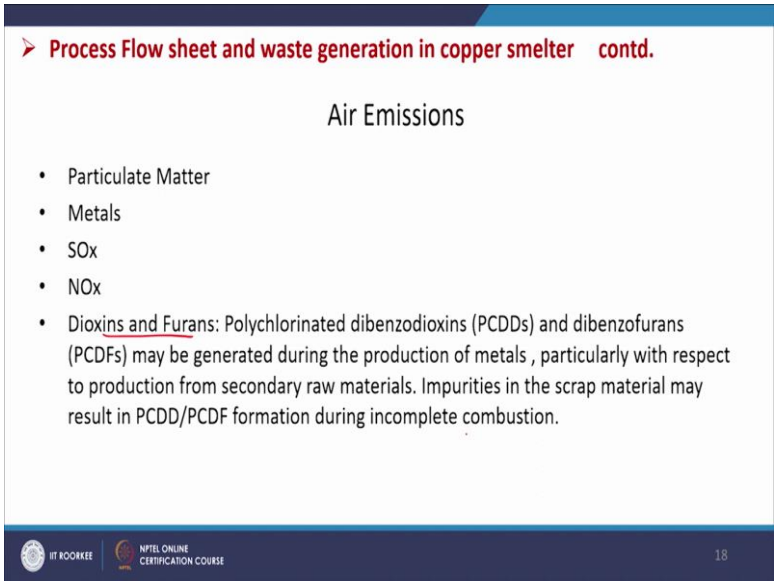

Now, we will discuss the air emissions. So particulate matter metals SOx, NOx are available in the air. Apart from that dioxins and furans are also present in this type of industry. Polychlorinated dibenzodioxins that is PCDD's and dibenzofurans, PCDFs may be generated during the production of metals particularly with respect to production from secondary raw materials, impurities in the scrap material, basically that is secondary raw material that may result in PCDD and PCDF formation during incomplete combustion. So, in that case, many organic compounds were present and those are converted to this.

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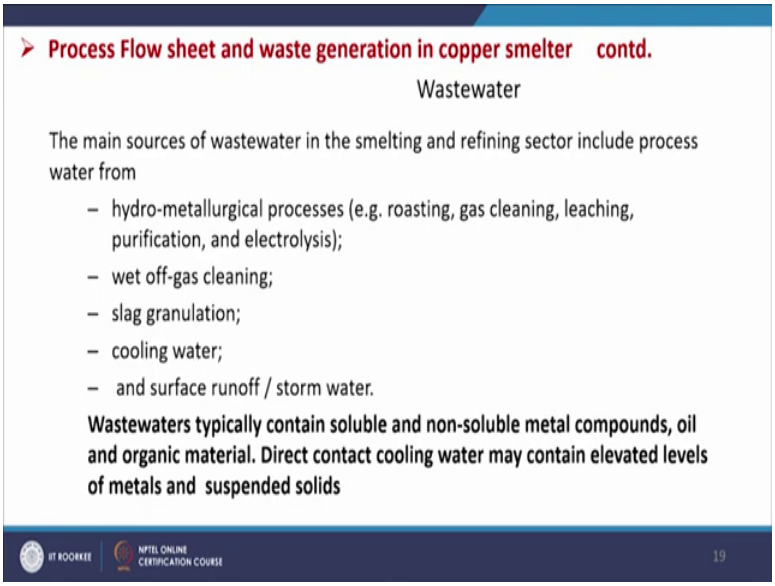

And the main sources of wastewater in the smelting and refining sector includes process water from hydrometallurgical processes, that is roasting, gas cleaning, leaching, purification and electrolysis wet off-gas cleaning, slag granulation and then cooling water and surface runoff, and stormwater. Wastewaters typically contain soluble and non-soluble metal compounds oil and organic material; direct contact cooling water may contain elevated levels of metals and suspended solids.

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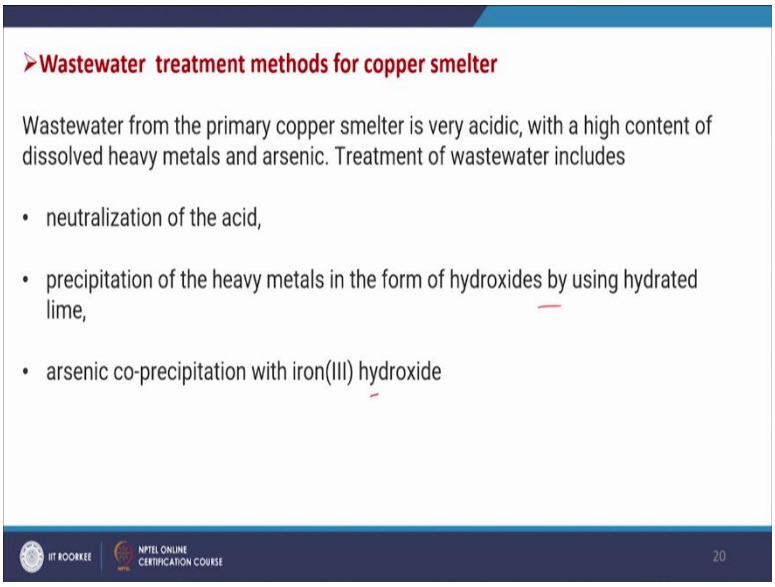

And wastewater from the primary copper smelter is very acidic with a high content of dissolved heavy metals and arsenic. So, this is one unique characteristics of this wastewater that contains arsenic and also its pH is acidic. So, for the treatment of this, we can neutralize it so that pH will be raised and the pH problem will be solved. And arsenic can be co-precipitated with iron(III) hydroxide and specification of heavy metals in the form of hydroxides by using hydrated lime. So, when we are increasing the pH and we are using the lime. So heavy metals can be precipitated. So, these are the special steps which are required for the metal removal in this melting industry.

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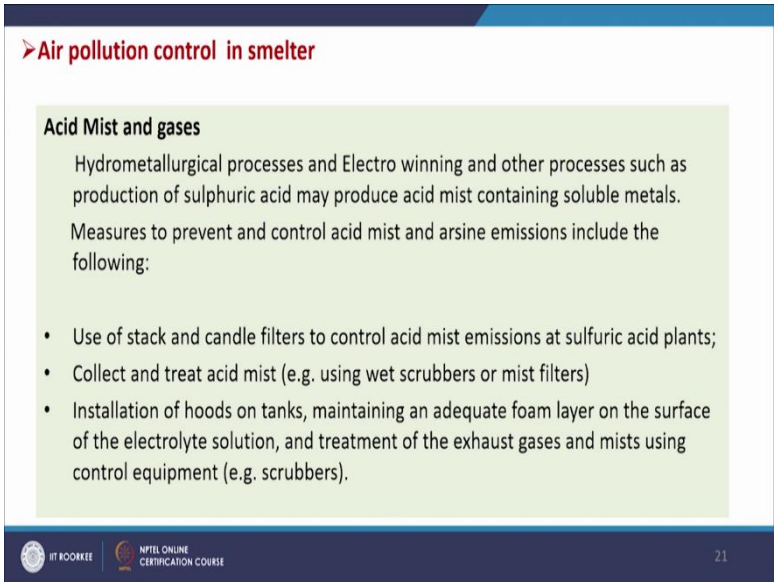

And here, if we see the air pollution, so then in air emission, acid mist, VOC particulate matter all are there. So acid mist and gases through hydrometallurgical processes and electro winning and other processes such as production of sulphuric acid may produce acid waste containing soluble metals. Measures to prevent and control acid mist and arsine emissions include the following that is use of stack and candle filters to control acid mist emissions at sulphuric acid plants.

In sulphuric acid plant already demister pad is used to remove the mists from the gas stream which is going out to the environment. And collect and treat acid mist using wet scrubbers or mist filters that is also one method. And installation of hoods on tanks, maintaining an adequate foam layer on the surface of the electrolyte solution and treatment of the exhaust gases and mists using control equipment. So, these are some measures we can take to eliminate the acid mist from the gases.

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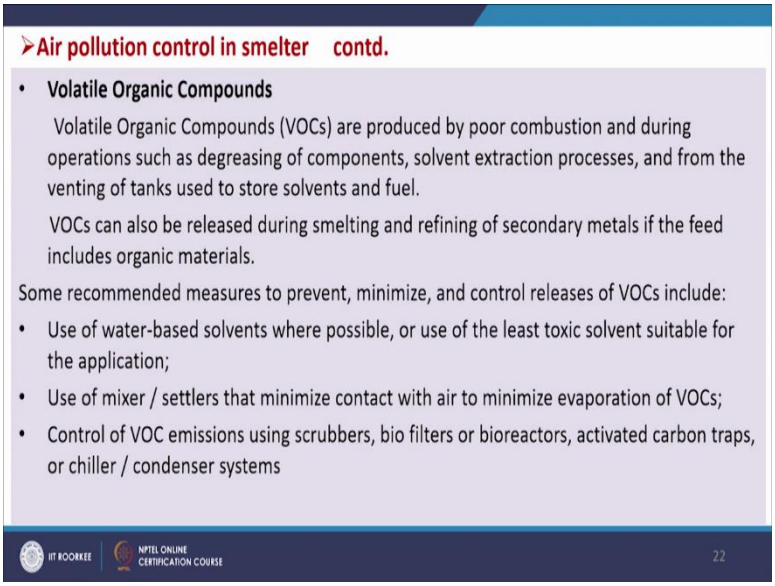

And volatile organic compounds another important pollutants which generated here. So that volatile organic compounds are produced by poor combustion and during operation such as degreasing of components, solvent extraction processes, and from the venting of tanks used to store solvents and fuel. And VOCs can also be released during smelting and refining of secondary metals if the feed includes organic materials. So, if we use the scrap, so, if you had organic material, then also you can get the VOCs.

Some recommended measures to prevent minimize and control releases of VOCs include use of water based solvents where possible or use of least toxic solvents suitable for the application because the solvents are the source of VOCs. So, if we use water, the less VOCs will be produced or if we use organic solvent, then those are not toxic in nature, then also, VOC productions will be reduced. And then use a mixer and settlers that minimize contact with air to minimize evaporation of VOCs and control of VOC emissions using scrubbers, bio filters or bio reactors, activated carbon traps, or chiller or condenser systems.

So, these are the different devices which are used to trap or to capture the VOCs and get it separated from the gas stream. And most important pollutant which it is generated in this type of industry is dioxins and furans.

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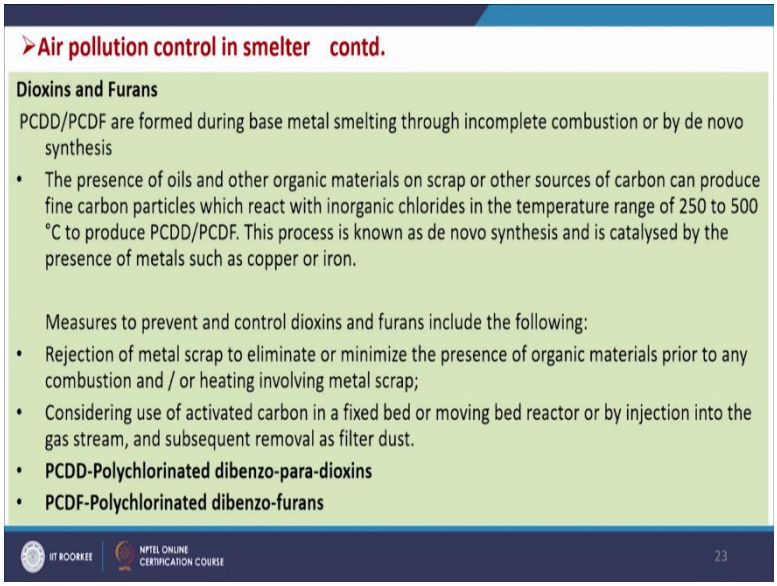

So, these PCDD and PCDF are formed during the base metals smelting through incomplete combustion or by de novo synthesis. The presence of oil and other organic materials on scrap or other sources of carbon can produce fine carbon particles which react with inorganic chlorides in the temperature range of 250 to 500 ^{o}C to produce PCDD or PCDF. And this process is known as de novo synthesis, and is catalysed by the presence of metals such as copper or iron.

So, measures to prevent and control dioxins and furans include rejection of metal scrap to eliminate or minimize the presence of organic materials prior to any combustion or heating involving metal scrap. Considering use of activated carbon in a fixed bed or moving with reactor or by injection into the gas stream and subsequent removed as filter dust. These are the different measures which can be implemented to reduce the dioxins and furans. And now we will see the noise pollution.

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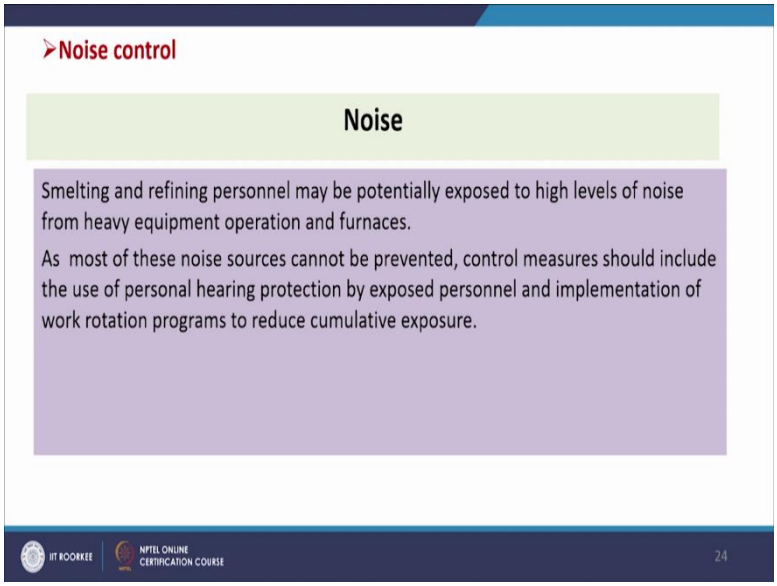

So, smelting and refining personal maybe potentially exposed to high levels of noise from heavy equipment operations and furnaces. As most of these noise sources cannot be prevented, control measure should include the use of personal hearing protection by exposed personal and implementation of work rotation program to reduce cumulative exposure.

So, these are the practices which are actually used in industry. So, people are normally not allowed to work more than 2 shifts. So, noise pollution is applicable for all type of industries so we need to identify where the noise is being created and we need to take action for the elimination of these noise and to reduce its intensity.

So, in this module we have discussed about the wastewater treatment and air pollution control and noise pollution control in different types of industries, up to this in this class. Thank you very much, for your patience.