Course Name: Industrial Wastewater Treatment

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Week - 01

Lecture 05: Neutralization & Proportioning

Hello everyone, today we will be dealing with another important tools and techniques that is neutralization and proportioning. The lecture 05 of module 1 which will basically focus upon the various methods used for neutralization, the various methods used for proportioning and the effects of neutralization and proportioning on the industrial wastewater treatment. We will be looking on these two techniques neutralization and proportioning in more details. So let us talk about neutralization process, this is one of the important process which is used to make the water near neutralized range because if we see in the most of the biological treatment system, chemical treatment system, the requirement of influent water that is to be slightly alkaline range 7 to 7.5. If the water is acidic, water is very alkaline in nature then it has to be brought to the near neutralized range so as to make it fit for further treatment unit operations.

So neutralization is not only done for making the wastewater amenable for different treatment system but it is also to comply with the effluent discharge standard that is IS2490 according to that. The effluent discharge should have the pH between 5.5 to 9. So this process if any waste stream in the industry which does not have much of pollution which can be discharged by neutralizing the wastewater so this technique is also used for meeting with the effluent discharge standard.

Also this is required because very highly acidic or highly alkaline water adversely affect the environment and also reduces the treatment efficiency of the secondary treatment process. So let us talk about the various methods what we use for neutralization so that basically depends upon the type of the waste stream we are generating in the industries that may be acidic waste stream that may be alkaline waste stream. So if acidic wastewater are generated so we have this system like limestone treatments, limestone slurry treatment then caustic soda treatment. If the wastewater is highly alkaline then we have like acid neutralizer like waste boiler flue gas we can use sulfuric acid we can use then we can also use carbon dioxide for neutralizing the alkaline waste. If in an industry both these streams are available like both alkaline and acidic streams are there then we have to identify them, segregate them and measure their pH and accordingly do the proportioning and neutralization so that the water becomes nearly neutral range.

So that is the different methods we adopt depending upon the type of the waste stream it is generated from the industry. So one by one we will be looking into more details of this treatment process, these methods of neutralization. So first of all let us talk about the limestone treatment. So limestone it has a very high neutralizing power and its action can be further enhanced if we increase the temperature. So this process basically is used for as a low cost process because limestone is comparatively cheaper than other neutralizer used for acidic wastewater.

So this process basically has lot of potential to neutralize the wastewater. So this is basically the chemical reactions $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3$, if this is the limestone we can represent it as a $CaCO_3$it reacts with the acid and formally it forms the $CaSO_4$ and this H_2CO_3. So here if we see if we use this limestone this calcium sulfate is basically generated which can enhance the hardness and TDS value into the wastewater. This is one of the basic drawback of this limestone treatment but the reaction is very powerful and can neutralize highly acidic wastewater in a most economical method. So the reaction basically continues as long as this lime is available as soon as this limestone are finished again we have to do the periodic replacement so that the fresh limestone are available for neutralization.

So this requires fresh replacement of limestone into the tank for neutralization at a suitable interval and then also the drawback if we talk that is the time of the treatment like used limestone sludge that is generated from the process of neutralization the disposal of this is a serious drawback and the problem for this method but this is relatively inexpensive hence this is most extensively used in the industry for neutralizing the acidic waste water. And this is basically you see that is the influent water which is entering through this pipeline this is a neutralization tank where these are the lime stones filled up and when the water enters through this pipeline here it comes in contact with the limestone and then it starts neutralization and after the neutralization the neutralized water goes through this pipeline and here you can see this is online pH monitoring system which will continuously monitor the pH level of the neutralized wastewater which is going through this pipeline so as to add certain the extent of neutralization as per our requirement. So this is a typical sketch of pH neutralization tank which is used in a pipe system. And then this is another treatment what we call is caustic soda treatment which is done for acidic wastewater if we compare with limestone this is more power pool neutralizer than the lime and the chemical reaction that takes place here that is $H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2 \quad + H_2O$ so here whatever the product like Na_2SO_4which is generated is soluble in the water and does not contribute to increase in the hardness of the water whereas CO_2 is released as a gas getting concentrated solution of the caustic soda that may have fast reaction with the acid waste and can result into faster neutralization. The reaction product as I discussed that are soluble in nature but do not increase the hardness however this method is relatively costlier because the chemicals what we use that is caustic soda which is costlier compared to the limestone so this is not very extensively used in the industry because of cost economics as compared to the limestone treatment.

Then we talk to the another method that is neutralizing using waste boiler flue gas this is basically a new concept that the industry has started with the concept of reuse of waste boiler flue gas for the neutralization purpose. so this is based on this chemistry like it the flue gas contains lot of CO_2which is dissolved into the H_2O from this H_2CO_3 ($CO_2 + H_2O \rightarrow H_2CO_3$) which again reacts with the alkaline wastewater so this alkaline wastewater $H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + 2H_2O$ say if it is $NaOH$ so it will form Na_2CO_3 and finally this will be converted into $2NaHCO_3$ ($H_2O.H_2CO_3 + Na_2CO_3 \rightarrow 2NaHCO_3 + H_2O$) so whatever the alkaline pH is a big acid is generated because of the waste boiler flue gas so this helps in neutralizing the alkaline waste history. So this is the purpose of the system which is used to reduce the water streams reducing its pH to near neutralized rates so for this we need to have a facility to be constructed blower is fitted in the stack which blows flue gases through a pipeline system that carries this to the treatment plant and then at the treatment plant this is diffused through neutralization. Then another treatment that is carbon dioxide treatment as we have seen earlier this is CO_2 is diffused into the wastewater this is based on the same principle as the boiler waste boiler feed gases are used it forms a weak carbonic acid which acts as a good neutralizer and this method also have very less operational difficulties so this carbon dioxide treatment is also can be taken as a alternative for the neutralizing the alkaline wastewater. Then we have another treatment for alkaline waste that is sulfuric acid directly we use sulfuric acid to the alkaline waste. So this is a very common method but is basically expensive because of the cost of sulfuric acid involved into the process. This is the chemical reaction $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$ states this is $NaOH$ which reacts with H_2SO_4 to form the Na_2SO_4 and then it reduces its pH value so this is very expensive method and it is difficult to handle because of its corrosive nature. So this sulfuric acid treatment need to be designed with a great care. The proportioning is basically provided to make the wastewater amenable for the biological treatment system like we see the biological treatment system mostly we use aerobic treatment system, anaerobic treatment system which required different CNP ratio. So if we see for anaerobic treatment system the CNP ratio is carbon nitrogen phosphorus ratio that must be 300:5:1 while for aerobic treatment system we require CNP ratio of 100:5:1 so this maintenance of this CNP ratio in the influent water that can be done by this technique that is called the proportioning.

Also to discharge the industrial wastewater into the municipal sewer like for a small scale industry if they are not able to meet with the treatment plant then they have to discharge their wastewater to nearby municipal sewer so they that sewer they also have regulatory standard that is IS2490 that the wastewater should be proportioned in such a way that they should not exceed their effluent discharge standards. So this is mostly required in case of a small scale industries and also to protect municipal wastewater or the industrial wastewater against the sudden overdose of the chemical that may inactive the bacteria that may adversely affect the process. To facilitate this process of proportioning we need to have design a holding tank and with the variable speed pump to control the effluent discharge so that the proper proportioning of the flow in the tank can be obtained and a proportion and finally mixed wastewater that will go as a effluent for the treatment system. So how this proportioning is performed how the flow is mixed how the calculations are done for that we have taken few examples both on the neutralization and proportioning techniques. So, one by one we will be looking on different numericals so this is the numerical one if we see a solution of zinc hydroxide containing 10^{-3} M of zinc as a solubility product $K_{sp} = 8 \times 10^{-18}$.

So at what pH will the zinc precipitate out of the solution. So, this is we have to determine at what pH the zinc can be precipitated out of the solution and the second case if the concentration of zinc is decreased like 10^{-5} then at what pH the zinc will be precipitated. So before going into the problem read it carefully and then note down what are given like the solubility product of the hydroxide that is given as $K_{sp} = 8 \times 10^{-18}$ then case 1 when the zinc concentration is $[Zn^{2+}] = 10^{-3}$ M what will be the pH when it will be precipitated out. Similarly, the case 2 if we see if the zinc concentration is further reduced to $[Zn^{2+}] = 10^{-5}$ M then what will be the pH at which the zinc will be precipitated. So we have two cases so one by one we will try to determine the required pH for precipitation of zinc.

So we have as we can see there is a solubility product of $Zn(OH)_2$ which is equal to $K_{sp} = [Zn^{2+}][OH^-]^2$and then here if we put the value of this Ksp that is 8×10^{-18} which is given here and then also put the value of zinc which is equal to 10^{-3} then we can solve this what is the molar concentration of hydroxide. So this is OH^- ions its molar concentration if the zinc concentration is 10^{-5} it will come out $8.94 \times 10^{-8} M$. Now we already know this H^+ into molar concentration of H ions into molar concentration of OH^- ions that is equal to 10^{-14} so if we put the OH value here in this equation so what we will get what is the H^+ ion concentration that is $1.12 \times 10^{-7} M$.

So this is for case 1 when the concentration of zinc is 10^{-3} M. So once we have determined this H^+ ion concentration we can find out the $pH = -log\,[H^+]$. so here if we put the value of H^+ ions that is 1.12×10^{-7} then the value of pH that will come out 6.95 similarly for case 2 the solubility product is given as 8×10^{-18} which is equal to the 10^{-5} put the value of zinc here zinc concentration then find out this OH value and by solving the same way we can get the pH value 7.95 for the case 2.

So this is how we can use this concept for getting the pH value when the precipitation of zinc can be taken out from the solution. Then this is another example you see a paper mill waste water having BOD of 940 mg/L need to be proportioned in such a way that its overall BOD comes to 500 mg/L. So here the overall BOD that should be 500 mg/L while the incoming BOD level that is 940 mg/L. Proportioning has to be done by domestic wastewater having BOD concentration of 160 mg/L and then we have to find out what is the amount of domestic wastewater flow that need to be diverted if its wastewater flow is 6.5 MLD. So here what we can see is we have given the flow of the paper mill wastewater let us take this is Q_1, Q_1 is equal to 6.5 MLD and similarly the concentration of incoming paper mill wastewater BOD that is 940 mg/L. Similarly for domestic wastewater which need to be used as a proportioning agent so that is the flow we need to find out how much flow has to be diverted to the paper mill wastewater so as to get the overall BOD concentration of 500 mg/L if the concentration of BOD for this domestic wastewater is 160 mg/L. So, in this case if we see we can find out the ratio of the two that is C_1/C_2 where C_1 is the concentration of BOD in the paper mill wastewater C_2 is the concentration of BOD in the domestic wastewater the ratio of the two if we see that is 5.875 means this C_1 that will be equal to 5.875 times of concentration of domestic wastewater.

So now if we proportion these two wastewaters and find out the equalized concentration so this $C = \frac{Q_1C_1+Q_2C_2}{Q_1+Q_2}$. So using this formula if we see the overall concentration of BOD we put here 500, Q_1 we have to determine what should be the flow of the domestic wastewater so $Q_1 \times$ 5.875 this is the concentration of the paper mill wastewater we keep here in terms of domestic wastewater concentration by replacing the value of C_1 equal to 5.875 here and then $Q_2 \times C_2 / Q_1 + Q_2$.

If we solve this put the value we will get Q_2 is equal to 1.23 into 6.5 that is equal to 7.99 MLD. So this is how we can calculate here to make a wastewater having BOD of reducing its BOD from 940 mg/L to 500 mg/L which is amenable for the secondary treatment process if we decide like this then we can mix the domestic waste water along with the industrial wastewater in such a ratio that it can have the composite BOD level as designed.

So this is how we can work out the proportioning of the different waste stream for meeting with the objectives. So this is another example there are two waste streams W_1 and W_2 which are generated from a chemical plant so consider the flow following data answer the following like what would be the pH after the mixing if the two streams W_1 and W_2 having different flow having different pH having different BOD value are mixed together what would be the pH of the mixed wastewater and then again another problem is given that what amount of then suppose the pH is not near neutral so what amount of this 10 M NaOH is required to bring the pH of equalized flow to 7.5 so after mixing you want to get the pH of the mixed wastewater is equal to 7.5 so how much of 10 M NaOH is required then in what proportion the two stream need to be mixed to get an equalized BOD concentration of 800 milligram per liter and also find Q_1/Q_2 the ratio of this Q_1/Q_2 that has to be diverted that has to be proportioned in such a way to meet with the overall objective of getting the equalized BOD concentration of 800 mg/L. So this is the problem now let us solve this let us talk about the first what would be the pH after the mixing so we have two waste streams the pH are given of the two waste streams if we mix them what will be the equalized pH so how to solve this so here if we see the given is 1 MLD flow that is 10^6 L/D we have pH definition pH is $-log\,[H^+] = pH$ so here we can determine directly the H^+ ion concentration and that is equal to $10^{-3}\ M/L$ by putting the value of pH=3 so here if we put the value of equal to 3 we get this value 10^{-3}.

Similarly we have to also determine the H^+ concentration in the waste stream W_1 here also the flow is given that is 10 MLD means 10×10^6 L/D and similarly we have the pH value that is equal to 10 so this pH here we have to put as a 10 so here this H^+ ion concentration in this case that will be 10^{-10}. Now if we mixed what will be the equalized H^+concentration so if we mix this is the flow 1×10^6into H^+ ion concentration this is the Q_2 flow 10×10^6 L/D $\times\ 10^{-10}$ which is the H^+concentration divided by $Q_1 + Q_2$ so we get this is the equalized H^+concentration so this H^+concentration if we find out equalized pH so this will be $-log\,[H^+]$ ion concentration and from this we can get the value of equalized pH that is 4.04 for the mixed wastewater so this is how to find out the pH after the equalization after the proportioning then the let us talk about the second problem so in the second problem if you see required pH of equalization tank we have fixed it should be 7.5 but after mixing here if we see this is 4.04 so this will require addition of alkali and for addition of alkali there is a NaOH given as per the problem that how much amount of NaOH that to be 10 molar NaOH to be added in order to bring its pH equal to 7.5 so total flow of the equalized based water will be the sum of the flow of the two base stream that will be 10+1= 11 MLD and then we have to find out this the amount of NaOH 10 M required so for this we know that is the required pH is 7.5 so from here we can get the H^+ion concentration similarly if we use this equation H^+ion concentration into OH^- ion concentration then the pH must be equal to 10^{-14} so here if we put this value of H^+ ion here we will get what is the OH^- ion concentration in this so this will be equal to $\frac{10^{-14}}{10^{-7.5}}$ which is the H^+ ion concentration and we get this is $3.16 \times 10^{-7}\ M$ of OH^- ion should be there ok to get this required pH of 7.5 so we need to have OH^- ion equal to this but in the equalized based water pH we have 4.04 so from here if we get what will be the pOH so if we subtract from 14 this pH value. so it will give the pOH that is 14 - 4.04 = 9.96 so this pOH will be this so from here we can directly get the OH^- concentration the existing OH^- concentration in the equalized based water and that comes $10^{-9.96}$ and if we further do it then we will get it equal to $109.65 \times 10^{-12}\ M/L$ so this is the OH^- ion present so this is required so how much additional is required so this minus this will be the additional OH required so now further if we solve this so additional OH required we have calculated that is $3.158 \times 10^{-7}\ M/L$ and if we see the molar weight of OH^- ion that is 1 + 16 = 17 g/mol and the total flow is also given that is $11 \times 10^6\ L/D$ then here we have this additional weight of OH required for this much of flow so this is flow is $11 \times 10^6 \times 3.158 \times 10^{-7}$ then OH requirement into 17 gram like 1 mole will have 17 gram so this much weight of additional OH will be required this comes to 59.05 gram per day if we convert in kg per day so it will come $59.05 \times 10^{-3} kg/d$ now the weight of OH^- ions if we see what is present in 10 molar NaOH so that is 17 gram for is the molar concentration molar weight of OH^- ions and this is 10 M so it will be 170 g/L and this we can write as $170 \times 10^{-3}\frac{kg}{L}$ so now if we divide with this this is the total requirement of OH^- ion this divide with the weight of OH^- ions per liter so we can get how much liter of this 10 M NaOH concentration of solution is required so this is 0.314 L/D. So, this is how we can calculate the requirement of additional alkali agent sodium hydroxide or potassium hydroxide for further neutralizing or bringing the pH to another level then again if we remember the question what will be the Q_1/Q_2 so here BOD level we have to fix that is to be BOD of the waste steam 1 that is 1200, BOD of waste steam that is 600 and we want to bring the BOD equal to 800 mg/L so what will be this Q_1/Q_2 so here we can use this the equalized mass concentration concepts $BOD_{eq} = \frac{Q_1 \times BOD_1 + Q_2 \times BOD_2}{Q_1 + Q_2}$ so here we need to have this equalized BOD = 800 put for the waste BOD concentration of waste steam 1 this is BOD concentration of waste steam 2 and Q_1 and Q_2 are their flow and divided by $Q_1 + Q_2$ and now after solving this we can get this Q_1/Q_2 that must be equal to 1 is to 2 means 1 is to 2 ratio the waste steam should be mixed so as to get this equalized BOD of 800 mg/L. So, these are few examples we have done in this lecture similarly there will be many more examples that you can refer into these references and practice at your home.

Thank you.