Physico-Chemical Processes for Wastewater Treatment
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Lecture 20
Coagulation and Flocculation - III

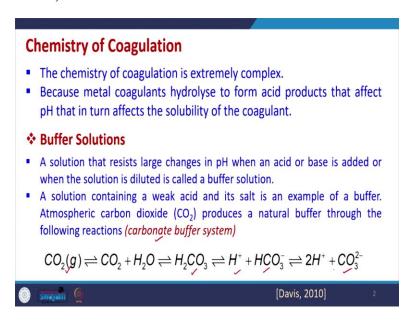
Good day everyone and welcome to this lecture on coagulation and flocculation. So, in the previous lectures, we started this particular section which is used in virtually all the water and wastewater treatment plants. So, in the coagulation, we add some additional materials which actually destabilize all those colloidal materials which cannot settle down easily. So, these coagulants are used in a number of ways. And in the previous lecture, we studied regarding the stability of the colloids, what are the different properties which should be measured in particular like zeta potential point of zero charge.

So, all those things we studied in addition, we studied the physics of the colloids and how the colloidal material, how the calculation works, and how the colloidal material is destabilized. So, we studied regarding all those parameters and various physics of the material we studied. And we found that there are four different mechanisms by which the coagulation works. So, one of them is like charge neutralization, another was adsorption on the coagulant itself. And inter bridging, then we have sweep coagulation.

And then there are other mechanisms also, which can work. Now, we will continue with the working of coagulants and we will try to study the chemistry of coagulation today in particular, how the coagulants behave in the water and how the chemistry changes, and how it works in our favour. And in addition, there are a number of parameters which affect the coagulant, in particular the dose, dose has lots of effects, in addition, the alkalinity of the water has lots of effects.

So, all those parameters in particular alkalinity, dose, pH, and the chemistry associated will be studied in this lecture. So, continuing with the chemistry of the coagulation, so, the actually the coagulation chemistry is highly complex, and in this case, whenever we are using any metal coagulants So, and if it is added in the water, it hydrolyzes to form various acidic products and that affect the pH and that in turn affect the solubility of the coagulant.

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So, suppose any metal coagulant is added and as soon as it is added the pH of the water changes and so, we may have optimized our condition with respect to one particular pH the coagulants are always decided on the basis of pH as well as their dose. So, if the it is already decided that okay the wastewater pH was in the range of 6 and we have decided a particular coagulant and once that coagulant is added that pH changes. So, if the pH changes actually the it will affect the later on coagulation behaviour. So, these things are very, very important and that should be well understood.

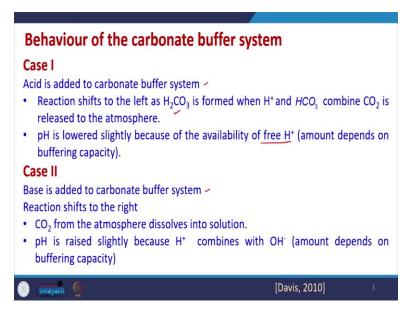
Fortunately for us, most of the water or wastewater have some buffering capacity and that buffering capacity is because of the CO_2 which is dissolved in the water. Now, what are buffered solutions? Buffered solutions are those which resists large changes in pH when any acid or base is added to the solution. And so, we always try to many times, add the buffer solution from outside in particular when we are performing some other type of reactions or otherwise in the liquid solution or any other type of solutions. But in this case, the natural buffering capacity is there because of the CO_2 which is dissolved.

So, the solutions generally the aqueous solutions have weak acid. And any buffer solution is like a weak acid and it is salts and they act together as a buffer. So atmospheric carbon dioxide, when it is dissolved in the water actually produces a natural buffer through the reaction which is given

here. And it is called cause carbonate buffer system. So, if carbon dioxide it is there and when it is getting dissolved in the water, it will form carbonic acid, and that carbonic acid may dissociate into a bicarbonate ion or carbonate ion.

So, these this reaction and vice versa also if suppose, we have a condition where bicarbonate ion and H plus ions are present and we add additional H plus ion, so, it will actually react with the bicarbonate ion and it will form carbonic acid. So, actually, whatever H we add, it will be used to form carbonic acid, but it will not change the pH because carbonic acid is getting formed. So, we have always in natural buffering capacity in water because of the dissolution of CO₂ in the water or to its solubility limit. Now, there are four different types of behaviours which are possible for carbonate buffer system.

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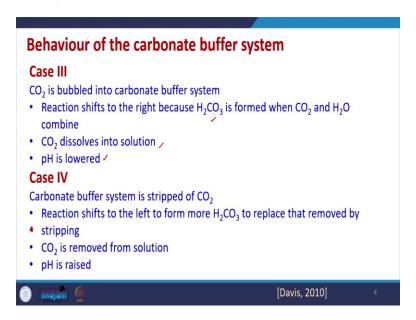


In the case one, suppose any acid is added to the carbonate buffer system. So, acid will react to the left as carbonic acid is formed. So, any acid will be there. So, we have additional H plus and that will react with the bicarbonate ion to form the carbonic acid and so, similarly, it is possible when two other, so, what it will do is that, when any acid is added the pH lowered is very less as compared to if this by carbonate buffer system would not have been there because the availability of free H plus will be very less and that will depend upon the buffering capacity of the water.

So, under this condition, if acid is added though the pH change should be high, but still the pH change will be very less because it will be taken care by the bicarbonate ion or carbonate ion, and respect to carbonic acid will be formed. If any base is added to the carbonate buffer system reaction will shift to the right and CO₂ from the atmosphere will dissolve into the solution.

So, amount of pH rise will be less because H plus will combine with OH minus ion and again the buffering capacity buffer will be maintained and the pH increase will be less. So, any if acid is added or base is added both condition the carbonate buffer system always provides good buffering capacity and pH changes minimal possible.

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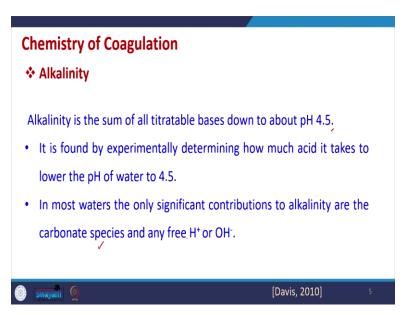
Second, third condition if suppose CO2 is bubbled into the carbonate buffer system, and this is the case where we like we have cold drinks, where higher amount of CO2 is bubbled into the water. Now, in this case, the reaction of the, the reaction will shift to the right because the carbonic acid will be formed and when CO2 and H2O under that condition when CO2 and H2O will combine. So, in this case, CO2 dissolves into the solution lowered, but it will not be lowered that but certain amount of pH certainly will get lowered.

Now, in the fourth case, the carbonate buffer system is stripped of the CO2 somehow suppose temperature is increased or otherwise and CO2 is coming out of the system. So, under that condition, the reactions shift to the left to form more carbonic acid to replace that removed by the

stripping, CO2 stripping.

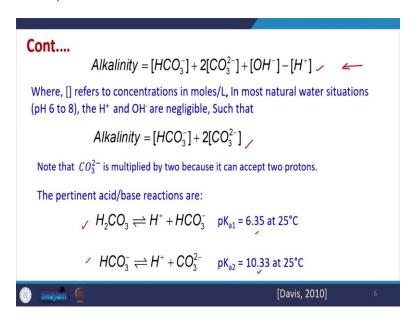
So, that is there a CO2 is removed, but because CO2 is removed the pH will be raised a little So, that is there. So, these are the different behaviours which are possible for carbonate buffer system. Now, in the chemistry of coagulation alkalinity is very important, though we have discussed alkalinity in detail earlier, we will still revise it a little bit.

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So, alkalinity is the sum of all titratable bases down to about pH of 4.5. And it is found experimentally that how much what we do is that we perform experiments and we try to see that how much acid is required to lower the pH to 4.5. And in most water the only the significant contributions to alkalinity are like carbonate species and any other H plus and OH minus ions. So, it is possible to consider other cations or anions also, but generally we consider only carbonate species for wastewater treatment.

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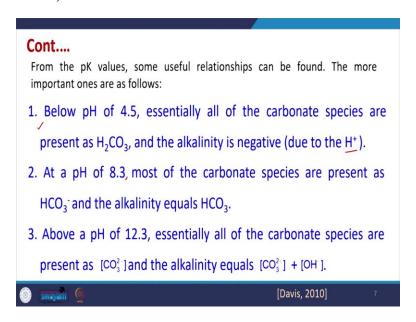


Now alkalinity was earlier also be defined, alkalinity by this particular equation where the parentheses refers to the concentration in moles per litre of the species respective ions and in most natural water situations around pH 6 to 8, the H plus and OH minus ions are negligible. So, under that condition we can consider like this, but this is more correct and we generally use this expression for finding out alkalinity.

Now, the acid-base reactions have already we have discussed a little bit in the previous like previous slide, but the reactions can be written like this carbonic acid breaks into H plus and bicarbonate ions at pKa value of say 6.35 And similarly, the bicarbonate and breaks into H plus and carbonate ions at the pKa value of 10.33 at 25 degrees centigrade.

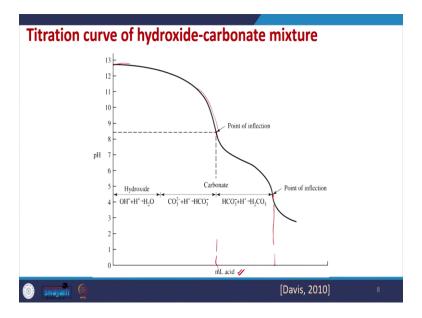
Now, both these pKa values can be used together and they give a lot of idea. So, what is done is that from the pKa values some lots of useful relationships can be found like the below pH of 4.5 all the carbonate species which are present are only in the form of H2CO3 and alkalinity is negative.

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So, under that condition that alkalinity will be negative not be positive and that will be only because of H plus that is there. At a pH so, all the species actually all the species everything will go off and only minus H plus will be there. So, alkalinity will become negative. At a pH 8.3. Most of the carbonate species are present as carbonate, bicarbonate ion and alkalinity equals to that of the bicarbonate ion. Above pH 12.3 essentially all the carbonate species are present as carbonate ion and alkalinity is equal to carbonate ion plus OH minus ion. So, we have above 12.3.

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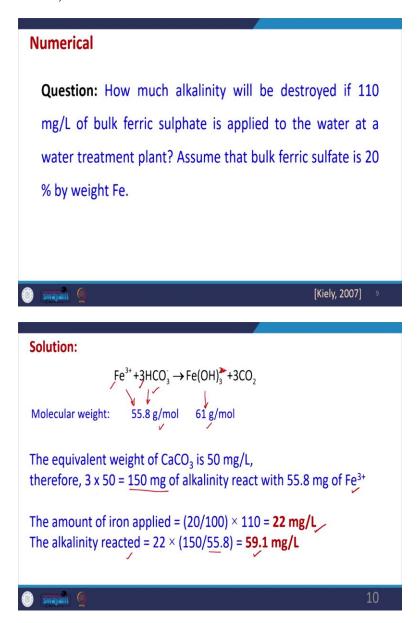


So, what is done is that any solution suppose we take we have to find out the alkalinity of water this we have studied earlier also. So, what we do is that we start adding some acid and try to measure the amount of acid which has been used. Certainly, we should know the normality of the acid beforehand and generally H2SO4 is used as a acid and we measure the pH. So, as soon as we will start adding the acid to any water which is having suppose high pH.

So, it will decrease the pH will decrease we can see from here the pH is decreasing. And at two points at two different points, we will be having some point of inflection. So, we always measured that how much volume of acid has been used up to this point and up to this point. So, two points are very important. And we measure the volume of acid which has been used to lower the pH of the water to first point of inflection and second point of inflection and those points of inflection give idea that whether what is the alkalinity.

So, this we have determined that alkalinity equations and we have determined salt problems also related to alkalinity previously. So I will not go further into this but that is very, very important for coagulation. We will just study within two slides, we will understand what is their importance. So, all the we can see that all the alkalinity goes off the second point of inflection, so that is there.

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Now going for that there is a one question, numerical question is given here that how much alkalinity will be destroyed if suppose 110 milligram per litre of bulk ferric sulphate is added to a water in a water treatment plant assume that the ferric sulphate is 20 percent and it is containing 20 percent by weight of Fe so this is being asked. So, they are asking that how much alkalinity will be destroyed.

So this is there. So what we have to do whenever we have to solve these equations, we have to look for the what are the reactions of like ferric sulphate so in ferric sulphate we have to look for

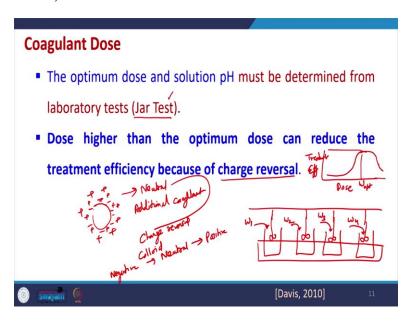
ferric and alkalinity what are the reactions. So alkalinity maybe bicarbonate carbonate. So in this case, this is the expression which is used. And in this case we find out the molecular weights of with respect to carbonates as well as the ferric hydroxide. So, we see that, okay this 2 plus will not be here. So, this ferric hydroxide the equivalent weight of calcium carbonate is 50 milligrams per litre this also we have studied earlier.

Now, what we see is that three times of alkalinity bicarbonate alkalinity is required when we compare with respect to ferric. So, under that condition so, that means, we will be requiring three into 50 that means 150 milligram of alkalinity will react with 55.8 gram milligram of Fe3 plus. So, this is the molecular weight of Fe, and this is the molecular weight of FeOH3. So, this okay and now, the amount of iron that has to be applied because it is only given that it contains 20 percentage of iron.

So, out of that 20 what we have to, out of 110 which is given here we can see that 110 milligram per litre of bulk ferric sulphate it will contain only 22 milligram per litre of ferric or iron. So, the alkalinity reacted will be calculated based upon the reaction stoichiometry and we can do it by because we are reacting only 22 milligram per litre of iron so, 22 multiplied by 150 which is the amount of alkalinity which is required and 55.8 is the amount of this the molecular weight of carbonate.

So, from bicarbonate if we solve it, we will be finding that okay 59.1 milligram per litre of alkalinity will react with this amount of iron if it is added. So 110 milligram per litre of ferric sulphate it is added. Now, from this question, we see that there is always a reaction of coagulants and it is ion with the different alkalinity and that alkalinity may be bicarbonate carbonate etcetera.

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So, and what is their importance, so, that also we have to study, before that there are some other things that we should study and in the coagulation the optimum dose that what should be the amount of coagulant that should be added is very very important. And this is so because we have to see that how much amount is required, which is good enough for destabilizing the colloids s. So, we know that colloids have some charge, so they are negatively charged. So, this is the negative charge that they have.

Now, what we do is that we add coagulant from outside and positive charge comes to the near the surface of the colloids and they become overall neutral. Now, if suppose we add additional coagulants beyond the optimal dose, so if suppose any additional coagulant is added to under that condition, what will happen the extra positive charges will be there for that will be more positive charge will be there and in this case, that charge reversal will happen and the charge reversal will happen and the colloids will become positively charged.

So, earlier the colloids was negative charge we converted into neutral and because of the addition of more coagulants it has become positively charged. So this which is not desirable. So, this is called charge reversal. If we add coagulants beyond the optimum dose, so we should in most of the water and wastewater treatment plants, they have some laboratories and these in these laboratories they perform these tests very regularly and these tests are called jar test. So in the jar

test in the same platform, like this is a platform so, we have different beakers which are kept here.

And in these beakers, they add different amounts of coagulants so these coagulants will be like suppose that dose is W1, then W2, then W3 and then W4. So, these type of dose will be there, certainly all will be containing some mixer and all are connected by a common rod. So, this is there. And after certain time, what they will do is that they will see the percentage removal efficiency or treatment efficiency. So, they will plot this type of graph. Like this is the dose and this is the treatment efficiency.

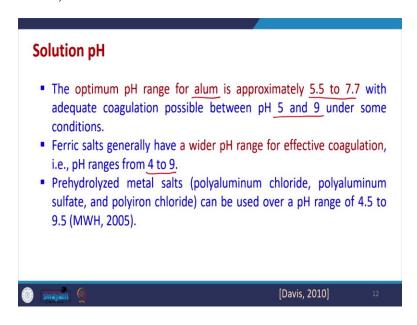
So, treatment efficiency will be like this. So, it is possible that it will may go like this. So, they are they look for the dose, which is having the maximum treatment efficiency, but, in the coagulation, if suppose, this process is performed for adsorption. So, this will go straight, but for coagulation, it is possible that after a certain time this coagulation, the treatment efficiency may decrease.

And so, that means, this dose which was optimum dose that should be used, we should never use the dose beyond the optimum value where the charge reversal may have occurred and it will decrease the overall efficiency of treatment. So, this is very, very important that we should always perform the jar test very regularly and try to find out the optimum dose. Similarly, the same way we can vary the pH, add the coagulant and cross-check that which pH is good for this particular water at which the coagulants may perform very well.

So, both optimum dose and solution pH may be optimized using jar test. Solution pH we should not vary that much, because we select the coagulant based upon the solution pH because we cannot change the pH that much of the that huge quantity of water, but still it has a lot of importance.

So, sometimes we may have some other streams so, we can mix the streams to change the pH. So, and how much mixing is possible in what ratio. So, through that pH change is also possible in some of the cases. So, under that condition, we can have an optimum pH range also. But generally, if the water pH is known solution pH our water pH known we can decide the coagulant.

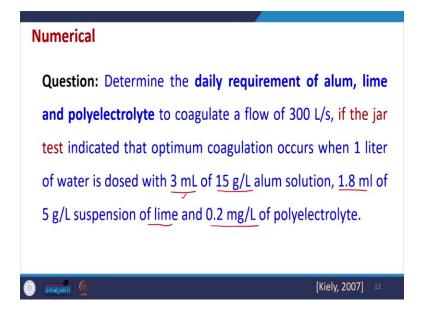
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Like for optimum pH range for alum as a coagulant is approximately 5.5 to 7.7 and with adequate coagulation possible between pH 5 and 9 also, so, under some condition. With ferric salts, they have a wider pH range under which they can work and it is from 4 to 9. And similarly, prehydrolyzed metal salts many polyaluminium chloride and polyaluminium sulfate, polyiron chloride all can be used in the wider pH range and they are very common because they have lots of metals which are metallic ions which are coming out.

So per unit amount they have more metallic ions. So they can destabilize the colloidal particles within the liquid solution very quickly. So, solution pH is very important and based upon that we select the coagulant certainly we perform the jar test, under different Coagulant doses, different pH ranges and cross-check that where is the maximum efficiency which can be obtained. So, this is possible.

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Now, this is another question that, determine that daily requirement of alum, lime and polyelectrolyte which may be required to coagulate a water flow of 300 litre per second. So, very, very high amount of water is coming. If that jar test indicated that the optimum coagulation occurs when one litre of water is dosed with a combination of coagulants and those combination of coagulant is like 3 ml of 15 gram per litre of alum solution. So, it tells that in the coagulation, we have different types of solutions which are available, like alum solution, Iron solution, Iron type of coagulants.

So, these and some may be directly available in the solid form. So it is possible so it has been cross-checked that if 3 ml of alum solution 1.8 ml of Lime which the lime solution is 5 gram per litre lime is added. So as to see the how the alkalinity actually behaves. So this we are going to study more in detail. Then 0.2 milligram per litre of polyelectrolyte. So we had three things added together as a coagulant per litre of water and the amount of water which is coming is 300 litre per second. So we had to cross check that what is the daily requirement of alum, lime and polyelectrolyte.

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Solution:

Daily flow rate = 300 \times 60 \times 60 \times 24 = 25.92 \times 10^6 \text{ L/day}

Alum requirement 3 mL of 15 g/L

= 45 \text{ mg/L} \times 25.92 \times 10^6 \text{ L} = 1166.4 \text{ kg/day}

Lime requirement 1.8 mL of 5 g/L

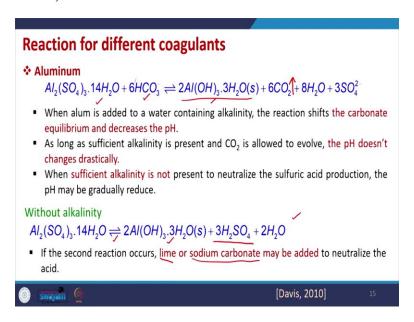
= 9 \text{ mg/L} \times 25.92 \times 10^6 \text{ L} = 233.28 \text{ kg/day}
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So, it is very easy question. So, daily flow rate is like per day this much is the flow rate. So, we can calculate very easily litre per day we can say like litre per day also okay then alum requirement is like 3 ml per 15 gram per litre. So, that means, in total, we require we require this much amount of a coagulant 15 into 3 and we have to cross check this with respect to the amount of water which is required per day. And solving we can find out okay 1.116 it is equivalent to around 1.1 ton of coagulant per day.

So, with this is very huge dose you can now cross see that how much sorry, this is yes, so, 1.16 ton of alum is required per day. Similarly, lime requirement is 1.8 ml of 5 gram per litre solution. So, total amount of lime which is required is 233 kg per day. So, we can perform the calculations very easily. And similarly, we can we can perform the calculation for polyelectrolyte also.

So, this is possible now, going further in this case we found that okay for each of the alum we are adding the lime also. So, the question may arise in the mind why we are adding the lime why only alum should have been enough. So, this is answered in the next slide.

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So, what is done in the actual condition if suppose we add alum. So, alum under normal condition when we have some alkalinity present in the water, so, it will react with that alkalinity and form the respective aluminium hydroxide via this reaction. Now, in this case what happens that when alum is added to a water which contains alkalinity that reaction at least saves the carbonate equilibrium and decreases the pH. So, this will always happen. Now, as long as the sufficient alkalinity is present to CO2 will be formed and this CO2 will evolve out and since if the CO2 goes off, that means, the pH will not change drastically, if this alkalinity is there and it will also save the equilibrium towards the right and we have more amount of aluminium hydroxide which will be formed.

So, when sufficient alkalinity is not present, like suppose this HCO3 is not present. So, under that condition without alkalinity the reaction will be like this. So, under this condition, what we see is that a lot of sulfuric acid is getting formed and this sulfuric acid is not desirable, because it will lower the pH of the solution. So, and this is also the amount of aluminium hydroxide will be lower because the reaction has not shifted to the right because the CO2 has not gone out.

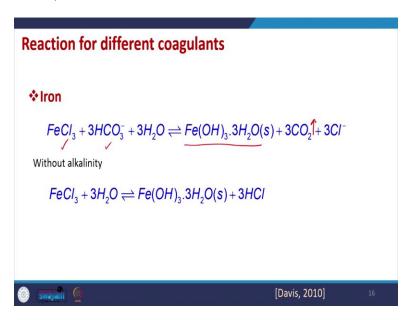
So, this equilibrium condition will be maintained and this equilibrium, so, amount of aluminium hydroxide per unit aluminium sulphate is will be less in the first case when alkalinity is present it will be higher and also it will shift because it the CO2 can go off in the second case, there will be

a drastic change in the pH if we do not add anything from outside. So, it is very important that we add some of the things from outside so that the this we can neutralize the acid which has formed.

So, we add lime or sodium carbonate from outside to neutralize the acid form otherwise the pH n will be drastic and our optimum pH condition may change. So, the behaviour of alum may also change. So, this way very important to have some alkalinity in the water if alkalinity is not there we have to add some alkalinity from outside and that alkalinity added is generally the lime alkalinity.

So we do this and through this we can properly optimize the coagulant dose. All the coagulant performed very well when certain amount of alkalinity is present. And if that much amount of alkalinity is not present, we had to calculate what is the alkalinity requirement and based upon that we add the lime or sodium carbonate from outside. So, this is done.

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Now, similarly for iron as a coagulant for this also, like ferric chloride is there, so we have bicarbonate and we have ferric hydroxide formation. So, in this case also CO2 will be formed, and that CO2 we will have to see that that CO2 goes off and it goes off the equilibrium shift and we will be having more ferric hydroxide formation.

Without alkalinity again HCL formation will be there and this HCL will actually lower the pH of

the solution and which is not desirable at all. So, that is why again, we will have to add some lime or sodium carbonate from outside so that we can neutralize the acids and we can, thus we can adjust we do not allow the pH change too much. So, this is there.

So we learned in this lecture that for efficient working of any coagulant certain amount of alkalinity is always desirable. If that alkalinity is not available, we have to add that alkalinity in the form of lime or any other or generally lime is added and that we can calculate later on. So, this is very very important consideration and we should add.

And similarly, there are many other things that we can calculate from this that how much amount of lime per day will be required, how much amount of precipitation will happen, because, this precipitate will form solid, so, it will form sludge. So, that means the sludge formation will be there. So, we can tentatively calculate that how much amount of sludge will be formed. And this sludge we have to see that how we can take away from the plant how we can settle it out.

So, all those things are later calculation, but it gives certain idea regarding all these parameters. We will solve some numericals and other things later on. And we will try to go further with understanding of different types of coagulants and how they work. So, thank you for this lecture.