Physico-Chemical Processes for Wastewater Treatment
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Lecture 57
Case Study Wastewater Treatment in Fertilizer Industry

Good day everyone and welcome to these lectures on Physico-Chemical Processes for Wastewater treatment. So, in the previous lectures, we have studied regarding the wastewater generation and treatment in few of the industries and that included the sugar industry and the fertilizer industry that we will be studying in today's lecture. So, already we studied regarding sugar and distillery. Now, fertilizers are backbone of any country and they essentially help in the growth of plants and because of which, we are able to survive as we are using grains as one of the major source of nutrient for any human being or otherwise.

Now, because of the process of develop process of fertilizer production, that means the Urea production in particular, via the Haber process, the tremendous population that is there on Mother Earth, and in particular in our country that is surviving. So, the Green Revolution only happened because we are able to produce a large amount of fertilizers which is being used in the fields for growth of various grains, etcetera.

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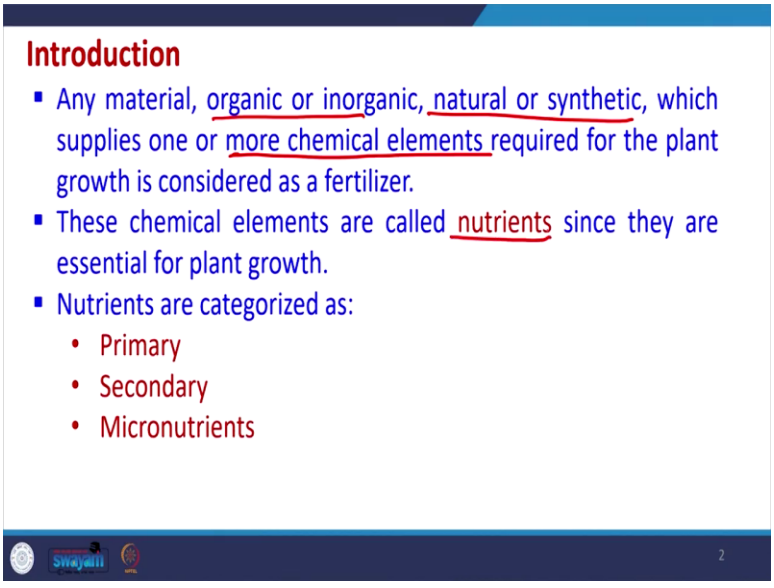

Now, what is fertilizer first? So, any material, which may be organic or inorganic, it may be natural or synthetic, this material which supplies one or more chemical elements, which are

essentially required by the plant for its growth is called as fertilizer. So, any chemical element if we supply additionally, which is not there in the field itself, and that is used by the plant for its growth, it is called as fertilizer, these are also called as nutrients, because, they are essential for the plant growth.

Now, there are nutrients can be categorized into three basic categories primary, secondary and micronutrients. So, essentially in 1970s 1980s, it was found that the nitrogen, phosphorus and potash, these were the three key elements which are actually missing in the soil. So, we need to supply all these elements from outside. Now, we understand that the fixing of nitrogen from atmosphere to the soil can be done only by a few plants and there is no other mechanism. So, that is why the Haber process via which we are we were able to synthesize ammonia and then ammonia was converted further into Urea is considered as one of the most important researches in the previous century, which is helping us survive on Mother Earth.

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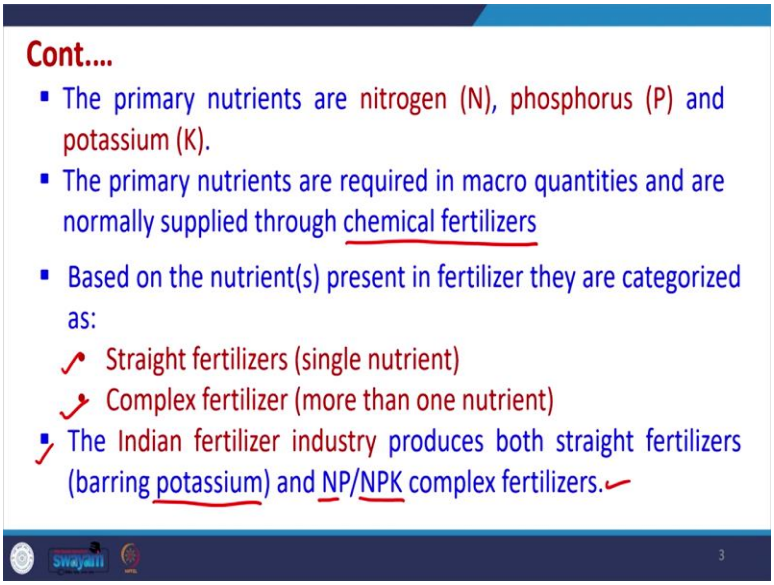

Now, going further, the primary nutrients are nitrogen, phosphorus and potassium. Now, within this there are the primary nutrients are required in large quantity or micro quantity by the plants for their growth and they are generally nowadays supplied via the chemical fertilizers. Now, based upon the nutrients, the fertilizers can be classified into straight fertilizers and complex fertilizers.

So, what are straight fertilizers which contain only one single nutrient, whereas complex fertilizers contain more than one nutrient. So, in the Indian fertilizer industry, we are actually manufacturing both straight fertilizers, barring potassium and we are also manufacturing complex fertilizers like nitrogen, phosphorus or nitrogen, phosphorus and potassium all mixed together as complex fertilizer. So, we have industries which are producing both straight fertilizers as well as complex fertilizers.

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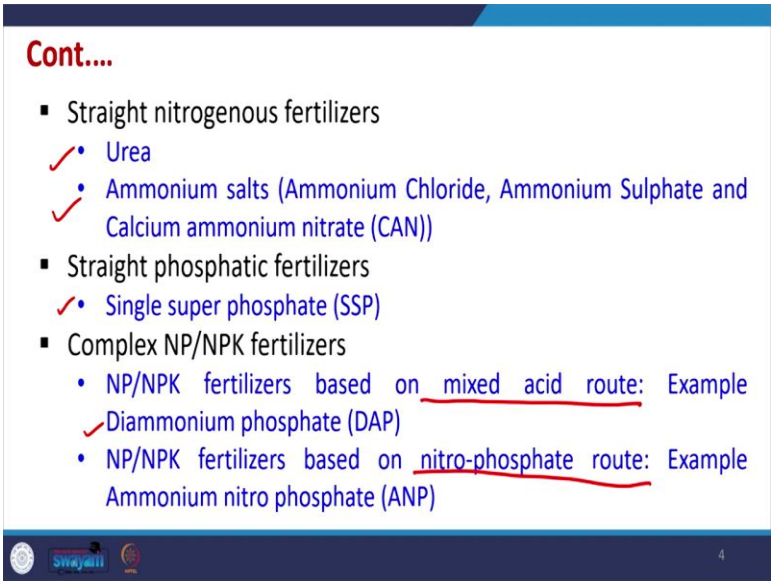

Now, straight nitrogenous fertilizers include urea, ammonium salts, so and these ammonium salts include ammonium chloride ammonium sulphate, calcium ammonium nitrate So, all these are straight nitrogenous fertilizers. Similarly, we have a straight phosphatic fertilizer also which is single super phosphate so, this is being produced in India.

Now, that complex fertilizers which are produced in India, they are based upon the mix acid route on the basis of nitro phosphate route. So, the example is Diammonium phosphate is based upon the mixed acid route, whereas the ammonium nitro phosphate which is manufactured it is based upon the Nitro phosphate route. So, these are the different types of fertilizers which are being manufactured within our country.

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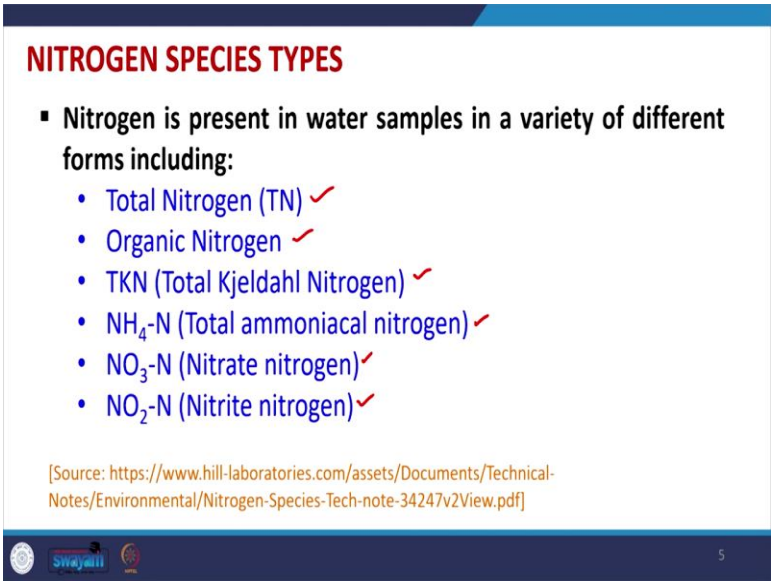

Now, in the water which is generated any water may contain nitrogenous species in different ways. So, it can contain various types of nitrogenous compounds straightforward like pyridine, picoline Urea many other types of nitrogenous compounds are possible. Now, in addition the nitrogenous element can be classified or the presence of nitrogen in water sample can be categorized into a different water quality parameters.

And these parameters are that what is the total nitrogen? How much amount of organic nitrogen is there? How much amount of total Kjeldahl nitrogen? then total ammoniacal nitrogen? so, nitrogen in the form of ammonia then total nitrate nitrogen and total nitrite nitrogen so, all these classifications are possible with respect to presence of nitrogen in the water sample.

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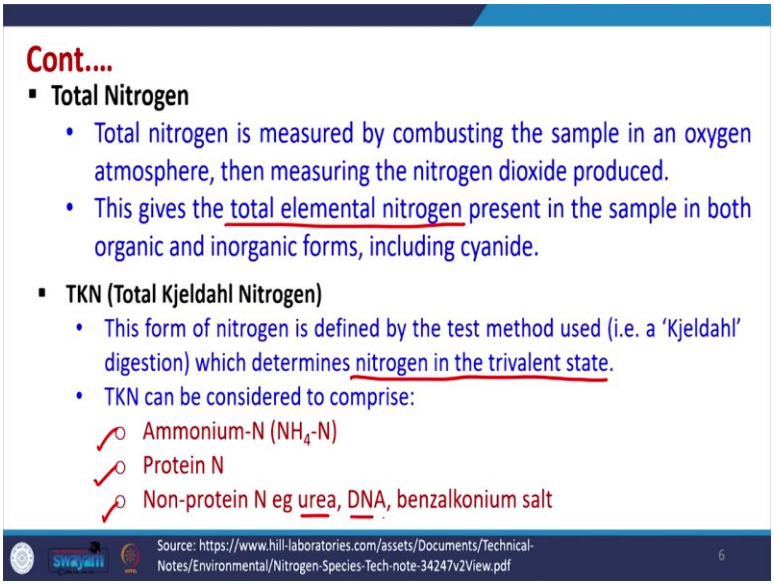

So, let us understand these also. So, total nitrogen is measured in particular in any wastewater from fertilizer industry or any other industry by combusting some sample in an oxygen atmosphere and then measuring their nitrogen dioxide produced. So, by a bag calculation we can find out the total nitrogen present in the water. So, this particular method gives the idea regarding the total elemental nitrogen present in the sample in both organic or inorganic form including the cyanide, so, we will be getting total elemental nitrogen present in any water sample.

Then TKN the total Kjeldahl nitrogen is very important parameter. So, actually, this form of nitrogen is defined by the test method which is used as Kjeldahl digestion method and which determines nitrogen in the trivalent state. So, we try to find out the nitrogen which is there in the trivalent state. So, TKN can be considered to comprise of ammonium nitrogen, proteinous nitrogen and non proteinous nitrogen including Urea DNA and other types of salt as well.

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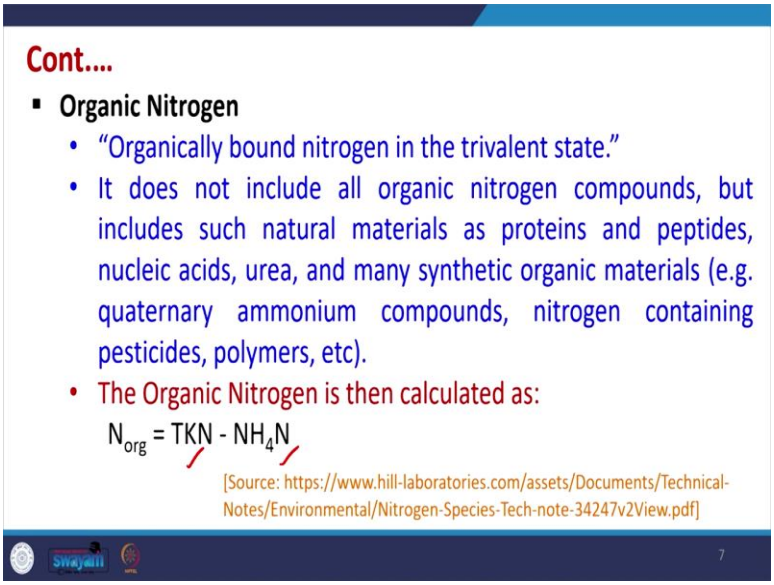

Then organic nitrogen, the organic bond nitrogen in the trivalent state we are considering with respect to organic nitrogen. It does not include all other organic nitrogen compounds, but includes such natural materials as proteins and peptides, nucleic acids, Urea and many synthetic organic materials example quaternary ammonium compounds, nitrogen-containing pesticides, polymers etcetera. So, all these compounds are considered the organic nitrogen is then calculated as the total Kjeldahl nitrogen minus ammoniacal nitrogen so, we subtract the ammoniacal nitrogen and we get the organic nitrogen. So, this is how it is find out.

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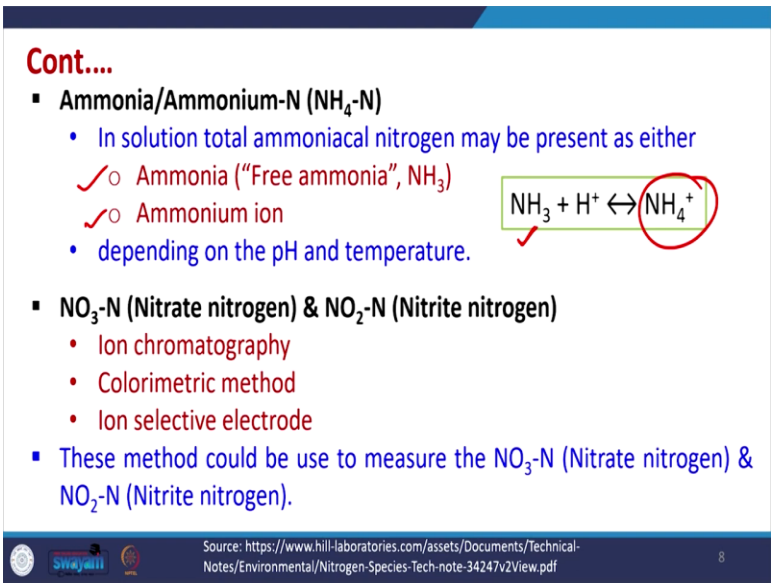

Now, the ammonia or ammonium nitrogen in solution that total ammoniacal nitrogen may be present as either ammonia which is free ammonia like here or it may can get converted into ammonium ion which is given here. So, depending upon the pH and temperature so, the ammonia or ammoniacal nitrogen actually measures both ammonia, free ammonia or ammonium ion. Similarly, nitrate or nitrite nitrogen can be found out by different methods including Ion chromatograph, colorimetric method, ion selective electrodes etcetera. So, these methods could be used for measuring any of the nitrate or nitrite nitrogen so, this is there.

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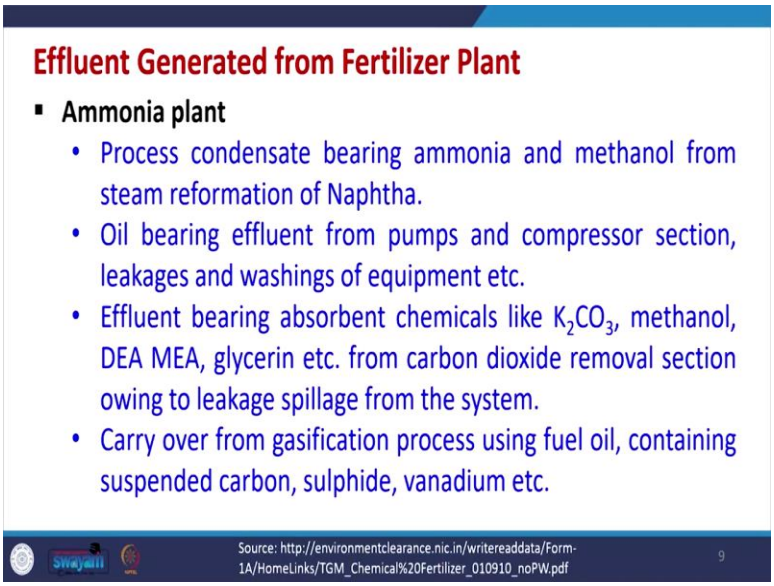

Now in the fertilizer plant without going much deeper into how the fertilizers are produced. There are different types of effluent that can be generated. So, the ammonia plant can generate effluent.

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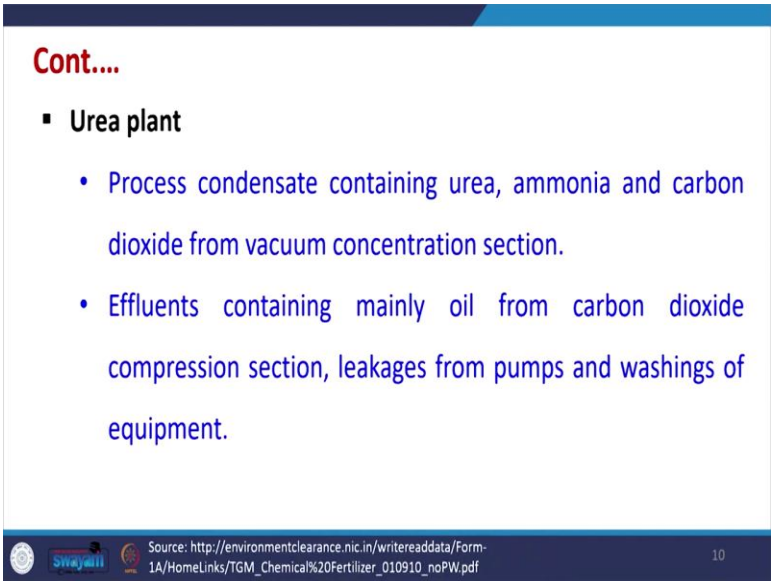

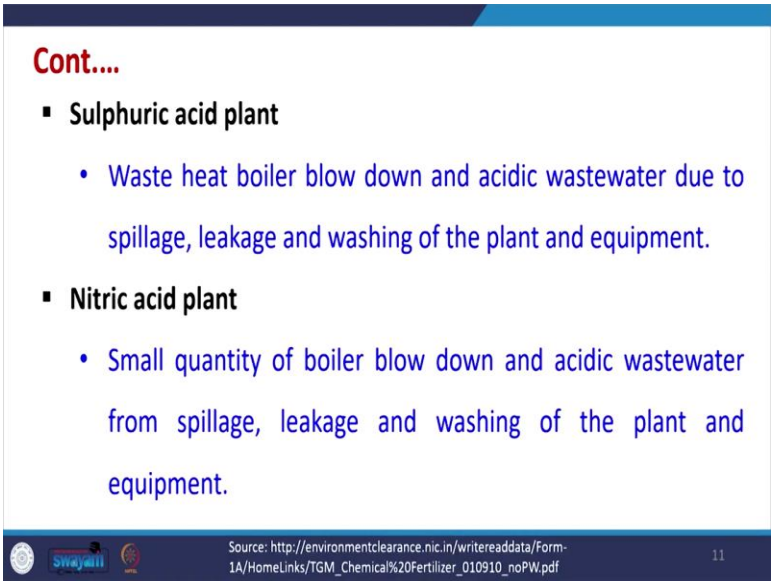

Similarly, there are other plants which can generate effluent including Urea plants sulphuric acid plant, nitric acid plant, single super phosphate plant, so, all these plants can generate different type of effluent.

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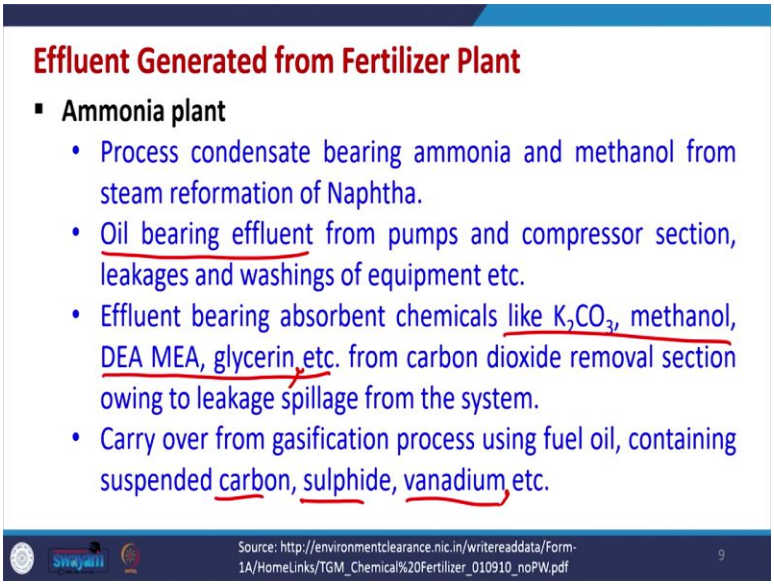

So, let us try to understand a little bit of the basics of this. So, ammonia plant, so, the process condensates bearing ammonia and methanol from the steam the formation of naphtha so, they may be present in the effluent which is generated from the ammonia plant then oil bearing effluent from pumps, compressors section, a leakage and washings of the equipment's etcetera will be present in this oil-bearing effluent.

Then effluent bearing absorbent chemical sets test K2CO3 methanol DEA MEA, glycerin etcetera from carbon dioxide removal section may be present and this is because of the leakage spillage from the system. So, these effluents will be containing this type of chemicals and this will be generated from the carbon dioxide removal section. Similarly, carry over from gasification process using fuel oil containing various types of carbon sulphide vanadium etcetera may be present. So, all these possibilities of effluent are there in an ammonia plant.

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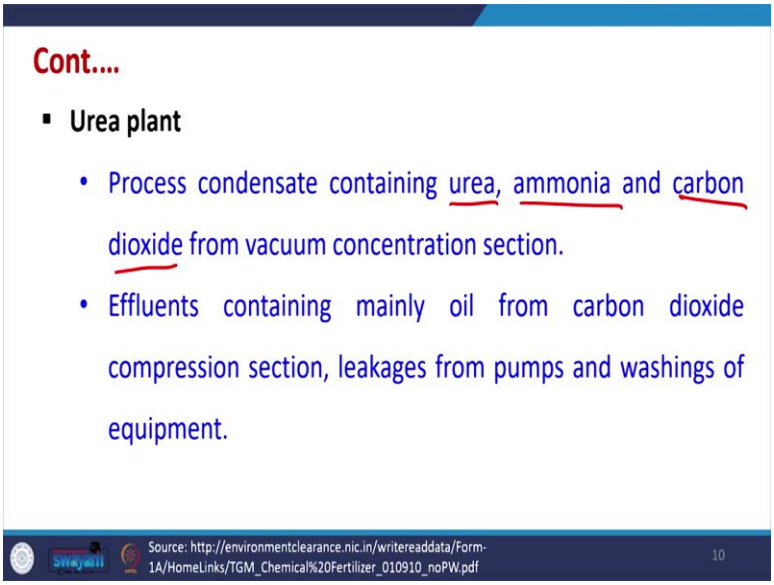

Similarly, Urea plant so, in the Urea plant process condensates containing urea, ammonia, carbon dioxide from vacuum concentration unit may be getting generated and that will be containing these compounds. Similarly, effluents containing many oil from carbon dioxide compression section, leakages from pumps and washing of equipment's may be present in the Urea plants so, these effluents may get generated in the Urea plant.

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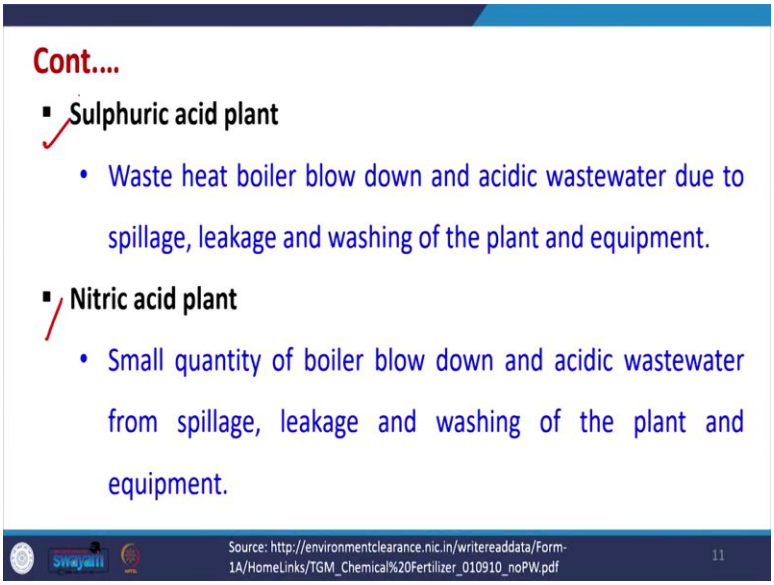

Similarly, in the sulphuric acid plant waste heat boiler blowdown and acidic wastewater due to spillage, leakage and washing from the plants and equipments may be there. For the nitric acid

plant a small quantity of boiler blow down so, that will be there. Then acidic wastewater from spillage leakage and washing of the plant and equipment will be presence. So, both have very similar type of wastewater getting generated.

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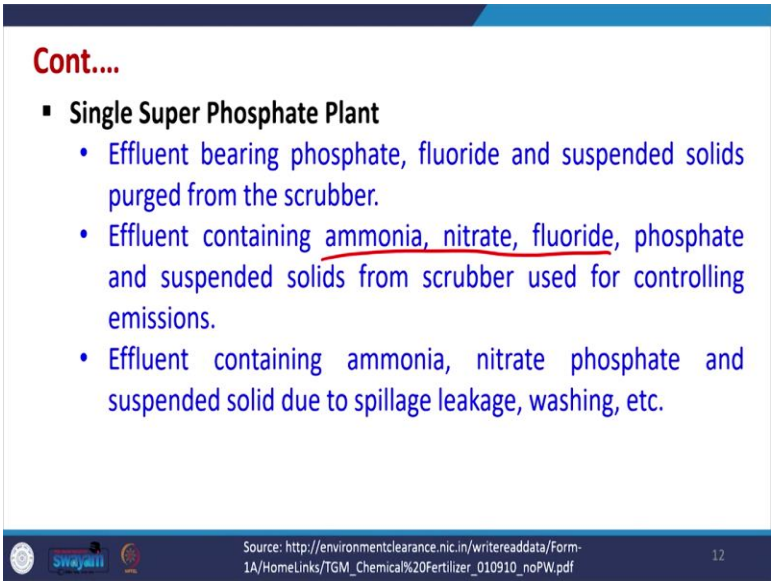

Then the single super phosphate plant. In this the effluent containing phosphate, fluoride and suspended solids from the scrubber may be getting generated also effluent containing ammonia, nitrate fluoride phosphate and suspended solid from scrubber which is used for controlling the emissions from there the effluent may be getting generated. Also, the effluent containing ammonia nitrate, phosphate and suspended solid may be getting generated due to spillage, leakage and washing etcetera. So, this type of effluence may get generated in different types of fertilizer plant.

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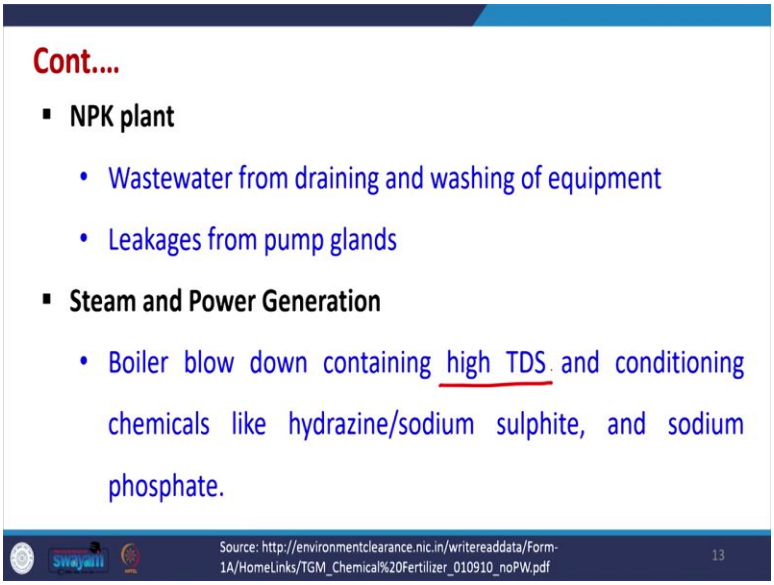

Now NPK plant the wastewater from draining and washing up equipment and also from leakages from pump glands etcetera. will be there. In the steam and power generation unit also, the boiler blowdown containing high TDS and conditioning chemicals such as hydrazine, sodium sulphite and sodium phosphate may get generated.

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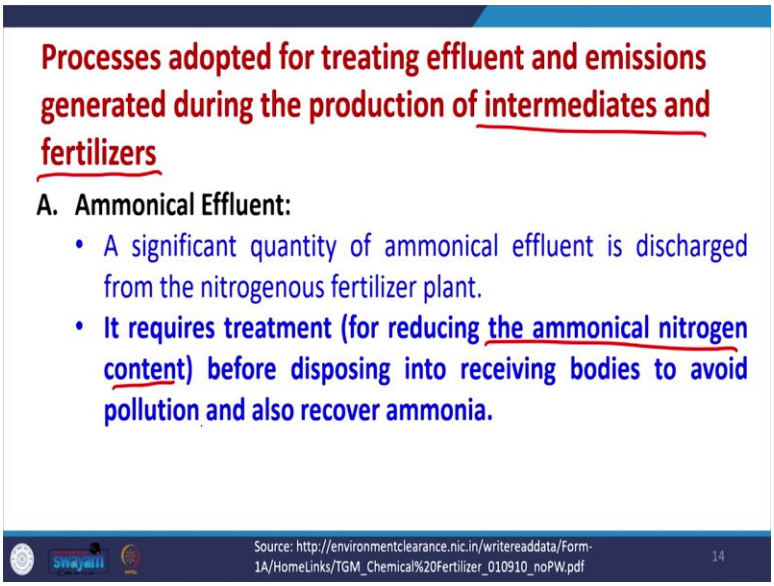

Now, what are the processes which are being adopted for teat meant of effluent and emissions generated during the production of intermediates or fertilizers in various fertilizer industries. So,

that are discussed here. So, one by one we will be discussing each of the plant and what are the various processes which have been adopted for treatment of such effluent.

So, in the ammoniacal effluent if it is getting generated in any of the plant, so, I saw how to tackle with this? A significant quantity of ammoniacal effluent is discharged from nitrogenous fertilizer plant. So, it requires treatment because we have to reduce the ammoniacal nitrogen content before this disposing this into receiving bodies to avoid pollution and also, we do this to recover the ammonia as much as possible.

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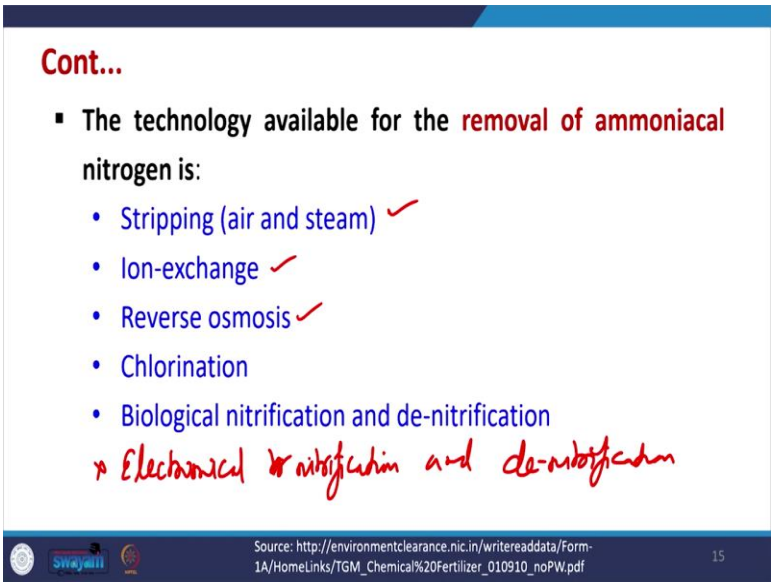

So, for doing this that technology available for removal of ammoniacal nitrogen includes a stripping, air and steam. Similarly, ion exchange units can be used for doing this. Reverse osmosis units have been used for treatment of such wastewaters, chlorination and biological nitrification and denitrification.

One more thing that we our self in our research group are doing a lot of work on electrochemical treatment or electrochemical nitrification and denitrification. So, this is also possible and this is this is under development stage, so this is also possible to do this both electrochemical nitrification and denitrification. So, this is possible and this technology is also getting slowly slowly developed for treatment of such effluence.

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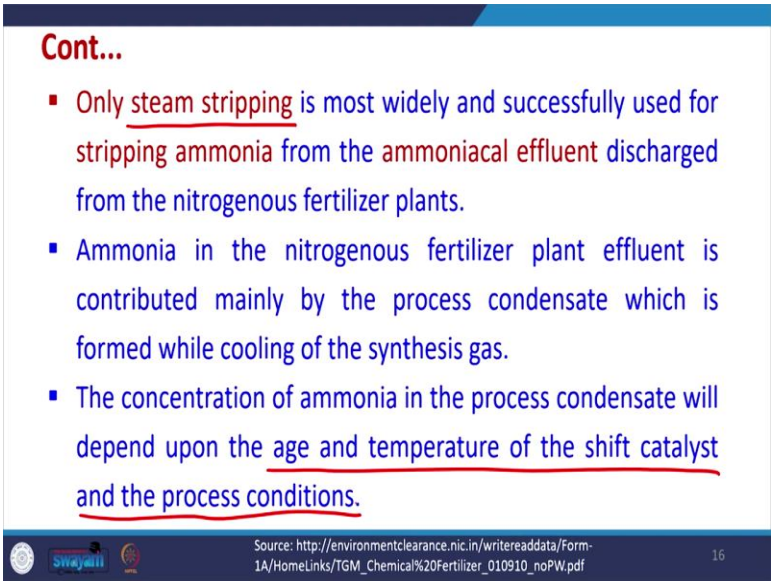

Now, only steam stripping is most widely and successfully used for stripping ammonia from ammoniacal effluent. So, this is this is the most common method which is being used. So, ammonia in the nitrogenous fertilizer plant effluent contributes is mainly from the process condensate and which is found while cooling of the synthesis gas. So, the concentration of the process ammonia in the process condensate it depends upon the air and temperature of the SIFT catalysis and the process conditions. So, if we can improve upon this certainly the concentration of the ammonia will get reduced.

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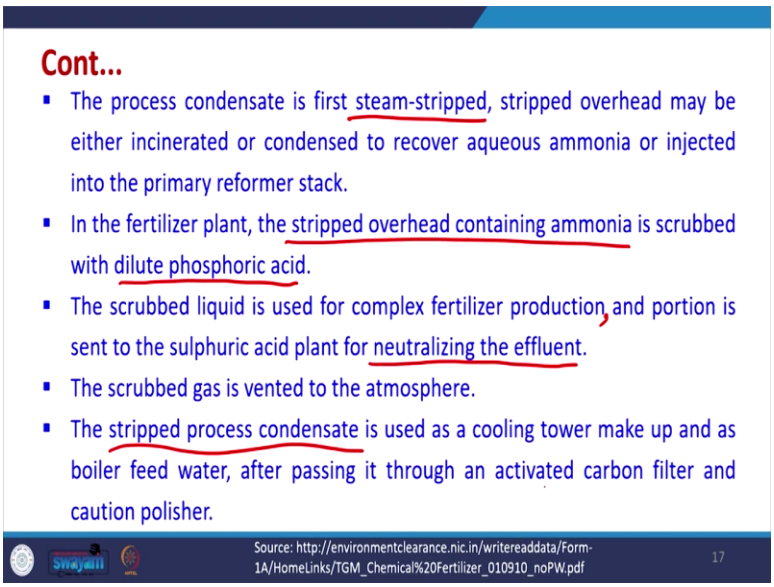

So, and so, far what is done is that the process condensate is first steam stripped and the stripped overhead is either incinerated or condensed to recover the aqueous ammonia or is injected into to the primary reformer stack in the fertilizer plant they stripped overhead containing ammonia is further escaped with dilute phosphoric acid. So, this is done the scrubbed liquid is used for complex fertilizer production and some other portion is sent back to the sulfuric acid plant for neutralizing the effluent So, we can use it for various purposes, this is possible.

The scrubbed gas is vented to the atmosphere. The stripped process condensate it is used as a cool is used in the cooling tower makeup also as boiler feed water after passing it through activated carbon filter. So, we have absorption unit which is there and some polisher is used before using the stripped process condensate in the cooling tower makeup or for boiler feed water. So, this is possible.

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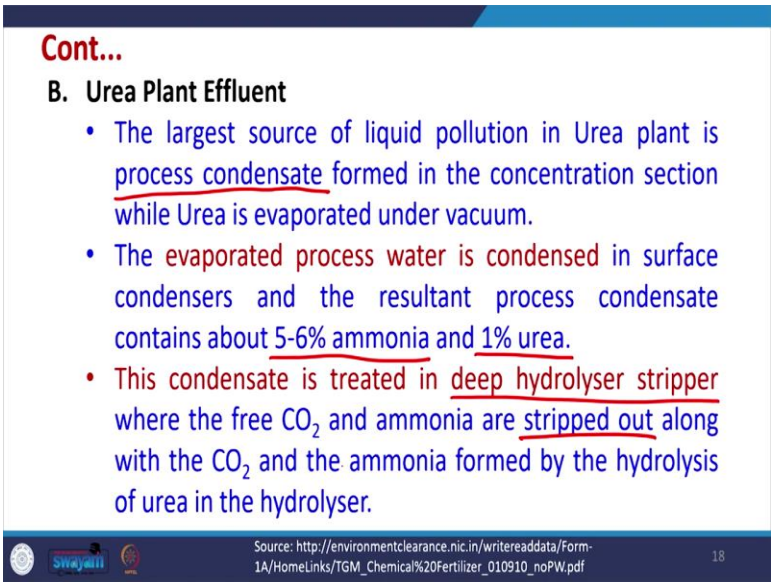

Now, going further Urea plant effluent. So, the largest source of the liquid pollution in Urea plant is process condensate which is formed in the concentration section while Urea is evaporated under vacuum. So, this is where the liquid pollution is happening. So, the evaporated process water is condensed in the surface condenser and the resultant process condensate contains 5 to 6 percent ammonia and 1 percent urea. So, the how it is treated? The condensate is treated in the deep hydrolyzer stripper section, where the free carbon dioxide and ammonia are

stripped off. So, they are stripped. Along with the CO2 and ammonia formed by the hydrolysis of the Urea in the hydrolyzer, so, this is this happens.

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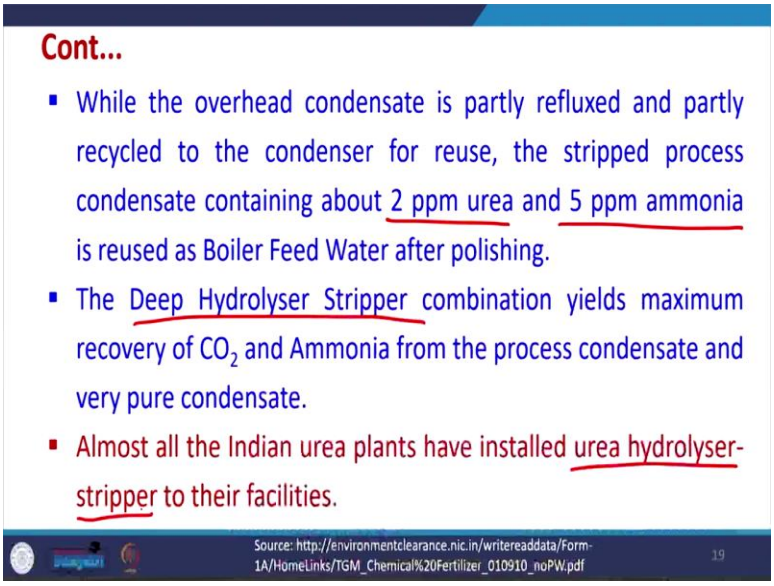

While the overhead condensate is refluxed and partly recycled to the condenser for reuse. The stripped process condensate contains about 2 PPM Urea and 5 PPM ammonia and you, it is reused as the boiler feed water after polishing again with activated carbon filter or further treatment. So, before using as boiler feed water, it may be treated a little bit. The deep hydrolyzer stripper combination yields maximum recovery of carbon dioxide and ammonia from the process condensate and we get very poor condensate. So, almost all the Indian Urea plants have installed this Urea hydrolyzer is cheaper in their facilities. So, this is there.

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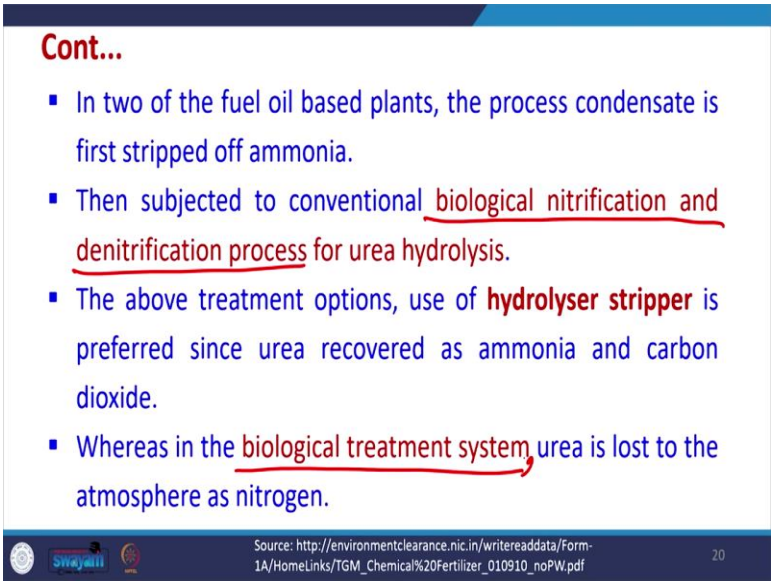

In the two of the fuel oil-based plants within India, the process condensate is first stripped of ammonia and then it is conveyed is subjected to conventional biological nitrification and denitrification for Urea hydrolysis. So, the above treatment options use of either hydrolyzer stripper is preferred since Urea recovered as ammonia and carbon dioxide whereas the in the biological treatment systems that if they are used Urea is lost to the atmosphere as nitrogen. So, hydrolyzer stripper is preferred because we have we can reuse the ammonia and carbon dioxide whereas, in the biological treatment system we are losing the Urea by converting it to atmospheric nitrogen, so this is there.

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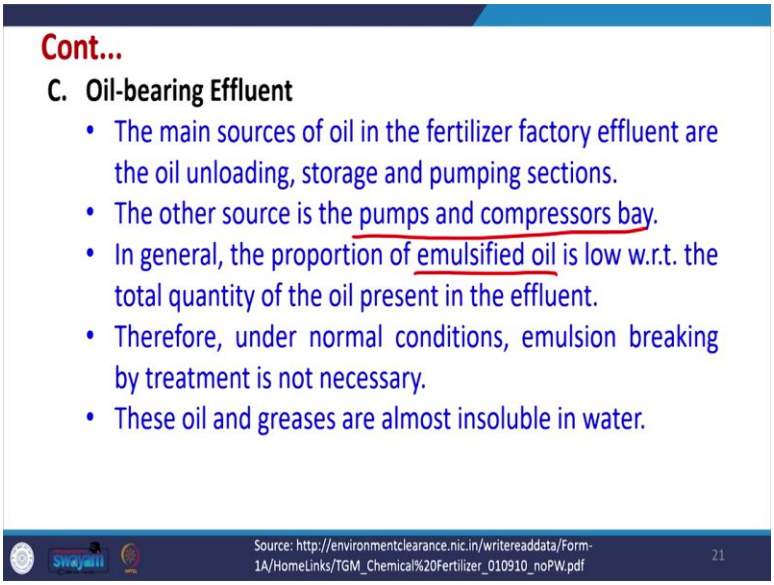

Then we have a lot of oil-bearing effluent which are getting generated in this fertilizer industry. So, the main source of oil in the fertilizer, factory effluents are the oil unloading storage and pumping sections the other sources are the like pumps and compressor bay. So, this is there. So, in general the proportion of emulsified oil is low with respect to total quantity of oil present in the effluent so, we will be having very less quantity of emulsified oil. So, therefore, under normal condition, emulsion breaking is not necessary. So, these are oil and grass greases which are there they are almost insoluble in water and we can use different methods for their removal.

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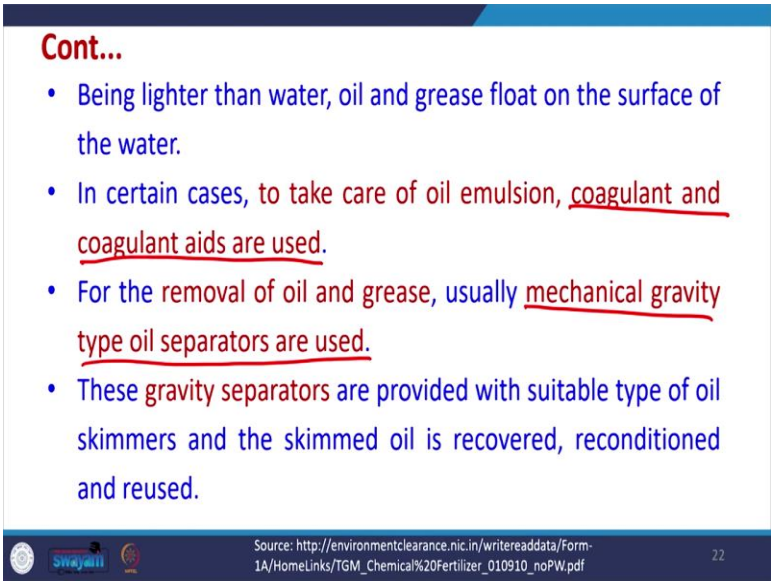

Now being lighter than water oil and grease floats on the surface of the water. So, in the certain cases to take care of oil emulsion, coagulant and coagulant aids are used. This is one of the method for removal of oil and grease, the mechanical gravity type of oil separators are also used. And these gravity separators are provided with suitable type of oil skimmers and the skim oil is recovered and reconditioned. In this method also, the electrochemical treatment in combination with mechanical gravity type of oil separators are also being researched and further for further use. So, this electrochemical with mechanical gravity type of oil separators they can be combined together for enhancing the efficiencies.

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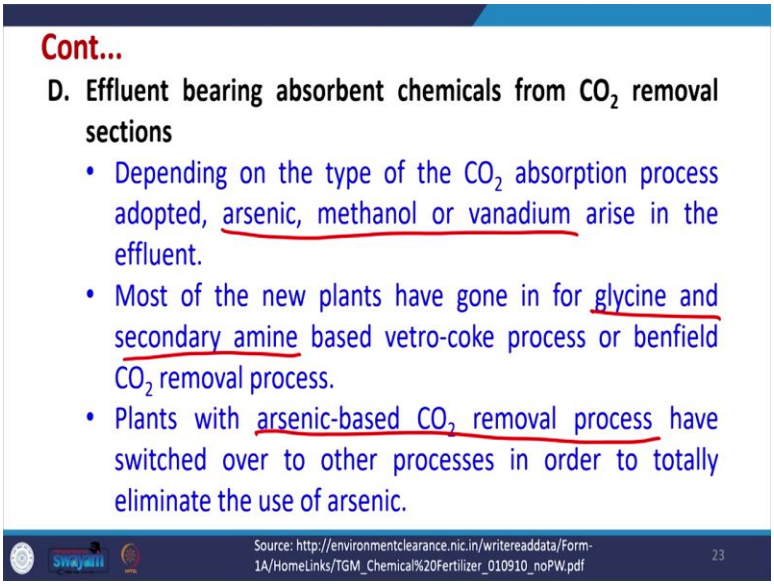

Now, effluent bearing absorbent chemical from CO2 removal section for such effluent So, depending upon the type of CO2 absorption process adopted arsenic, methanol or vanadium may arise in the effluent. So, most of the new plants have gone in far glycine and this secondary amine based Vetro-coke process our likes or Benfield CO2 removal process, so, plants with arsenic based CO2 removal processes have switched over to other type of processes in order to totally eliminate the use of arsenic, but still it may be present.

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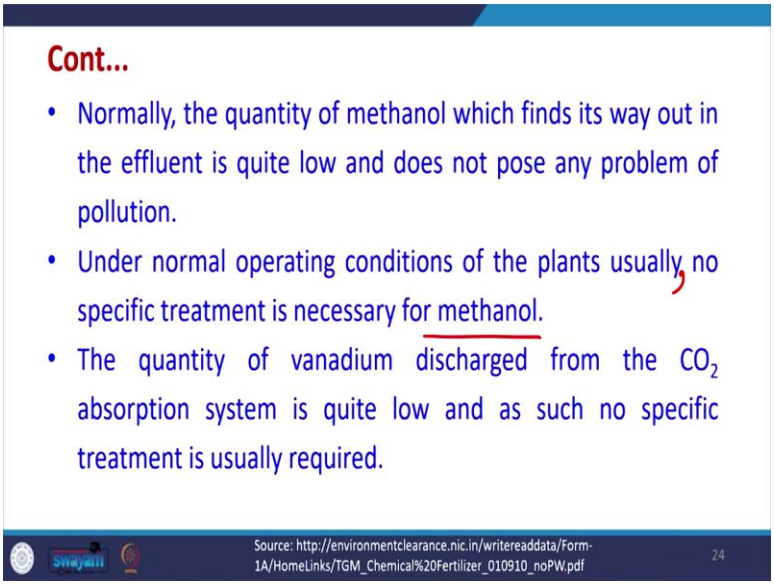

So, normally the quantity of methanol which is present in the effluent is low and does not cause that much problem. So, under normal operating plant a no specific treatment is done with respect to methanol but arsenic certainly we have to remove. The quantity of vanadium which is discharged from this system is also low and no specific treatment is required.

So, in general a common effluent is good enough. So, we can adopt any other technologies with respect to arsenic and vanadium removal along with methanol absorption. So, that is possible to treat such effluent. So, we can use adsorption, we can use coagulation-flocculation. So, any of the common techniques can be considered for treatment as such effluent.

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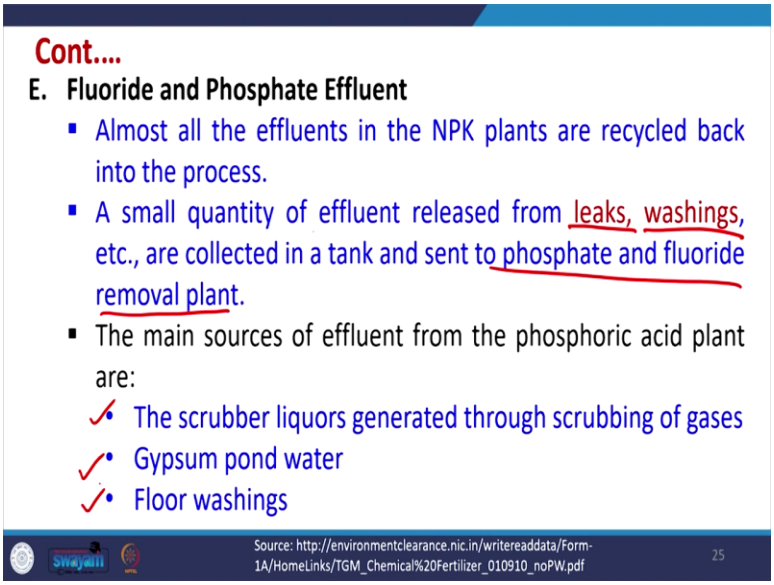

Now, fluoride and phosphate effluent. So, almost all the effluent in the NPK plants are recycled back into the process itself and a small quantity of effluent is released which is containing the leaks, washings, etcetera. And it is collected in a tank and set to the phosphate and fluoride removal plant because they will be essentially containing phosphates and fluoride. The main source of effluent from phosphoric acid plants are the scrubber liquids generated through a scrubbing of gases. The gypsum pond water and the floor washing so all these are the main sources of effluent which are getting generated.

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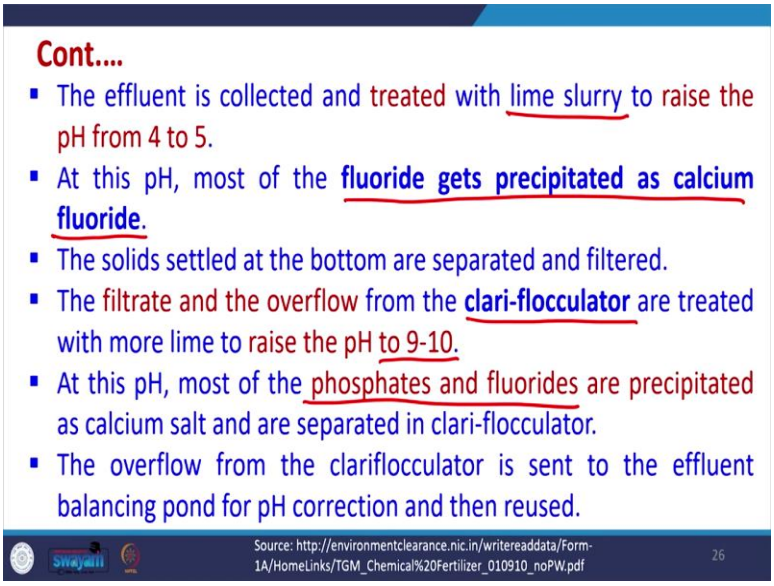

So, what is done is that, that the effluent is collected treated with lime slurry. So, we are using lime slurry to increase the pH from up to 4 to 5. Then at this pH most of the fluoride gets precipitated as calcium fluoride. So that will go as calcium fluoride. So, we are already using lime slurry, the solids settled at the bottom are separated and filter.

The filtrate and overflow from the clari-flocculator is treated with more lime to raise the pH to 9 and 10 and at this condition the phosphates and fluorides are further precipitated as calcium salts and separated from the clari-flocculator. So, the overflow from the clari-flocculator is further sent for in the balancing pond for pH correction and then further reuse itself in the industry itself, so this is there.

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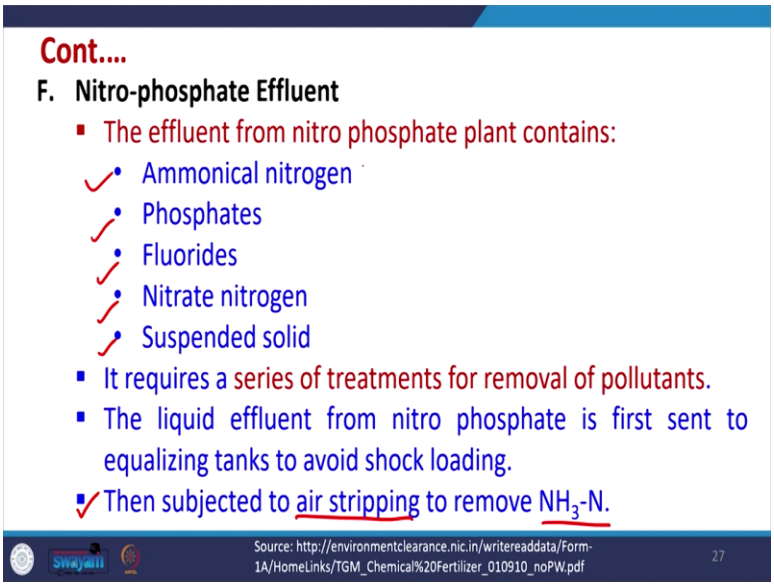

Now, then there is a nitro phosphate effluent may get generated and at this will contain ammonical nitrogen, phosphate, fluorides, nitrate, nitrogen and suspended solid. So, it will require a series of treatment for removal of these pollutants. So, depending upon the concentration of these pollutants present a different strategies may be adopted to treat such effluent. So, that liquid effluent from nitro phosphate is first sent to the equalizing tank to avoid a shock loading and then it is air stripped to remove the armonica nitrogen. So, first this may be removed. So, this is there.

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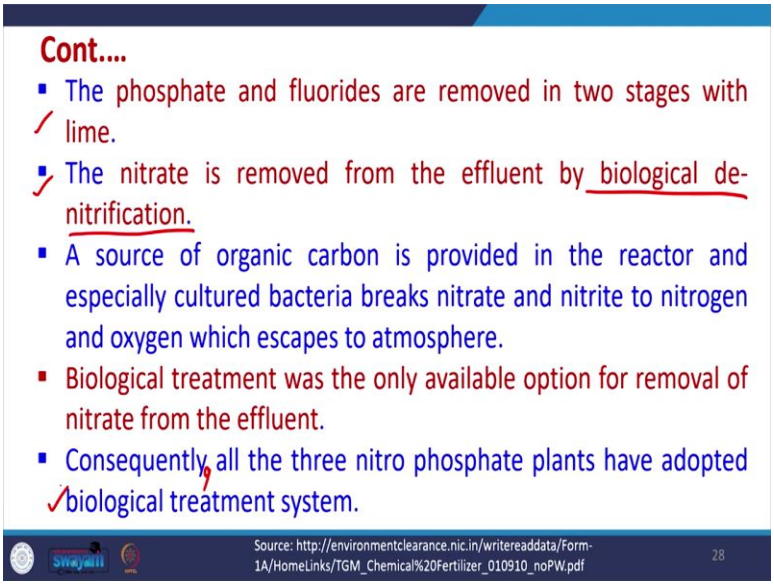

The phosphates and fluorides are removed in two stages with lime as we have discussed earlier. The nitrate is removed from the effluent by biological denitrification process. So, this is done. A source of organic carbon is provided in the reactor and specially cultured bacteria breaks nitrate and nitrite to nitrogen and oxygen which escapes to the atmosphere in this biological denitrification.

Biological treatment was the only option available for removal of nitrate from the effluent till now, but there are other technologies including electrochemical technologies, which are a lot of research is going on and they may come into picture soon. So, this is there. So, now in most of the plants, because all the 3 nitro phosphates plants have generally they are using right now biological treatment options, but other options are also coming into the picture.

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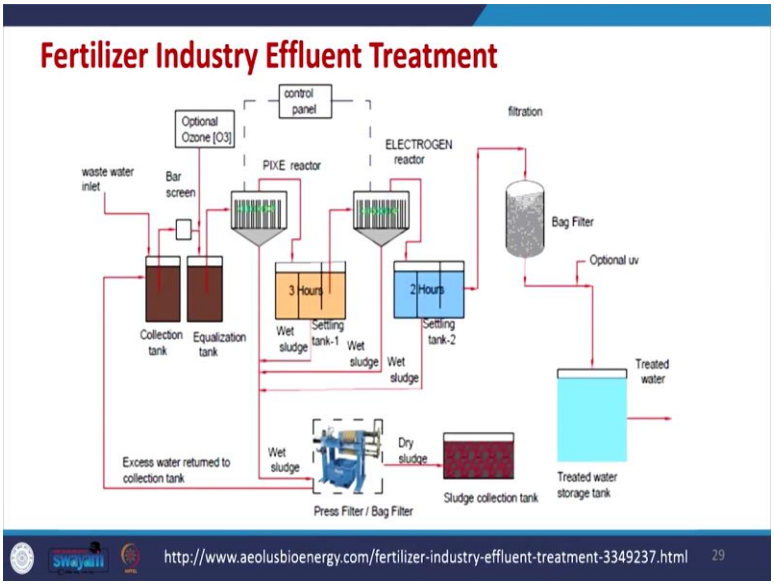

So, this is a common fertilizer industry effluent system maybe there. So, we may have different types of treatment unit depending upon the requirement. So, we are not discuss that.

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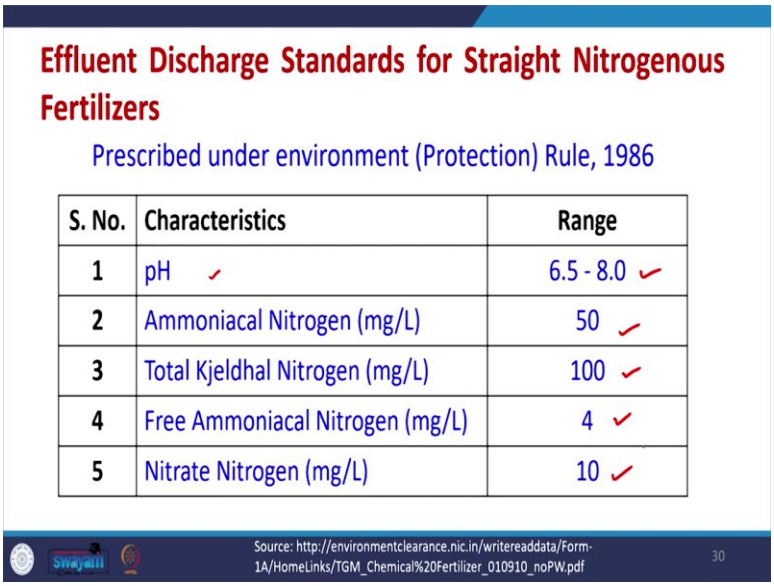

Now, effluent discharge standards for a straight nitrogenous fertilizer. There are different a government of India has stipulated certain standards. So, after treatment, the effluent should always comply to these range of characteristics. So, what are their range, so, pH should be between 6.5 to 8, the Ammoniacal nitrogen should be less than 50. The total Kjeldhal nitrogen

should be less than 100, the free ammoniacal nitrogen should be less than 4, nitrate nitrogen should be less than 10. So, this is there.

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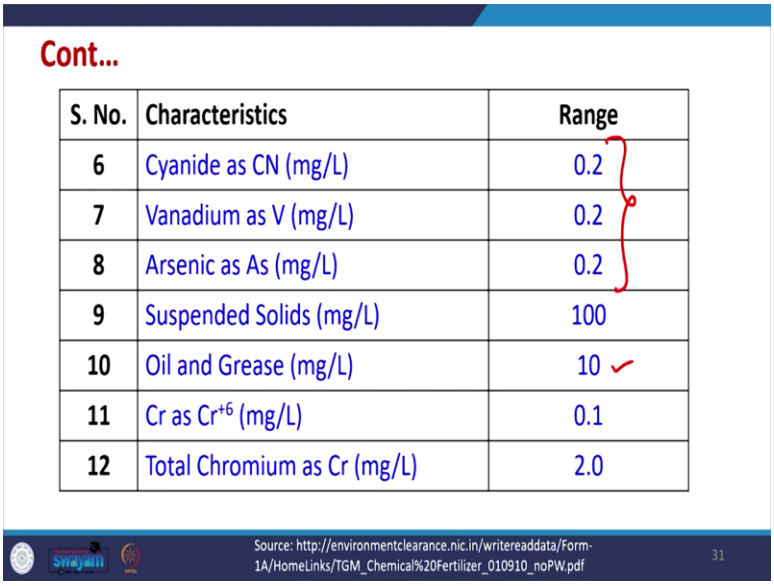

Similarly, Cyanide may be present. So, Cyanide, vanadium, arsenic all have to be less than 0.2 milligrams per liter, suspended solid is allowed maximum 100 milligram per liter. So, oil and grease have to be less than 10 milligram per liter. Similarly, chromium and total chromium may also be present. So, that have to be limited to 0.1 and 2 milligram per liter.

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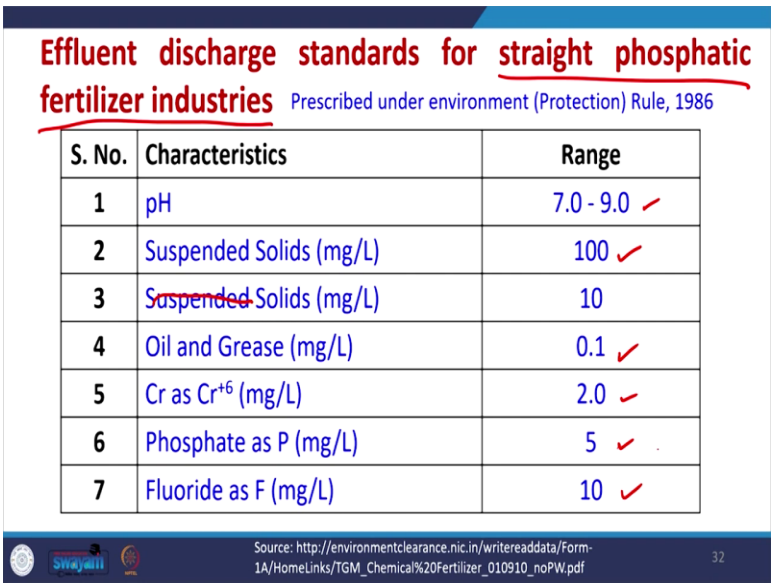

And for straight phosphatic fertilizer industries, the respective standards which have been prescribed are there. The pH should be between 7 to 9, suspended solids, Sorry, there is a mistake here. So, suspended solids should be less than 100 milligram per liter. Oil and grease should be less than 0.1, chromium and chromium as chromium 6 should be less than 2 milligram per liter. Phosphate and fluoride also are limited up to 5 and 10 milligram per liter.

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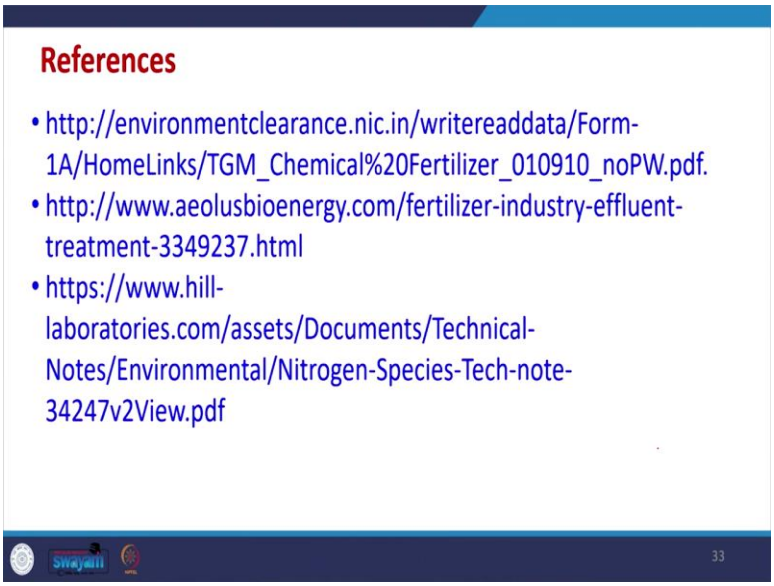

So, these are the various references which have been used in this slide making. Some fertilizer industry is one of the most important industry for any country and its growth and because of which the whole of the population is surviving and without food, without food grains we cannot survive and with India's growth, the fertilizer industry is bound to grow. Now, India is also trying to make triple super phosphate and different other types of fertilizers as well.

So, this industry is bound to grow and with this the challenges associated with treatment of water and generated in these industries is also bound to grow. So, accounting for these water and new type of challenges, the new technologies are also slowly and slowly coming into picture except for biological nitrification or denitrification the most of the processes used in the treatment of fertilizer industry wastewater are Physico Chemical or Electrochemical.

So, this is a great area of research and All India treatment technologies are available but there are many other challenges. For this also, we should always perform research and understand the

characteristics of the water which is getting generated, then only we can properly develop technologies for treatment of such waste. So, we will end this section. Thank you very much.