Course Name: Industrial Wastewater Treatment

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Week – 10

Lecture 48: Treatment of wastewater produced from Refineries and Iron & Steel (Coke Ovens)

Welcome you all. Today I am going to deliver lecture 3 of module 10 which is on the treatment of wastewater produced from refineries, iron and steel industries, especially coke ovens. So in this slides what we are going to cover is like the type of coke oven plants, the basic introduction, their uses and then also we will be looking into the making process like coking process, what are the process diagrams and then we will be looking into the various sources and the characteristics of wastewater produced and finally we will be looking about what are the various contaminants which are found in coke oven a plant, their toxic effects and then environmental concerns and finally we will be going through the various byproducts, major outputs of the coke oven plants.

So let us discuss about the brief introduction about the coke oven plants. So, this the basic objective of the coke oven plants is to produce the hard coke. So, this is produced by the process of coking of coal to produce the hard coke and in this process, what happens the coal is converted into coke by heating in the oven at a temperature of around 1200 to 1300 ℃ up to an incubation period of 16 to 36 hours. So in this incubation period what happens at this temperature when the coal is heated in essentially like in absence of oxygen then what happens whatever the volatile organic compounds which are present in the coke as a contaminants they are removed through the vapor forms and driven off leaving a carbon rich material that we say that is the hard coke and these volatile matter leaves the coke oven chamber as a hard fuel gas which we can require and use as a fuel gas. So, this is then cooled off and collected separately as a coke oven gas in a byproduct recovery type of plant while it is discharged through the stacks in case of non-recovery type of coke oven plants. So, this coke oven gases whatever is generated either can be recovered as a fuel gas or in case of non-recovery type of coke oven plants this is discharged through the stacks and finally the hard coke is taken out and sprayed with a lot of water which results into generation of a liquid stream that we call the coke oven effluent which contains a lot of variety of compounds organic, inorganic compounds and is contaminated with toxic compounds.

So, this we are going to look in more details. So, before we go into more details let us talk about the various uses of the coke. So, coke is primarily used as a fuel and helps in smelting of iron, steel and aluminum in iron and steel industry, aluminum industry. So, this is a basic fuel that is used in the iron and steel industry in the smelting operation and the other uses of the coke involves like synthesis of calcium carbide then also manufacturing graphite and its electrodes. As we discussed the coke oven gas is also produced as a fuel gas so this can also be used as a fuel gas and finally, we can require out various byproducts from the coke oven effluent like this

naphthalene, benzene, ammonium sulfate, coal tar. So these are variety of byproducts we can recover we can sell it out. So, these are like the different uses of the coke oven plants the objective of the coke oven plants.

And then let us talk about the types of coke oven plants basically they are two types of coke oven plants one is non-recovery type and another is like recovery type of coke oven plants where byproducts are recovered. So, byproducts which are recovered they are basically phenol, ammonia, fertilizer, coal tar, naphthalene. So, these are many byproducts they can be recovered out of the coke oven effluent in the byproduct recovery type of plants and there is also called coke oven gas which can also be recovered as a fuel gas. So, this is basically the recovery process that is carried out in byproduct recovery type of coke oven plants, where non-recovery type of coke oven plants the fuel gas which is generated the coke oven gas which is generated is discharged through the stacks and not goes for recovery of byproducts. But if we compare the two types of coke oven plants like non-recovery and byproduct recovery type of plants so basically in the byproduct recovery type of plants the process and the methodology that is used for recovery of phenol, ammonia, fertilizers and coal tar they are basically nowadays costlier than they are produced from their conventional process. So, that's why the recovery for phenol, ammonia as a fertilizer, coal tar, naphthalene, this benzol, so these are various types of byproducts which can be recovered but because of their cost economics nowadays the recovery of these byproducts from coke oven effluent that is obsoleted and in the modern type of coke oven plants this coke oven gas that is recovered as a fuel gas and used as a fuel.

So let us talk about the various steps what we use in cooking of the coal in a coke oven plant. So, first step that is basically charging. So charging is the process of loading of coal into the ovens and this is basically carried out by a loading cart which has a capacity of around 4 to 5 tons which moves above the coke ovens on a laid-down tracks and from the mid of the coke oven from the top there is an opening through which this all the loaded coal will be loaded into various ovens. So, this step basically involves the loading of coal into the coke ovens and then the second step what we say that is the coking of coal. So, in this step what we do we used to heat the coal to a temperature of around 1200 to 1300 °C till it becomes red hot and this is done for an incubation period of around 24 hours to 36 hours even sometimes it goes up to 48 hours depending upon the quality of the coal. So, this coking process gets completed and it takes like one and one and a half days time like 24 to 36 hours and then after incubation period is over then whatever red heated coal that is taken out with the driving cars. So, this driving car is provided with each coke oven wherein the coal is loaded initially and then after the heating after cooking of the coal inside the coke ovens they are taken out with the help of this driving car and then finally when this red heated coal comes out of the ovens then lot of water is sprayed over the red heated coal, so as to bring down its temperature to atmospheric temperature. So, it basically requires a lot of water and then generates a lot of effluent wastewaters which may contain a lot of suspended solids, phenol, ammonia and many other toxic compounds like cyanide, isocyanate. So, this is a rich wastewater contains a lot of variety of toxic compounds organic matter suspended solids so that is generated and termed as a coke oven effluent. So these are basic process and after quenching of the coal this is again screened out different size of coal is separated and then is sent for sale in the iron and steel industry, aluminum industry and many other clean coal operations.

So let us see the flowchart of the coke oven plants which are based on the non-recovery type coke oven plants so in this if we see that the first unit operation that is coal handling and preparation and briquetting plants where the mined out coal that is crushed and the screened out after screening a particular size of the coal is taken out and then it is blended with the good quality of the coal if it is required if the quality of the coal which is mined-out is not having a lot of carbon content, a lot of ash content then it has to be blended with the good quality of the coal and after this blending operation is over then this blended coal that is taken to the storage tanks where this coal is stored and after this the coal is loaded into coke oven batteries. So, battery here is basically referred to as a series of coke ovens in a row termed as one battery and there are number of batteries. So, this coal from the coal storage is loaded into various coke ovens, various batteries wherein this is red-heated to a temperature of 1200 to 1300 °C for a period of 24 hour to 36 hour, which is basically the incubation period during this period whatever the volatile organic compounds present into the coke that gets evaporated and rest of the coal red-heated coal basically that is quenched out and then the coke is produced. So here after if we see for this after coal is charged into this coke oven battery so this combustion has to be initiated this has to be done by adding the combustion here and some lean gas or coke oven gas can also be used for initiating the fire inside the oven and once it is done then it is heating is to be done in a pyrolysis condition, no further addition of the combustion here is required and this basically as I told coking process will generate a lot of fuel gas and that flue gases comes to the coke oven gas manifold collection system, from where it can be sent to the by-product recovery plant or if it is a non-recovery type of plant so this is basically discharged through the stacks and here after cooling after quenching of the coal whatever the coal comes out that is screened out separated into various size range. So, this is like blast furnace coal the large largest size of the coal that is taken for the blast furnace coke and then the medium size of the coal that is referred to as nut coke and the finer size of the coke breeze which are generated in the screening operation that is referred to as coke bridge. So, these all are basically referred to as coke and of different size and they are depending upon their applications they are used in iron and steel industry, aluminum smelters and various other furnaces and other heat applications.

And this is basically the flow chart for by-product recovery type of coke oven plants so here if we see this is basically the coal which comes out after the blending after the coal preparation plants. So, this is basically loaded into this coke oven batteries and as I said this after coking process is done this will produce the hard coke here so hard coke is separated and during this coking process as I told there will be lot of flue gases that will be generated. So, it has lot of calorific value the flue gases which are generated from this coke oven battery has a temperature range of around 700-800 °C. So, this heat value of the coke oven gas that is captured and used as a fuel gas. So, here is one application and the other way also if the byproducts are to be recovered so first of all this has to be cooled down so here this is done in a gas collection system where lot of flushing liquid is sprayed over this coke oven gas so as to reduce its temperature to around 70 °C, 60 °C. So, after reducing this temperature whatever the tar present into this coke oven gases in the form of vapor so that gets precipitated here in the next unit operation that we call tar precipitator. So this precipitated tar that will go to the separator where from this the clean coal tar that will be separated and this coal tar then will go for distillation process for further purification and then finally purified form of this tar is produced where rest of the coke oven gas that goes

through the gas exhauster and then it goes to the gas cooler where temperature of this coke oven gas that is again reduced and then it is purged through the 6% sulfuric acid in a saturator, so which this process of saturation with the acid that basically converts this ammonia present in the flushing liquids into the ammonium sulfate fertilizer form. So, this will generate ammonium sulfate solution which will then be crystallized through centrifuge dryer so this is how we can require here the ammonium sulfate as a fertilizer and then rest of the coke oven gas after recovery of this ammonia in the form of ammonium sulfate, it goes to the acid catchers where all the acids that will be separated and then after separation of acid purified form of benzol that will be recovered out. So, these are the basically the flow chart the process diagram for a coke processing plant which operates on the basis of byproduct recovery.

Then let us talk about the coke oven gas which is an important byproduct that has to be recovered so as I said when it comes out from the coke oven battery it has a temperature range of around 800 to 900 °C and this hot gas that is immediately quenched by direct contact with the spray of water in the flushing system for cooling down the temperature so this process basically that is termed as the quenching process and this process generates a lot of coke oven effluent or the flushing liquor which contains a lot of ammonia and then this is collected separately for the recovery of ammonia and sulfur present into this flushing liquor and the cooled gas after this process that is saturated and has a temperature of around 70 to 75 °C and then this gas is collected through the gas collection manifold system for recovery as a fuel. So, this is like how this coke oven gas that is processed for recovery of ammonia and sulfur and also as a fuel.

So, this is the major byproducts which are generated from the process that is the ammonia in the form of ammonium sulfate is generated which is sold in the market as a fertilizer. And if we see the overall its generation, so it generates around 12 tons per day of ammonia and the second byproduct that we generate that is the light oil and if this is recovered so this is required and sold in the market and in terms of volume if we see this is around 12,500 gallons per day of this light oil is required and also if we see another byproduct that is the coke oven gas which is used as a fuel at the coke oven battery and also in the steel works so this also generated its amount that is around 50 million is standard cubic feet per day. So, this is the amount of coke oven gas that is generated. And then another byproduct that is basically the tar that is generated and which is sold into the market. And if we see this is basically 29,000 gallons per day of tar that will be generated in the process and is finally sold in the market.

So, let us talk about the wastewater generation and its composition. So, here if we see the world average if we see globally this coke oven plants they generate around 400 to 500 liters per ton of coke. Whereas in India if we see that is the average is little lower side that is 300 to 400 liters per ton of coal for Indian conditions. And in terms of contaminants if we talk that is basically if in terms of color this is having a brownish color, having high BOD and COD, then having phenol is also there, cyanide is there, isocyanates and then NH_4–N these are the major contaminants they are found in the coke oven effluent and they have all their environmental and health impacts and that need to be treated before the coke oven effluent they are discharged into the environment.

So, before going into the more details let us see the characteristic of the coke oven wastewater which is generated globally. So, here we have this is Australia, Germany, China, Spain and India.

So with respect to our country how this wastewater generation and their composition varies so here these are basically the water different water quality parameters like the strength of the wastewater in terms of BOD, COD, total suspended solids, TKN, ammonia nitrogen, total phosphorus, phenols, isocyanate and then cyanide. So, this is like if we analyze this overall variation of the wastewater generated from coke oven effluent globally. So, what we see on an average the characteristic varies within the typical range some of the countries like in terms of BOD if we see, so BOD in our country that ranges from 100 to 800 mg/L, but in case of Germany this is having the maximum BOD in case of Germany where BOD level goes 1600 to 2600 mg/L and similarly is the concentration for COD, COD also here is very high in Germany whereas in India this is up to 500 to 2000 mg/L. In terms of suspended solids if we see that is very-very less like up to 50 mg/L, but in terms of nitrogen this is 200 to 300 in case of Australia in case of Germany this is by up to 500. So, in terms of ammoniacal nitrogen, the concentration of the ammoniacal nitrogen in Indian coal that is very-very high that is around 400 to 1400 mg/L, but in other countries if we say other than this Spain so concentration lies within 200 to 300 mg/L but in case of Spain it can go up to 1100 mg/L. So, what I mean to say is like large variation in the characteristic of the coke oven effluent generated from different countries that may be attributed to the quality of the coal and the origin of the formation of the coal wherein these contaminants vary depending upon their geological conditions and the conditions when the coal that has been formed so this is all a lot of variation in the wastewater we can see.

And then this is like the toxic effects of these contaminants found in the wastewater. So, if we see it causes taste and order problem if it is discharged into the receiving water body and then also it contains a lot of oil and grease, so it forms a oil slicks due to the lot of release of oil and grease into the receiving water bodies and because of formation of oil slicks onto the surface the DO concentration of the receiving water body also reduces because of its high BOD and COD. Then it contains a lot of toxic compounds like phenol, cyanide, isocyanates. So, they have toxic effects and health hazards to the various aquatic lives and the human beings exposed to that water body. And then that is also like the phenol, cyanide they are carcinogens so they have carcinogenic effects also and it contains a lot of coal tar that may get deposited that may get precipitated on cooling and that may cause choking of the pipe. So, these are various toxic effects and environmental concerns associated with coke oven plants.

And then these are the environmental norms so if we see the characteristic this is the characteristics of the effluent and for discharge of this effluent on to the water body. The CPCB has given different norms and then IS2490 that is the effluent discharge standard it has different norms whereas this global standard that is given by USEPA. So, these are the different norms that has been given for the that the coke oven effluent should follow before it is discharged into the environment. So, if we see in terms of pH, so initial pH that is slightly alkaline in nature but it has to be discharged in a pH range between 6 to 8 as per CPCB and 5.5 to 9 as per IS2490. Similarly, the ammoniacal nitrogen initially it is present up to 1400 mg/L but in the discharge in the treated effluent it should not be more than 50 mg/L as per CPCB standard, whereas this effluent discharge standard permits only up to 5 mg/L. So, these are different standards made for this coke oven plant similarly for cyanide it is present in a concentration from 10 to 50 mg/L but it's very toxic and it's it should not be more than 0.2 ppm as per CPCB norm and the similar norms that has been given by the IS2490. Whereas the global norms that is a little bit liberal compared to our

Indian norms so that is up to 0.5 mg/L and then we see the phenol that initially there in the wastewater is in the tune of 300 to 1000 mg/L, but it should not be more than 1 mg/L in a treated effluent and this if we see IS2490 norm so it should not be more than 5 mg/L. So, before it is discharged it has to be treated and bring down to its environmental norms for its safe disposal without causing any harms to the receiving water bodies and environment. So again if we see the BOD and COD level here, so BOD and COD level is up to 1000 mg/L whereas COD is 2000 mg/L, so BOD as per CPCB norm it should not be more than 30 mg/L and similar is the norm affixed by effluent discharge standard that is IS2490 and this as per the USEPA norms it should not be more than 25 mg/L. So, depending upon the conditions depending upon the countries the different environmental norms are there and similarly for COD if we see that is up to 2000 mg/L and for this parameter there is no norms fixed by CPCB, IS2490 and USEPA and then similarly is the suspended solids that is up to 50 mg/L. So, here if this is well within the prescribed norm so there is no need of removal of suspended solids into the wastewater and if we talk that oil and grease that is one of the important contaminants and that need to be taken care of so because this is present up to a concentration of varying from 10 to 250 mg/L, but as per the discharge norms it should not be more than 10 mg/L and similar is the norms given by IS2490, so this oil and grease basically that forms a layer of oil, oil leaks onto the surface of the receiving water body then it is discharged into the receiving water body and when it forms the oil leaks it acts as a barrier for diffusion of oxygen, penetration of UV lights which are very essential for survival of aquatic plants and life within the receiving water body so this oil and grease that is one of the severe problem in the coke oven plants and that should be make sure to be removed less than 10 mg/L, so as to avoid the contamination of receiving water bodies.

So, these are the references that can be referred.

Thank you.