Course Name: Industrial Wastewater Treatment

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Week – 10

Lecture 49: Treatment of wastewater produced from Refineries and Iron & Steel (Coke Ovens)

Welcome you all. Today I am going to deliver lecture 4 of module 10, which is on the treatment of wastewater produced from refineries, iron and steel industries, especially from coke ovens. So, if we recall in our previous lectures we have gone through the various types of coke oven plants, recovery type, non-recovery type of coke oven plants, their unit operations and the sources of wastewater generated, their characteristics. So now in this lecture we are going to cover basically the two major waste streams, one is coke oven gas and another is the wastewater liquid effluent which is generated from the coke oven plants, their treatment and also looking into the composition and various types of contaminants which are present. Then finally we will be looking about the various recovery process which are used for recovery, the various byproducts like coal tar, then naphthalene, then ammonia as a ammonium sulphate as a fertilizer and many other products which can be recovered from the coke oven plants and finally we will be dealing with the treatment process which are used for management of the waste streams, liquid streams generated from the coke oven effluent.

So let us first talk about the various sources of pollution in the coke oven plants. So, in different stages there are a lot of emissions, if we see charging means that is initiation of the floor after coal is loaded into the coke ovens, so it is fired, so this during this time lot of smokes along with the particulate matter, carbon dioxide, carbon monoxide and many other poly aromatic hydrocarbons which are emitted in the flue gases, they are generated and they are taken out from the vent pipe and central manifolds and then it is discharged through the stacks into the atmosphere. So this kind of emission we say that is the charging emissions and then combustion emissions like when the coking process is done, basically the volatile matters which are present in the coal that gets converted into vapor forms along with the emissions of various gaseous products like carbon monoxide, hydrogen, ammonia, water vapors along with various size of dust, so they together is termed as the coke oven gases which are emitted from the top of the coke ovens and collected through the central manifold system and then is taken for the recovery of various byproducts. Then another type of emissions which we talk about in the coke oven plant that is diffused emission, so these are the emissions which takes place due to the leakage of the flue gases from the coke ovens because the flue gases under the coke ovens they remain under very high pressure, so if there is any leakage, so lot of emissions that goes as a diffused emission into the atmosphere and then at the time of pushing out of the red heated coke from the coke oven plants from the coke ovens after the completion of the incubation period, so when the coke is pushed out of the oven into the pusher car, the soot blows out of the door due to its opening and this type of emissions basically they are classified as pusher emissions that is taking place at the

time of opening up the door at the time of taking out the red heated coke from the coke ovens, so this type of emissions they are directly discharged into the atmosphere. And then another type of waste stream that is basically liquid streams, these are all like in the form of flue gases, gaseous emissions and this is basically the liquid in the form of waste water in the form of coke oven effluent, this is basically generated as a flushing require when quenching of the red heated coal is carried out with the water, so lot of liquid streams they are generated and this is referred to as coke oven effluent which may contains lot of contaminants like phenol, cyanide, isocyanate, lot of organics, inorganic compounds, so this coke oven is extremely polluted kind of waste effluent which is generated from the coke oven plants.

Then let us talk about the various types of contaminants which are commonly found in the coke oven gas. So, first of all we will be looking into the coke oven gas which is one of the waste stream, so which contains lot of contaminants which can be recovered to produce various useful byproducts, so like if we see the type of contaminants, tar is present in the form of vapors, then light oil, light oil basically referred to as consisting of mixture of benzene, toluene and xylene, they together is referred as light oil, so this light oil is separated and is processed for recovery of benzene, toluene and BTX. Then there is the naphthalene vapors, that are also present in the coke oven gas, so when we cool down this coke oven gas temperature, so this naphthalene gets precipitated and can be removed out. Similarly, there is a lot of ammonia gas which is generated during this coking operation, so this ammonia gas is separated through ammonia stiller and then is taken for recovery of various byproducts, so this we are going to study in more details in the forthcoming slides. And then another type of gaseous pollutants which are present in the coke oven gas that is hydrogen sulphide, then there is hydrogen cyanide, so these are the various contaminants, they are found and finally we used to process this coke oven gas for recovery of these byproducts.

So, let us see what are the different recovery process and before going into that let us see what are the basic composition of the coke oven gas in the dry basis and the wet basis. So, here if we see this coke oven gas contains lot of hydrogen, then it contains 25% of methane and this carbon monoxide also it contains around 6%. So, this together hydrogen, methane and carbon dioxide they are flammable in nature, so they add calorific value to this coke oven gas and hence this coke oven gas after recovery can be used as a fuel gas and if we see this wet basis, so there is if we see in the saturated condition, it contains around 47% of the moisture and rest is like the hydrogen, methane, nitrogen, carbon monoxide and carbon dioxide composition. So here what is important to see that is around 47% when it is in moist condition in saturated conditions, so it contains around 47% of the water vapors, so these water vapors basically in the first stage that has to be condensed out the temperature of the coke oven gas has to be reduced, so that 50% of the gaseous compositions overall gas volume can be reduced, so this can be done by condensation of water present in the coke oven gas.

So let us see about the various treatment techniques that are basically adopted for recovery of byproducts from this coke oven gas. In the first stage we do condensation of water, so this when the temperature of the coke oven gas is cooled down in a primary cooler, so whatever the water vapors they are there they will be condensed out and there are naphthalene, there are tar particulates, so they will also be condensed because of the cooling of the temperature of the coke

oven gas, so they are basically separated and removed from the rest of the coke oven gas and then finally this thaw and naphthalene they are processed for recovery like tar separators, this is basically used for separation of the tar particulate by way of flushing of water, so flushing of water will reduce the temperature and that will cause all tar particulates to precipitate down in the form of solids. So then still after this precipitation there are very finer size of tar particulates, they are not precipitated in the tar precipitators, so this electrostatic precipitators are used where this tar aerosols they are removed which otherwise will cause choking in the pipeline and fouling of equipment, choking of nozzles wherever it is used as a fuel, so this is like a process where this fine particulate matter aerosol size of the tar particulate matters, they are removed in the electrostatic precipitation process, then there is a removal of this naphthalene by condensation process similar to the tar, so this naphthalene also condensed the coke oven gas temperature is reduced and this naphthalene gets precipitated and they can be removed from the rest of the coke oven gas and then there is ammonia slippers, so ammonia slippers basically used for removal of ammonia, separation of ammonia gas from rest of the coke oven gas, so this is performed by stripping of this liquor with the steam, so all the ammonia that gets separated along with the steam from the wastewater or the flushing liquors. And then finally the next process that is removal of the light oil by the adoption column for recovery and sale of the benzene, toluene and xylene, followed to this there is again we used to recover out this hydrogen sulphide by scrubbers and then finally this is recovered as elemental Sulphur using this Claus process. So, these are the different processes which are used for recovery and separation of various byproducts.

So, one by one we will go in little more detail of these processes, so this is basically the process flow chart of recovery of various byproducts from the coke oven gas. So if we see this is like the coke oven battery where all the coke oven gases they are generated and then they are taken to the central manifold system where it passes through the primary coolers, so when it passes through the primary cooler the temperature of this coke oven gases is reduced by when this coke oven gas comes in contact of water, so this tar precipitators are there to remove out the tar from the flushing liquors which is generated after cooling of flushing of this coke oven gas with the water and this tar is separated here and then finally whatever this rest of the coke oven gas that passes through this electrostatic precipitators where aerosol size of particulate matters or the tar particles they are removed and after this you can see there is another unit operation that is called exhauster where basically this exhauster helps in maintaining and controlling the pressure which renders these flue gases to be derived from the central manifold system to the byproduct recovery plants and then you can see like there is a recovery and removal of this H_2S and ammonia using various scrubbers. So, this you can see this is ammonia strippers where this ammonia will be separated and then using this Claus plant so whatever the H_2S that gets scrubbed out that is taken to the Claus plant for recovery of Sulphur in the form of elemental Sulphur and then you can see whatever the waste water that is generated is going for the biological treatment system after this recovery of ammonia and then the rest of the coke oven gas then passes through the light oils using the wash oil so this light oil gets absorbed on to the solution and then this is dissolved here and whatever this BTX that is separated is sent for recovery plant to recover out the benzene, toluene and xylene from the liquor and finally this BTX is sold in the market. So, this is basically the entire process diagram which takes place in a coke oven plant for recovery of byproducts from the coke oven gases.

And these are basically the different unit operations how they work like if we explain about the first unit that is like the primary cooler where this tar gets precipitated in the tar precipitator so this tar precipitators are used basically for removal of this tar particulate matters from coke oven gas by condensation of coke oven gas where this tar gets precipitated and these units they can be installed before or after the exhauster and rest of the tar aerosols are very fine particulate matter which are not removed which are not settled in the tar precipitators they are taken out to the next unit operation that is electrostatic precipitator where this very fine size particulate matters they will be removed and basically removal of this tar particulate matter that is very important because if they are not removed they would contaminate and foul the downstream process like it would foul the gas line and choke the burner, nozzles if allowed to continue along with the coke oven gas and that's why this tar aerosol that has to be removed in the further unit operation in the electrostatic precipitators basically which uses this high voltage electrodes to charge these tar particles and electrostatically they are separated these are the charged particles that is attracted and then this is removed in the by the process of electrostatic attraction.

Then the another process if we see this ammonia as I said a lot of ammonia is present in the coke oven from coke oven gas that has to be removed using the water scrubbers where this water is used as a scrubbing liquid to remove out to dissolve this ammonia present in the coke oven gas. So along with ammonia there also the hydrogen sulfide, hydrogen cyanide that will also get dissolved into the liquor and this liquor is taken out for recovery of this sulfur the recovery of this ammonia and this ammonia whatever is recovered out after this ammonia stripping process that is sent for recovery. So, this can be recovered in the form of ammonium sulfate fertilizer so in this process what happens this ammonia is made to pass through this H_2SO_4 solution, that is 6% strength solution and this is kept in a saturator where this coke oven gas is containing this ammonia will be bubbled and this ammonia basically will react with H_2SO_4 and it will form ammonium sulfate later this has been crystallized and sold in the market as a fertilizer. So this is one of the process wherein ammonia that can be recovered in the form of ammonium sulfate which is used as a fertilizer and then the another process of recovery of this ammonia that is like the catalytic converter so this catalytic converter uses catalytic cracking process of ammonia which breaks down this ammonia in the form of nitrogen and hydrogen which are recycled back into coke oven gases to aid its calorific value this process is used for improving the calorific value of the coke oven gas when this coke oven gas is used as a alternative of fuel gas. And there is another process called that is the PHOSAM process which is developed in US and basically in this process what we use we use a mono ammonium phosphate solution which will absorb this ammonia present in the coke oven gas and which later it will be separated in the form of anhydrous ammonia so this is a PHOSAM process that is used for recovery of ammonia and the last alternative is the incineration of ammonium vapors which is usually not an option because of the strict rules and regulations that restricts the emissions of NO_x and SO_x, because if this is incinerated this ammonia will form various oxides of nitrogen and the sulfur present in that gas that will also cause a generation of oxides of sulfur, so this will cause a lot of air pollution and that's why as per the regulations this alternative is nowadays obsolete.

Then if we see this is the process of removal of ammonia the flowchart so here if we see this coke oven gas that is that enters from the bottom here it goes on the top and from the top if we see we used to flush out a lot of cooled water and flushing liquors so when this coke oven gas comes

in contact with a lot of flushing water so whatever ammonia that gets dissolved into the water and this flushing liquid is then taken out to the ammonia is still are where this ammonia that will be stripped out using this steam and the pH condition that has to be maintained here as pH equal to 10 to 11. So, this basically pH is adjusted by adding lot of caustic soda into this and in this stripping process whatever this ammonia that will be separated and then it will be converted in the form of anhydrous ammonia.

So, this is the process of removal of ammonia from the coke oven gas and then this is like the flowchart for the PHOSAM process so this process if we see that consists of ammonia absorber, ammonia stripper followed by fractionator and then in this ammonia absorber what happens this coke oven gas along with the vapors which are coming from the ammonia stiller, they are sent to a ammonia absorber this contains a lot of phosphoric acid which is used as a media for absorption of this ammonia so this ammonia gets absorbed here and whatever the rest of the coke oven gas that goes out of this ammonia absorber and this after absorption this goes to this detarrer, where this temperature is cooled down and then tar is precipitated, tar is removed out and then this this basically again it goes for this stripping of ammonia which is there in this flushing liquors. So, here from the bottom steam is sent here and this liquor comes down so when it comes in contact with each other whatever this ammonia that stills out and then this is stills out ammonia basically goes to the fractionator where this steam is used and this ammonia whatever comes out here that along with the steam get fractionated here. So, here in the fractionator whatever the ammonia gas comes that is stripped along with this steam and this when it is cooled out whatever the water condensate that forms the wastewater streams and whatever the ammonia that comes out that is like an hydrous ammonia which can be liquefied and in the liquid ammoniacal form it can be stored. So, this is like the PHOSAM process where first of all ammonia is absorbed in the solution then it is stripped out in the vapor form and in the fractionator finally it is like the water stream the water vapors are separated from the ammonia vapors and this water vapors they are generated in the form of wastewater here, whereas this liquid ammonia that is generated after separation of the ammonia purified form of ammonia condensation of this ammonia so that gets converted into liquid ammonia and this is the stored for further recovery process.

Then this is another process what we call that is catalytic cracking of ammonia in the catalytic converter. So, this process essentially involves a catalytic converter. So this catalytic converter whatever the vapors comes from ammonia is stiller and whatever the coke oven gas along with the air that is fed here into this catalytic converter where this whatever the fraction of ammonia present in the vapor coming from the ammonia is stiller present in the coke oven gases they basically get catalytically converted cracked and broken into nitrogen and hydrogens after conversion of this ammonia into nitrogen and hydrogen so this is passed through a waste heat boiler which uses and recover out the heat energy associated with the flue gases generated from the catalytic cracking reactors so this heat is utilized for generation of energy for generation of steam and then after the recovery of heat from the waste boiler the rest of the coke oven gases is taken to the tail gas cooler where this coke oven gas is sprayed with lot of water onto this incoming coke oven gases so this comes in direct contact with the water here in the cooler and its temperature gets cooled down and whatever the cool tail gases which are generated after this cooling operation that is basically is stored as a raw coke oven gas for supplying into the supply line and whatever the flushing liquor basically which is generated that is basically referred to as

condensate which may contain a lot of ammonia and other contaminants, so that becomes a waste stream to be treated along with the coke oven effluent.

So, this is basically the ammonia recovery as a fertilizer this option where this ammonia is separated and then it is saturated with the H_2SO_4 acid to form the ammonium sulfate. So, this is like the solution we use sulfuric acid 6% sulfuric acid. So, this sulfuric acid in the form of 6% solution that is sprayed over the coke oven gases and when this coke oven gases comes in contact with this saturator so recovery of ammonia in the form of fertilizer is done by using two process one is by using an absorber where the sulfuric acid solution that is sprayed into the gas and as the reaction with the ammonia this forms the ammonium sulfate or this can also be achieved by a saturator where this coke oven gas is bubbled through a solution of sulfuric acid and when it comes in contact with this ammonia it forms the ammonium sulfate and this can be recovered and sold in the market as a fertilizer ammonium sulfate crystals they are separated out from the solution and sold in the market as a fertilizer but nowadays this is obsoleted because the conventional process for production of this ammonium sulfate fertilizer that becomes more economical than the process we use here for recovery of ammonia and then production of ammonium sulfate fertilizer. So, because of this reason these days, these processes are obsoleted.

Let us talk about the naphthalene removal process which is done in the final cooler which removes the heat of compression which is generated from the coke oven plant during its flow to the exhauster so this final cooler typically cools the coke oven gases by when it comes in direct contact with the cooling medium either with the water or the wash oil so this wash oil also that is used as a solvent for this naphthalene so this naphthalene gets dissolved in the wash oil and gets separated and after cooling these naphthalene crystals that gets condensed out and for absorption we can use this which we have separated in the tar precipitators. So, this is like a closed loop cycle along with the tar precipitator so this naphthalene and tar which are present in the vaporized form they are basically precipitated and removed.

And then you see the recovery of BTX that is benzene, toluene and xylene together which we say that is the light oil so this recovery of light oil is basically uses the wash oil where this removal of light oil that takes place from the coke oven gas and then after this is absorbed in the wash oil then this is taken to the stiller where the light oil will be separated and then it will be cooled down to produce the crude light oil and this can be sold for further refining in the market off-site or within the plant also it can be refined in the by-product recovery plant using several distillation process wherein this benzene, toluene and xylene they are separated at different stages of distillation. But nowadays there is a practice because this light oil basically the benzene, toluene and xylene is left to the coke oven gas if it is used as a fuel gas because presence of this benzene, toluene and xylene they will add on its heating value its calorific value so nowadays in case of no option for recovery of this light oils they are left into the coke oven plants to be used as a fuel.

So this is basically that the desulfurization process of the coke oven gas so here we use a number of process for desulfurization of coke oven gas that is vacuum carbonate process then we have ammonia wash process then we have sulphiban process and finally we have this Claus process they are used for recovery of sulfur so in the first process where this hydrogen sulfide is absorbed from the coke oven gas using a solution of potassium carbonate that's why this process is referred

as vacuum carbonate process where later on H_2S that is dissolved into this solution that is stripped out in a stiller so this is one process where this H_2S are the sulfur vapors they are absorbed from the coke oven gas and then finally they are separated from rest of the coke oven gas in the another process called ammonia wash process hydrogen sulfide is absorbed basically using a solution of ammonia so ammonia here it is used and this ammonia then gets stripped out in ammonia is stiller so this process often combined with the ammonia removal system so as to remove both ammonia and H_2S then this ammonia basically that is recovered either in the form of various kinds of by-product and this H_2S also that can be recovered in the form of elemental sulfur in the Claus process and then you see that is the Sulphiban process where this hydrogen sulfide is absorbed from the coke oven gas using a solution of mono ethanol amine that is amine then it is stripped out so this process basically removes out the ammonia. And then this Claus process, where the H_2S is converted into the elemental sulfur using biological process and finally this can be used for production of sulfuric acid.

So, after the treatment of coke oven gases the wastewater which is generated from the coke oven plants they are taken out and then that has to be treated using various treatment systems so among various treatment system if we see there are physiochemical treatment system, nano filtration system, adsorption system, then bioaugmentation system, biological treatment system, phytoremediation system, advanced oxidation process like ozonation, photo catalysis then air stripping. So, these are number of process if we see this air stripping process that is used for removal ammoniacal nitrogen from the wastewater. And this physiochemical treatment like in the coke oven plants if we see there are a lot of toxic compounds like cyanate, cyanide, thiocyanate they are present in the wastewater, so they are treated using physiochemical treatment process. Then the biological treatment process mostly activated process that are used for removal of phenol, organic contents, BOD-COD from the wastewater and then in the biological treatment system there is an notification and denitrification system that is the conventional system which is also used for removal of the monocle nitrogen present in the wastewater. So, there are various alternatives which are used for the treatment of coke oven wastewater.

So, one by one we will look among various alternatives which are used for coke oven plants so overall if we see the entire treatment consists of the chemical treatment which basically is used for removal of cyanide present in the wastewater so this is used by oxidation process where a chlorine, sodium hydroxide that together it needs with the wastewater where this chlorine acts as a oxidizing agent and then it converts the cyanide into nitrogen. And then there is a two-stage aerobic biodegradation process which are used for removal of phenol removal of organic matter present in the wastewater and then there are nitrification and denitrification system which are used for the treatment of a monocle nitrogen present in the wastewater and finally if we see by using this treatment process we can remove COD up to 95% BOD up to 96%, phenol around 98% and then cyanide also we can remove more than 94% so after this treatment if we see that the treated effluent meet with the discharge standards which are prescribed for coke oven effluent but as we know this coke oven plants they work on the zero discharge principle so whatever the treated effluent comes out that has to be again recycled back into the plant for various operations where butter is required like quenching process, scrubbing process and then cleaning and washing process. So, these are like the various treatment alternatives which are used for the treatment of coke oven effluent.

And then this is like the chlorination process that is the physio-chemical process, chemical treatment process which are used for removal of cyanide. So, here if we see this is predominant mode of cyanide removal from the wastewater and in the first stage whatever the cyanide present in the coke oven effluent that is oxidized by this sodium hypochlorite which is added in the chemical treatment process for oxidation of cyanide and this reaction may be brought about the direct addition of sodium hypochlorite also addition of chlorine and the sodium hydroxide solution. So, this oxidation process either we can do by direct addition of chlorine or the chlorine gas along with the sodium hydroxide. So, this is the chemical reaction and in the secondary stage process what happened this whatever the cyanide that is produced after conversion from the cyanide so that is again oxidized to the carbon dioxide and finally this nitrogen gets converted into dinitrogen gas. So, these are the two process which takes place wherein this cyanide gets finally converted into carbon dioxide and nitrogen. So, here if we see this cyanide in the first stage that is converted into cyanate this is the chemical reactions where this sodium cyanide reacts with the sodium hydroxide and chlorine because this reaction happens in the alkaline conditions so this NaOH has to be added so that this can react with the chlorine to form the NaCN and then this will convert this sodium cyanide into sodium cyanate $NaCN + 2NaOH + Cl_2 \leftrightarrow NaCNO + 2NaCl + H_2O$. So this sodium cyanate will be produced and then in the second step this sodium cyanide whatever is produced in the first stage that again gets oxidized by chlorine to carbon dioxide and then finally this nitrogen is produced so whatever the cyanide that was present in the wastewater that has finally converted into the carbon dioxide and nitrogen ($2NaCNO + 4NaOH + 3Cl_2 \leftrightarrow 6NaCl + 2CO_2 + N_2 + 2H_2O$) using this two-stage oxidation process wherein this we can use either chlorine gas along with the sodium hydroxide or we can directly use this sodium hypochlorite for oxidation of this cyanide finally into carbon dioxide and nitrogen gas and then there is a cyanate also that is present in the wastewater.

So, this cyanate that is again is hydrolyzed using this key enzyme that is Cyanase and using this process whatever this thiocyanate that is present in the wastewater that gets converted into cyanate and this cyanate again then gets converted into ammonia and carbon dioxide. So this process basically that is carried out by aerobic microorganism under aerobic conditions. So wherein this hydrolysis of carbon and sulfur bond there in the thiocyanate that breaks down and then finally this is converted into ammonia and carbon dioxide ($SCN^- + H_2O \rightarrow CNO^- + H_2S$ (Hydrolysis of the C−S bond) and $CNO^- + HCO_3^- + 3H^+ \rightarrow NH_4 + 2CO_2$) and then the other pathway for removal of this thiocyanate. So, here basically that is the carbonyl sulfide pathway where this thiocyanate hydrolyze is used as a enzyme for degradation of this thiocyanate and in this the thiocyanate that will convert it into H_2SO_4 in the second step, first step this will produce carbonyl sulfide this COS and this ammonia and this hydroxyl ion ($SCN^- + 2H_2O \rightarrow COS + NH_3 + OH^-$), so this finally whatever this carbonyl sulfide that is produced that will be finally converted into H_2S and this H_2S ($COS + H_2O \rightarrow H_2S + CO_2$), when it is again comes in contact with oxygen, so this will get converted into H_2SO_4 ($H_2S + 2O_2 \rightarrow H_2SO_4$). So, this process basically is aerobic biodegradation route of thiocyanate which can lower the pH of the effluent through the oxidation of reduced sulfur H_2S into H_2SO_4. So, this process finally reduces the pH of the treated effluent so this has to be further neutralized in order to make it to the effluent discharge standard.

So, these are the various processes which are used for degradation of thiocyanate this is basically the flow chart for the treatment of coke oven effluent so here if we see that is the coke oven wastewater so wastewater which is produced from the quenching operation with the wastewater which is produced from the scrubbing operation ammonia stiller, so they all are taken to the equalization tank and they are mixed together so this tank basically acts as a equalization tank where the concentration and the flow of the wastewater is averaged and this is also used for removal of some inhibitors which are basically affecting the nitrification and denitrification process so this goes for denitrification process where whatever the nitrate that will be converted back into the nitrogen gas and then these are the two-stage aerobic treatment process where this COD, BOD which are present as the organics like phenols they will all be reduced here so these are activated process activated sludge process where this BOD, COD and the phenol together they will be removed and then this is finally nitrification process whatever the nitrogen ammonia remains there that will be finally converted into nitrate and then finally this passes through the settling tank where all types of refractory compounds and the sand and silt particles they will be removed out after settling and then whatever the treated effluent that has to be further reused and recycled within the plant as a process water as a water to be used for a scrubbing purpose water to be used for quenching purpose so this is all recycled to get the zero discharge concept within the plant.

So, these are the references you can use.

Thank you.