Course Name: Industrial Wastewater Treatment

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Week – 10

Lecture 46: Treatment of wastewater produced from Refineries and Iron & Steel (Coke Ovens)

Welcome you all. Today I am going to deliver my lecture 1 of module 10 which is on treatment of wastewater produced from refineries and iron and steel industries. So under this we will be covering about the basic introduction about the iron and steel industry, the basic introduction about the production process, their growth patterns and the contribution of different countries in the globe towards the total global production of iron and steel which is one of the major construction material used in infrastructure development and then we will be also looking about the various unit processes which are used in the production of iron and steel in the industry and from these operations lot of waters are used and that results into generation of various waste streams within the plants. So, we will be looking about the different sources of the wastewater and the major contaminants which are found in their wastewater and then finally we will be looking into the detailed characterization of the wastewater produced from different unit operations from this industry.

So, let's start with the basic introduction about the iron and steel industry we see that the total global production of steel at present that is around 1.9 billion ton/annum of which the India contributes significantly to about 120.29 million ton/annum. And if we see in India the growth of this industry, we will see there are the seven major integrated iron and steel plants in India of which majority of the plants comes under the SAIL, which is the Steel Authority of India Limited the under which at least five out of seven major integrated plants. Then if we see this industry uses large amount of water that results into generation of wastewater at different proportions from different unit operations and on an average if we see in our country like per ton of steel production it will require around 25,000 to 60,000 liter of water and of raw material if we talk that is around four to five tons of iron ore that will be used along with this. There are other raw materials like fuels coke that is used and then there are limestone used as a flux material in the blast furnace of the iron steel industry. So, there are number of raw materials or bits the important ore that is magnetite or hematite.

So, if we see the global production of steel we can see pattern that Asian country that contributes to around 60 to 70 % of the total iron ore production and rest is of the world and the major sector after Asia that is the Russia which is the global leader in production of iron and steel. And if we see the country wise US is the largest producer of iron and steel followed by the India which is the second largest country producing iron and steel followed by Europe and finally the fourth place that comes that is China.

And the important raw material that is the iron ore which is required for this iron and steel industry. So there are various types of iron ores and this table shows the composition of various ores which are naturally found and which are mined out for production of iron and steel. So, the most purest form and most abundant form that is the magnetite which is basically having the steel gray or the black color and its composition if we see that is the most oxidized form of iron that is Fe_3O_4 which contains around 62 to 72 % of the iron and the second ore that is found that is a hematite in this category also there is the two types of this hematite one is red hematite another is a brown hematite and if we see this red hematite as the name indicates it is earthy or rocky red color and its composition if we see that is the ferric oxide which is Fe_2O_3 and also contains a good amount of iron that is around 60 to 70 % of the iron comparable with the magnetite and then the another type of hematite that is found is brown hematite which is basically brown in color and it's basically the hydrated form of this ferric oxide and that contains around 42 to 60 % of the iron and other than the hematite and the magnetite there is a Siderite or Spathic, that is basically crystalline gray color and its composition if see that is in the carbonate form that is $FeCO_3$ and this also found in terms of in the name of iron stones which is also having gray to light brown color and they have got the like the not very pure form of ore having iron ore content from 35 to 48 % in the Siderite and in iron stones it also varies from 30 to 42 %.

So, this is basically the flow diagram of the production process which are used in iron and steel industry. So if we start that is the coal mines basically the coal is used as a raw material here in the plant as a fuel. So, this coal is basically mined out, so there are having the integrated mines associated with the iron and steel industry. So, they may have this open cost mines, they may have underground mines so whatever the mined-out coal comes out from the mine that we say that is runoff mines, which basically contains lot of impurities and other inorganic impurities which contains quartz, silica and clay and other kinds of foreign materials. So, which basically increases the ash content of the coal. So, this coal which is mined out from the coal mines is first taken to the coal washery. So, this coal washery is the second unit operation in the iron and steel industry where this coal is washed out using the water as a washing media and then here basically that is the process of removal of the impurities present in the coal so that its carbon content can be further increased and the ash content of the coal can be reduce. So, this process is done by washing off coal so in coal washery again there are number of unit operations starting from crushing of the mined-out coal into a particular size then screening, then rinsing has to be done and then washing has to be done. So, finally this dry coal is produced which is mostly free from the inorganic impurities which are associated with the mined-out coal. So here since we use lot of water so that is one of the streams that is generated that we say that is the coal washery effluent, so this effluent contains lot of fine coals along with the sand and silt particles quartz particles. So lot of inorganic impurities are present in the suspended forms this contains around a lot of suspended solids. So, this wastewater is stream that is taken and segregated and then after the treatment it is again recycled back for this washing operation and then following to this after the coal is washed out. Then it is taken to the coke oven plants where the coke is converted into hard coke which is basically rich in carbon. So this process is carried out in the coke oven plants where this washed out coal is fed into the furnace, where it is heated in pyrolysis conditions to a very high temperature around 1100-1200 °C. So as all the volatile organic compounds which are present in the washed out coal they are removed in the form of this byproduct in the form of coke

oven gas which is the byproduct for recovery of various chemicals so this process converts the washed out coal into hard coke. So, this again has a number of unit operations which include the last operation which is the quenching of the heated coal, which comes out of this furnace. So, here lot of water is sprayed over this red heated coal so as to cool down its temperature to ambient temperature and then during this process the coal gets a lot of thermal resistance against the temperature. So, this process of quenching basically generates a lot of effluent which basically is one of the polluted waste streams which are generated which contains lot of toxic compounds like phenol, ammoniacal nitrogen, this also contains a lot of cyanide, isocyanate having lot of BOD and COD. So, this waste water is a particularly polluted waste stream which is generated and then it is treated separately in a coke oven plant. And this coke basically is used as a raw material here and in this basically the iron and steel industry. This is the blast furnace where this coke is used as a fuel and this there is a limestone quarries also similar to the coal because this lime is also one of the important raw materials used as a flux in the blast furnace along with the coke and the iron ore for the process of converting this iron ore in the form of pig iron for removing its impurities. So, this limestone quarries again they are mostly open cast and they are integrated with the iron ores steel industry. So, here whatever the mined out lime that is taken into the storage and this from storage this limestone is added into this blast furnace along with the coke and then the major important ingredients that is going to be fed into the blast furnace that is the iron ore and this basically in the form of magnetite or in the form of hematite that is sent to this blast furnace where this basically the entire iron ore along with the flux material and coke basically used as a reducing agent. So, here if we see the composition of this iron ore, so they are most oxidized form of iron, so here in the blast furnace we try to reduce this iron and ore to a lower oxidation stage so as to produce the purest form of the iron. So, all this mixture of this coke, limestone and this iron ore that is taken into the blast furnace, so blast furnace again it is a civil structure made of steel and lined with the refractory brick which acts as an insulator for the entire blast furnace structure, so inside this we used to have a temperature of 900 to 1200 °C. At this temperature this smelting of this iron ore is carried out so this operation basically results into the molten stage of iron which is purest form that is separated from rest of the impurities and this iron ore is then molded in the various types of ingots. So, this basically produced the pig iron and this pig iron is then becomes the raw material for the another shop which we say that is steel smelting shop. So, this basically is steel smelting shop where basically we used to convert this pig iron in the form of molten stage in the LD arc furnace. So, here whatever the this molten steel that is produced that is converted in the form of ingots and then these ingots basically they are different shapes of the iron molds they are generated and then they are soaked into a soaking pit and after this the next process these plastic ingots they become again the raw material for different unit operations like a part of this goes to the blooming units, a part of this goes to the billet mill and then finally the pickling is done. So, here this plastic ingots when it goes to the blooming mills basically here convert this purest form of iron this plastic ingots in the form of different shapes, different circular shapes, sheet shapes and then maybe round shape of bars so this shaping of the this steel that is carried out in the blooming mill where it uses lot of water and this basically led to the generation of oily and scale bearing waste streams, which are produced basically from this blooming mill and then it goes to the next unit where this is converted into in the form of mill house. So after this blooming mill it goes to the rail and structural mill where this different shapes of again the iron and steel that is produced in the form of I sections, in the form

of sleepers, like rail sleepers, in the form of channel sections, in the form of columns which are used normally in the infrastructure development as a steel. So, this is the final end product that is mostly generated after blooming mill and then a part of this plastic ingots basically that goes to the slab mills where the different shapes of the slabs they are casted and then from these slabs big size of slabs are then further divided into plates seats and tin plate that is in the different mill house that is called as the plate, sheet and tin plate mill house and after this shitting is done, plating is done then we need to have surface treatment of this finally finished product so, as to remove any other impurities if still present and to prepare the surface ready for painting ready for coating ready for plating. So, this is the process of carrying out surface treatment this is called as the pickling. So, this pickling is basically uses lot of organic acids, high molecular organics, organic acids which generates again the waste streams after cooling which is done in the cold rolling process. So this waste streams contains lot of heavy metals and mineral acids which are present in the wastewater and finally this end products are generated and then again if we see another section of this plastic ingots which are produced from the soaking pits that again goes to the billet mills, there number of billets they are produced or different shapes and size in the form of round in the form of circular in the form of square shapes, rectangle shapes and then again this pickling operation is done basically. And finally, we have wire mills we have pipe and tube mills so here basically different diameter of wires are produced and then here different types of pipes different diameter of pipes they are finally generated as a final end product. So, this is basically the overall process for production of iron and steel industry. And here if we see in the blast furnace if we see after whatever the flue gases that are generated from the blast furnace that contains a lot of particulate matter dust. So, this has to be passed through the dust separator, dust catcher. So, here basically this whatever the coarser fraction of the dust that is removed and then the rest of the flue gases after removal of this coarser fraction that goes to the gas washer house where the water is sprinkled over this flue gases. So, this water makes the particulate matters wet and because of their gravity then they used to separate down at the bottom then maybe the filter media. So, filter medias are also used so they will be attaching all these dust particles and finally from the bottom we will have a lot of wastewater will be produced from the washing of this flue gases and here this you see after this washer house when this flue gases comes out it contains a lot of moisture, so it is basically the wet gas which is relatively clean free from the particulate matters and still there will be very fine particulate matters aerosols that will be present. So, that can be removed by this electrostatic precipitator. So, this is one of the air pollution controls equipments where charge neutralization takes place and finally these charged particulate matters they are captured and the clean gas that is taken out and discharged into the atmosphere through the chimney. So, this is basically the entire process diagram which are used in an iron and steel industry for production of iron and steel different shapes, different size and different types of iron and steel products from different types of mills and shops.

So here we will basically introduce about the basic unit operations which have been used in the iron and steel industry. So as I said this is the blast furnace this blast furnace basically that is the furnace which is a tall stack made of steel lined rail and structural with the refractory bricks and this is basically designed for converting iron ore into the pure molten form of iron through the application of heat and the presence of flux and the coke as a fuel so this is the process which basically converts the iron ore which carries out the smelting of iron ore and produces more

refined form of iron in the form of pig iron and this pig iron basically if we see this is produced on smelting of iron from this blast furnace where this coke and limestone is used as a flux material in the blast furnace and this is basically this pig iron is then is taken to the soaking pit where it will be converted into the plastic pig iron and like in ductile form of iron and when this will be sent to different shops melting shops and mills for production of different types of iron and steel products. So, this is pig iron that will be basically sent first to the steel is smelting shop where this steel is smelting is basically shop that is where the steel is made by melting of this pig iron in a LD converters which is basically a refractory lined vessel which converts the this pig iron into this molten form of this iron this is also referred to as hot metal bath this is done by oxidation process by blowing lot of oxygen into LD converters so in the presence of this oxygen this iron again gets oxidized. So, the process of again converting this iron into steel that is basically not a reduction process but in contrary to this that is basically the oxidation process and then if we see that is the next operation after this hot metal broth is produced from steel smelting shop. So, this is basically converted into the ingots and the ingots and the continuously cost material from the melting plant that basically is used here as a raw material and converted rolling is done basically for forging press and the billet mills here all rectangular, square, round shapes of billets strips etc., they are produced from this process. And then if we see there are billet mills also there are pickling mills also. So, this billet mills basically this is used for costing of iron into various desired shapes like billets in this process molten metal is basically powered in different types of molds and allowed to cool and solidify in a different and desired shape. So, these billets can also be formed through the extrusion or rolling which involves passing of metals through a die to create a more uniform and consistent product from the billet mills and then basically this pickling process as I told this is the process of treatment of the surface of the metal which is derived from this melting shop and this basically used to remove the impurities such as stains inorganic contaminants any rust or scale formations. So, this is removed by using high organic acids so this basically a solution called pickle liquor which is usually contains the acid is used to remove these stains or impurities present onto the surface of the metals. So basically, these are the various unit of process which are used in the iron and steel industry.

So, here I'll show you the process flow diagram of a Durgapur steel plant, which is one of the major largest iron and steel plants in our country. So, here if we see starts from this from the top this is the storage of the iron ore, this is the storage of the limestone and here this coal is stored this is converted into the coke and then it all this three raw material that goes together they are mixed in a sintering plant and after mixing they are filled into this blast furnace and here heating of this coal is done basically this coke that produced a lot of carbon monoxide and then this carbon monoxide helps in reducing of this iron ore. So, this reduced form of iron ore that we say that is the pig iron that will be produced. So that this will go for casting and so here we'll get the pig iron pellets and then this molten broth produced from the blast furnace if we see that is going for the conversion into the ingots and conversion into the CC billets and then CC billets they are formed in different shapes and size and then it goes for the production and here this CC billets again if we see that goes to the merchant mill and where it is converted into different diameter of bars and round shape different shapes of the bars and here again if we see this ingots again if we see that goes to the blooming mill where this is converted in the form of thick seeds of different shape and size so there is a section mills, there is axle forge, there is axels so here this is medium

structures they are made like this I-sections, channel sections and then T-sections. So, different sections of medium structural steels they are produced from this blooming mills and then this billets which are produced then goes to the merchant mills again from this and this goes to the billets mills to produce the billets which can also be directly sold to the market and then finally goes to the scalp mill for producing the different scalps of the iron and steel. So, this is the real unit operations that are involved in a Durgapur steel plant. So, this is based on the real case study.

So let's now talk about the various types of wastewater and their major contaminants produced from iron and steel industries. So, if we see the first one that is the coal washery effluent, that is produced from the washery plants and then there is a coke oven effluent that is produced from the coke ovens and then the another major streams that is produced from the blast furnace, then we have effluent also produced from the hot rolling mill and then we have similarly billet mill effluent and then the wastewater which is generated as an effluent from the pickling shop. So, there are various based streams which are generated and we will be looking into its detailed characteristic and the major contaminants which are found in these types of waste streams.

So, if we see that is the coal washery effluent, so this coal washery effluent if we see the flow so this basically produces 0.18 m^3 of wastewater or the effluent per ton of coal which is being washed out in the washery. So, this generates around 180 liter of wastewater out of one ton of coal and in terms of pollution, if we see that contains lot of total solids and out of total solids if we see the major fraction that is of suspended solids. So, here if we see this total solid ranges from 1000 to 25000 mg/L. So normal range that is around 5500 to 6000 mg/L out of this the major fraction that is of suspended nature that is 800 to 24700 mg/L and then we have also some dissolved solids in the form of hardness basically in the form of calcium carbonate present, so that is around 230 mg/L. Similarly, if we see the pH, so it generates slightly alkaline streams of the wastewater. So, this wastewater if we see majority of its pollutant if we see that is the lot of suspended solids that are produced from this wastewater, so this sediment load has to be removed before this water is again recycled and reused in the washing operation.

And then this is basically the spent ammoniacal liquor which is produced from the coke oven plants after quenching is done. So, here if we see in terms of flow so it generates around 140 liter per ton of coal comparatively higher than the coal washery plants and again in terms of its pH if we see that is slightly alkaline pH of the effluent which is 7.5 to 8.5 but this effluent basically contains lot of toxic and hazardous compounds that is like cyanides are there, phenols are there and then thiocyanates are there thiocyanates are there sulfites are there so here if we see that phenols around from 900 to 1000 mg/L. Wherein if we see in terms of cyanide it contains 10 to 50 mg/L which is very toxic and hazardous to the human health and as well as living being and then it also contains thiocyanates also sulfates in the form of thiosulfates and sulfides apart from this there is also high content of chlorides which are found in the coke oven plants. So, basically this is most polluted stream that is generated from the coke oven plants apart from these toxic compounds if we see the ammonium concentration that is the total free ammonia 300 to 350 mg/L but if we see the total nitrogen content that again it ranges from 1000 to 1400 mg/L. So, this is like very polluted streams generated from the coke oven plants.

And then if we see this is the characteristics of benzol plants which are used for recovery of benzol. So, here if we see this plants again generates a very low amount of wastewater like only 20 liters that will be generated per ton of the coal being carbonized and then here if we see this again generate the wastewater having pH varying from 6 to 8.5. It also have traces of phenols ammonia and it has lot of organic contaminants as well as where BOD ranges from 300 to 800 mg/L. So, this is like the waste stream which is generated from a typical benzol plant waste.

And then we use water also in the blast furnace, so here again there will be lot of waste water that will be generated so here in terms of volume if we see around 500 liter per ton of this iron that will be produced in terms of pH if we say so this is again a slightly alkaline stream of the waste water that is generated and in terms of solids if we see again we'll see the total solids that is very high that is varying from 1000 to 10,500 mg/L out of which most of the solids they are suspended while the total dissolved solids ranging from 346 to 500 mg/L in terms of hardness also it is not very hard water so it contains the hardness from 80 to 118 mg/L as a $CaCO_3$ and in terms of chloride also it is not very high that is hardly 210 to 250 mg/L. So, this is a typical waste water characteristic which are generated from the blast furnace.

And then this is basically the wastewater or streams which are generated from the hot rolling mill process. So, here again if we see in this process lot of water is used so that is the maximum volume of the waste water that is produced from this hot rolling mill process that is 7 m^3 per ton of ingots which are processed. So, this around 7,000 liter of water will be produced per ton of ingots and it also generates alkaline waste stream pH varying from 7.8 to 8.1 but it has very low solid content that is not very high that is 346 to 500 mg/L out of which the hardness contributes to around 80 to 118 mg/L and then the major problem with this base stream that is the oil and grease which is produced in this process that is very-very high. So, there is a special treatment system must be provided for removal and separation of this oil and grease material from this wastewater.

So then we see here this is waste water which is produced from a typical power plant waste so this is basically the blow down wastewater which is produced from the boiler. So, here also if we see in terms of volume this is 0.13 m^3 per ton of steel produced and this waste steam is highly alkaline having pH range up 10 to 11 having a lot of silica content that is 50 to 70 mg/L and ample amount of phosphorus equal to 40 to 60 mg/L and it also contains chloride that is around 70 to 140 mg/L. So, this is basically the alkaline stream, so that has to be neutralized and the excess phosphate that contained blow down water from the boiler so that has to be removed.

So, these are the references you can use.

Thank you.