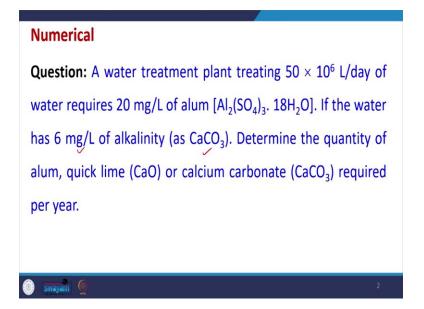
Physico-Chemical Processes for Wastewater Treatment Professor V.C. Srivastava Department of Chemical Engineering Indian Institute of Technology, Roorkee Lecture 21 Coagulation and Flocculation – IV

Good day everyone and welcome to this lecture and in the previous lecture we studied regarding the Coagulation and Flocculation's. We will continue with the same and in the previous lecture we studied that how the chemistry of Coagulation is highly related to alkalinity. And we found that until unless there is a certain amount of alkalinity which is present in the water the Coagulation system does not works well. And we require a certain of amount of alkalinity to be present in the water otherwise we have to add that alkalinity from outside so that the optimum condition with respect to treatment is maintained.

And the coagulants performance actually get enhanced only if certain amount of alkalinity is present. So, now we are going to solve one problem and understand the relationship further. And also, through this we can understand that how we can perform simple calculation with respect to requirement of different amount of coagulants, lime and other parameters as well. In the previous lecture also, we studied that optimum dose is very important and optimum dose is obtained via performing a jar test.

And in the jar test we have within the jar test apparatus 5 6 jar tests are kept and within each of the jar we have the same water but different amount of coagulants which are added. And through this we get to know that what is the optimum amount of coagulant which is required. So, coagulant solution pH so depending upon that coagulant is decided and alkalinity. So, these are very very important parameters with respect to treatment. So, we are going to solve one problem starting today.

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And in this case, it is being told that a water treatment plant has to treat 50 into 10 raised to 6 liter per day of water that means 50 million liter per day of water and for treatment of that water 20 milligram per liter of alum has been found to be optimum dose. Now, if the water has itself a alkalinity of 6 milligram per liter, so we performed a test we found that the water is having 6 milligram per liter of alkalinity as CaCO3. Now, we need to find out the quantity of alum, quick lime or calcium carbonate which is required per year. So, how much quantity of these will be required per year and from that we can calculate the cost also so this is we are going to perform.

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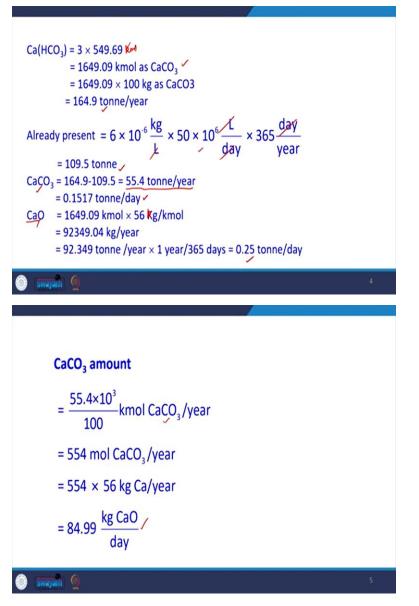
Solution: $Al_{2}(SO_{4})_{3} \cdot 18H_{2}O + 3 Ca(HCO_{3})_{2} \longrightarrow 2Al(OH)_{3} + 3 CaSO_{4} + 18 H_{2}O + 6 CO_{2} \uparrow$ $3 CaCO_{3} + 3 H_{2}O + 3 CO_{2} \longrightarrow 3 Ca(HCO_{3})_{2}$ Alum = $20 \frac{\text{mg}}{\text{L}} \times 50 \times 10^6 \frac{\text{L}}{\text{day}} \times 365 \frac{\text{days}}{\text{Year}}$ = 3.65 × 10¹¹ mg/ym 1 ton = 906.7 kg $= 3.65 \times 10^5 \text{ kg/m}$ 1 tonne = 1000 kg = 365 tonne/year Conversion of kg to kmol = 549.69 kmol

So, for alum this is the reaction which is there with respect to like if we add alkalinity so alkalinity is in the form of bicarbonate and so this is the reaction which is possible. And here we found calcium sulphate which is will which will go into the sludge aluminum hydroxide which will also go down CO2 which will go outside. And because of that the reaction will shift towards the right and will be having more aluminum hydroxide. Now, this calcium carbonate actually that we add it also reacts to form calcium bicarbonate and which is actually the one which the alum reacts.

So, alum dose has been given to be 20 milligram per liter and we have to treat 50 into 10 raise to 6 liter per day of water. So, this liter liter goes off so milligram per day and this milligram per day in a year we have 365 days so that also goes up so we have we can calculate so this will be the amount which is required per year.

Similarly, we can convert this amount into kg per year and we can convert this into amount ton per year. Remember the one mistake many people commonly do that there is a unit which is written as ton so this is called as short ton. So, this is equivalent to 906.7 kg whereas the this user metric ton is 1000 kg so this unit should be always be remembered.

Now, conversion we can convert to kilo mole also, this much amount of kilo mole of alum it will be required per year so this is the so we you can tentatively see 365 ton per year that means 1 ton daily of alum is required. So, cost wise also we can if you can find out a per kg or per ton so this will be the cost incurred per day on alum only. Now, during this reaction we find that we required certain amount of calcium carbonate and that calcium carbonate will be from that calcium bicarbonate will be from calcium carbonate. (Refer Slide Time: 05:56)



So, this bad calculation also we have to perform so how much amount of calcium bicarbonate is required it is three times the moles which is required by the with respect to alum. So, alum mole requirement is 549.69 and the calcium carbonate will be three times of that so that is how these three times into 549.69.

So, we get in mole that will be in mole sorry kilo mole because it was kilo mole so this is in kilo mole and as CaC03. Now, for calcium carbonate the molecular weight is 100 so that means multiplied by 100 and then further divided by 1000 so we get 164.9 ton per year of calcium bicarbonate is required.

Now, already how much amount of alkalinity is present so it is being it has been given that 6 milligram per liter of alkalinity is present, so this is 6 milligram per liter is equivalent to 6 into 10 raised to minus 6 per kg. And for water the amount is this this was the amount of water treated and again day per year so if he goes off so 109.5 ton of alkalinity is already present. Now, so that means we have to add 55.4 ton of calcium carbonate or this alkalinity from outside and the this is the ton which is required per year. So, from this we can calculate this is the requirement.

Now, for CaO also we can calculate from the kilo mole and after some calculation will be finding that the amount of calcium oxide which is required will be 0.25 ton per day. So, these calculations have been made on the stoichiometry requirement and as well as with respect to the molecular weight which is there for each of them for so calcium oxide also so this is there. So, this lime may if lime calculation is required this is possible if carbonate calculation is required this is there. So, these are the additions per day or per year we can calculate so this is possible.

Now, calcium carbonate also through this we can perform so 55.4 into 10 raised to 3 kilo mole per calcium carbonate per year. So, this has been converted into mole and then mole into calcium so amount from calcium into calcium oxide so this is the requirement per day. So, this way we can perform the calculations for all these requirements which are there.

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Solution: $Al_2(SO_4)_3$. $18H_2O + 3 Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 + 3CaSO_4) + 18 H_2O + 6 CO_2$ $3 \operatorname{CaCO}_3 + 3 \operatorname{H}_2 O + 3 \operatorname{CO}_2 \longrightarrow 3 \operatorname{Ca}(\operatorname{HCO}_3)_2$ Alum = $20 \frac{\text{mg}}{\text{L}} \times 50 \times 10^6 \frac{\text{L}}{\text{day}} \times 365 \frac{\text{days}}{\text{Year}}$ $= 3.65 \times 10^{11} \text{ mg/sec}$ 1 ton = 906.7 kg = 3.65 × 10⁵ kg/m 1 tonne = 1000 | = 365 tonne/year Conversion of kg to kmol = 549.69 kmol

COAGULATION REAGENTS

Numerous chemicals are used in coagulation and flocculation processes. Desired characteristics:

- Effectiveness
- Cost -
- Reliability of supply -
- Sludge considerations
- Compatibility with other treatment processes
- Secondary pollution
- Capital and operational costs for storage, feeding, and handling

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- Coagulants and coagulant aids commonly used are generally classified as inorganic coagulants and polyelectrolytes.
- Polyelectrolytes are further classified as either
 - synthetic-organic polymers
 - natural-organic polymers
- The best choice is usually determined only after the jar test is
- done in the laboratory.

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Now, going further what are the different types of coagulants and other things that we use commonly in the water treatment plant. So, there are numeric chemicals which can be used for the coagulation and flocculation. The essential desired characteristics are listed here first thing they should be highly effective at the solution pH for that particular water which may contain different amount of organic inorganic pollutants etcetera. And it should be able to settle down maximum amount of uncertain able matter. So, that is there certainly cost is very very important since the amount of these coagulants which is required is very high there should be a reliability of supply.

The supply should be thoroughly maintained there is a sludge consideration also because we see in the previous question that lot of these sludge is formed and we can in fact perform calculation of these sludge's also that how much amount of sludge that we have to handle per day from coagulation unit itself. Similarly, from primary secondary treatment also sludge will be generated so all is clubbed together to know that how much how many trucks of sludge will be generated per day how much ton of sludge will be generated per day.

So, sludge consideration is very very important, compatibility with other treatment process because after coagulation also we have secondary treatment or tertiary treatment, so this is very important consideration that we should not add something which should affect the secondary treatment processes so this is very important consideration. Then the secondary pollution which happens because of the sludge which is getting generated so that is also very important. Then we have lot of capital and operational cost for storage, feeding handling these much amount of chemicals so these are the essential consideration.

The first two three are more important as compared to other but others also have lot of role to play. Now, coagulants and coagulants aids which are commonly used they can be classified as inorganic coagulants which are very very common and then polyelectrolytes also. So, both polyelectrolytes inorganic coagulants they are all used.

Now, within poly electrolytes there are natural organic polymer and then synthetic organic polymers so this is possible. The best choice is always determined using the jar test and also checking whether what is the cost. So, we have to optimize on the cost and that can be done very quickly it is not very difficult in the laboratory. Some inorganic coagulants along with the associated advantages and disadvantages are listed here.

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Common inorganic coagulants along with associated advantages and disadvantages

Name	Advantages	Disadvantages
Aluminum Sulphate (Alum) Al ₂ (SO ₄) ₃ .18H ₂ O		
Sodium Aluminate Na ₂ Al ₂ O ₄	Effective in hard waters; small dosages usually needed	10 N. 10

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The following table lists several common inorganic coagulants along with associated advantages and disadvantages.

In some applications, floc	
In some applications, floc	Not commonly used; little full-
formed is denser and faster	scale data compared to other
settling than alum	aluminum derivatives
Effective between pH 4-6 and	Adds dissolved solids (salts)
8.8-9.2	to water; usually need to add
	alkalinity
Effective between pH 4 and	Adds dissolved solids (salts)
11	to water; consumes twice as
	much alkalinity as alum
	Effective between pH 4–6 and 8.8–9.2 Effective between pH 4 and

Name	Advantages	Disadvantages	
Ferrous Sulphate (Copperas) FeSO4.7H2O	Not as pH-sensitive as lime	Adds dissolved solids (salts to water; usually need to add alkalinity	
Lime Ca(OH) ₂	Commonly used; very effective; may not add salts to effluent	Very pH-dependent	

So, like alum is the most common coagulants and so here aluminum coagulants are listed alum and sodium aluminate. So, alum is like highly effective in the pH range of 6.5 to 7.5 it can go up to 5 also and it is easy to handle and apply and most commonly used coagulant it is one of the most commonly used coagulant. And but it has disadvantage that it adds lot of dissolved solid or salts to the water if by combining with the carbonate alkalinity that is there and certainly sometimes we have to add lime also from outside. Similarly, sodium aluminate is very good for hard water only small doses may be required for hard water often it may be mixed with the alum also.

So, alum is common sodium aluminate may be added with the alum itself and it is high costlier as compared to alum and it is ineffective in soft water so this is there. For hard waters we may add sodium aluminate extra from outside. Similarly, poly aluminium chloride is another aluminium related coagulant and which is very commonly used and, in some applications actually it is more used because it will form flocks which are highly denser and it settles in much lesser time as compared to alum so that means the settling tank will the cost of the settling tank will be much lower.

And we can handle more amount of water in the same volume of the settling tank, so this is possible. And it is more used in the chemical and process industries where complex type of wastewater are there. Certainly, some disadvantage is there with respect to using for the water treatment. Some other iron related coagulant are like ferric sulphate, ferric chloride so these are common so they have different pH ranges under which they operate. Certainly, their pH ranges

are broader as compared to lm coagulants but the requirements are also different they add lot of salt to the water so the secondary pollution becomes very important.

Usually they require more amount of alkalinity so the alkalinity has to be added from outside so that adds to the amount of ah dissolved solid which are getting generated so this is there and they consume around higher amount of alkalinity. Similarly, ferrous sulphate and lime also are added so ferrous sulphate is not much pH sensitive as compared to lime but they also I have the disadvantage that they add solids to the water.

Similarly, lime is generally we have to add the lime if enough alkalinity is not present so that is always there they do not add salts to the effluent but they still generate large quantity of sludge so this is the problem. If we have overdose of lime then that will actually result in poor quality of treated water that is also very important consideration and during the addition of lime so we should be properly selecting that how much amount of lime has to be added. Then we have lot of polyelectrolytes also which are used so water soluble polymers they contain lot of ionic charge along with the polymer chain so they may be added.

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Polyelectrolytes

- Water-soluble polymers carrying ionic charge along the polymer chain.
 Natural and synthetic polyelectrolytes.
- Natural polyelectrolytes include polymers of biological origin and those derived from starch products, cellulose derivatives, and alginates.
- Depending on the type of charge, when placed in water; the polyelectrolytes are classified as anionic, cationic, or nonionic.
 - Anionic—ionize in solution to form negative sites along the polymer molecule
 - Cationic—ionize to form positive sites
 - Non-ionic—very slight ionization

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And they may be along with that they may be natural polyelectrolyte they may be the man made or synthetic polyelectrolytes so that is possible. So, within natural polar electrolytes they contain polymers of biological origin and those which are derived from like starch products, cellulose, alginates etcetera. So, different types of polyelectrolytes are available depending upon the type of charge that they generate when they place in water they may be anionic cationic or non-ionic so they may form negative sides they may form positive sides or only a little ionization when they are added in the in the water. So, different types of poly electrolytes are available.

Commo	n organic po	lyelectr	oly	tes	
Polymer Type	Name	Mol.wt.		Available form	Typical use
Nonionic	Polyacrylamide	1×10 ⁶ 2×10 ⁶	to	Powder, emulsion, solution	As flocculent with inorganic or organic polymers
Anionic /	Hydrolyze Polyacrylamide	1×10 ⁶ 2×10 ⁷	to	Powder, emulsion, solution	As flocculent with inorganic or organic polymers
Cationic	Poly(DADMAC, diallyl dimethyl ammonium / chloride)	200 500×10 ³	to	Solution	Primary coagulant alone or in combination with inorganics.
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So, these are the common organic polyelectrolytes which are listed here non-ionic, ionic and cationic. And these are the different types of poly electrolytes which are very common and they have used as flocculants also along with the coagulation they help in the breeze and combining together all the flocks which are formed. So, they help they work as a flocculants also and they help in the overall improvement in the overall treatment efficiency. And these electrolytes may be available in the powder form emulsion form or solution form so depending upon the requirement they work differently and they are available differently also their molecular weight range is also different.

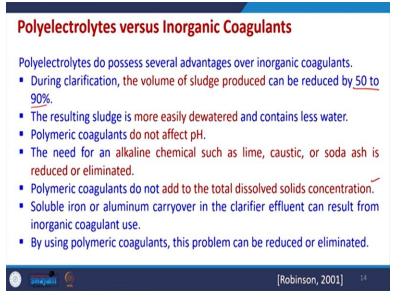
So, we have to be highly knowledgeable while using this type of polyelectrolytes and whether we require anionic or cationic that will be known from zeta potential and other characterization studies. So, we have to understand overall the both the physics and chemistry of the coagulation process the water as well as the coagulants. So, if we know these things the chemistry in particular we can properly select the coagulants or the polyelectrolyte or coagulants aids also so many times coagulants adds are also added.

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Polymer Type	Name	Mol.wt.	Available form	Typical use
Cationic	Quaternized Polyamines	10 to 500×10 ⁴	Solution	Primary coagulant alone or in combination with inorganics.
Cationic	Polyamines	10 ⁴ to 10 ⁶	Solution	Primary coagulant alone or in combination with inorganics.

These are other types of organic polyelectrolytes like quaternized polyamines these are polyamine simple polyamines and they may be used as a flocculant they may work as a primary coagulants also but the efficiencies will be lower it may be possible. So, it depends upon the what type of water pH is there and how much amount of dose is required so depending upon that.

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So, there are always a dilemma between polyelectrolytes versus inorganic coagulants so several both have some advantages and disadvantages. Polyelectrolytes in particular during clarification the volume of sludge with polyelectrolytes gets reduced by 50 to 70, 90 percent. So, this is good

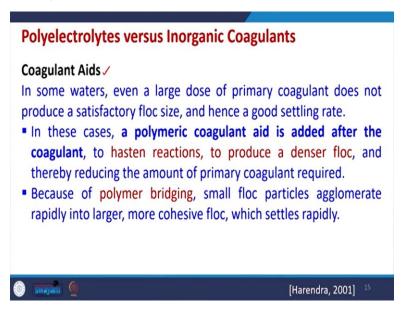
advantage of poly electrolytes, so that is why industries generally use lot of pole electrolytes the resulting sludge is denser and can be easily dewatered.

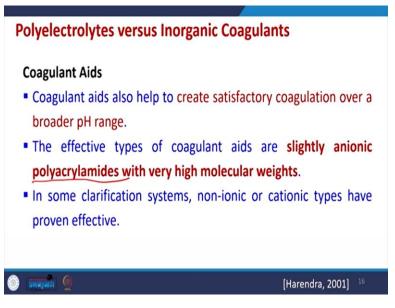
So, that means it is very easy to handle the sludge in case of a use of polyelectrolyte as a coagulant. A polymeric coagulant do not affect the pH that much as compared to inorganic coagulants so that is another advantage, so we may not have to add that much amount of lime also from outside.

So, that means the need for alkaline chemicals such as lime caustic or soda, ash is either reduced or eliminated ah totally while using the polyelectrolytes. And polymeric coagulants do not add to the total dissolved solid concentration which is there. So, these are the various advantages of polyelectrolytes as compared to inorganic coagulants.

Similarly, soluble iron or aluminium they are carried over in the clarifier refluent and if they are carried where they can result from and generally they will result from inorganic coagulants. So, they may add to the secondary pollution so this is also a problem which is not that much which is there in the polyelectrolyte. So, these problems the problems related to inorganic coagulants can be easily minimized by using polymeric coagulants.

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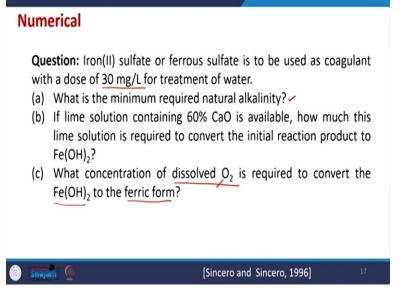




In addition to these coagulants we use lot of coagulants aids as well so sometimes in water even after adding large dose of coagulant the satisfactory flock size will never get formed. So, under that condition we have to add certain coagulant aids from outside actually which help in the formation of the bigger flocks. And this way they produce a denser flock and thus the settling is very quick they can get removed very quickly and during this these coagulant aids actually help in polymer bridging etcetera.

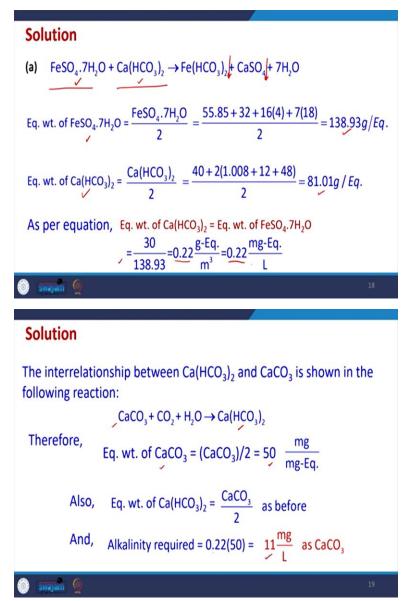
So, they enhance the overall treatment efficiency they enhance the settling time or reduce the settling time and thus the size of the overall treatment unit becomes smaller with the use of coagulant rate. So, we many a times we have to a add coagulant aids from outside so this is very very common. And the effective type of coagulants aids which are very common are slightly anionic poly acryl amides so with this these polyacrylamides are very very common with very high molecular weights so they help in the bridging as well as they help in the denser flock formation.

So, they are used non-ionic and cationic types are also available which can be used depending upon the requirement. So, this way we can we understood that there are coagulants there are coagulant aids and now will continue with the last section in this particular coagulation and will try to understand that with some one question. (Refer Slide Time: 22:42)



So, this numeric question is like we have iron second sulfate or ferrous sulphate which is to be used as a coagulant. And the optimum dose has been given to be 30 milligram per liter for treatment of a water. Now, what is the minimum required natural alkalinity so this is the first question always it will come when we are you using any type of this coagulant that what is the minimum required natural alkalinity.

If that alkalinity is present or not otherwise we have to add and similarly there is a question that always be required some amount of dissolved oxygen if that is not available then also there will be some formation. So, we can which is required to convert the ferrous hydroxide into ferric form so ferrite hydride ferrous hydroxide into ferrous ferric hydroxide how much amount of dissolved oxygen will be required. (Refer Slide Time: 23:35)



So, let us try to solve this question so we have ferrous sulphate and again we try to see the reaction of ferrous sulphate with calcium bicarbonate. So, we have this iron bicarbonate which gets formed during this reaction and we have calcium sulphate which gets formed which gets removed. Now, the equivalent weight of ferrous sulphate as well as calcium bicarbonate has been found here so you can see here the calculations have been performed.

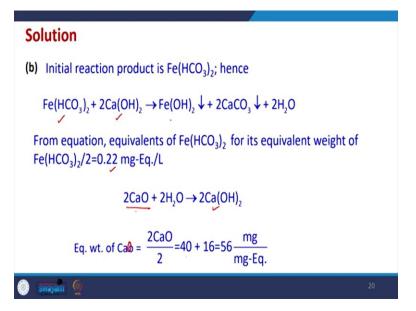
And this is like 138.93 gram per equivalent and similarly 81.01 gram per equivalent for these ferrous sulphate as well as calcium bicarbonate. As per the this equation we require same

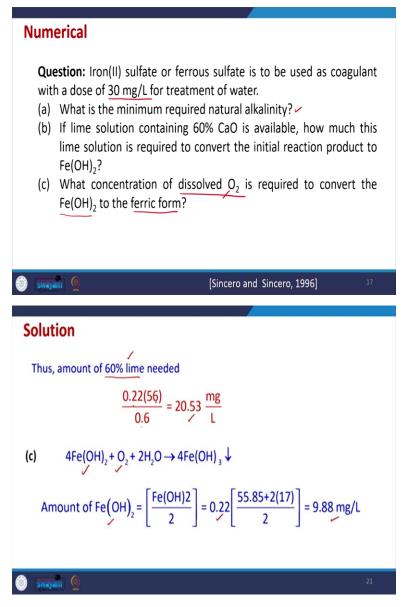
equivalent of both so equivalent weight of calcium hydroxide calcium bicarbonate and ferrous sulphate requirement is same.

Now, since we require 30 milligram per liter of this, so we can calculate for 31 divided by 138.93 so we can solve, so this is 0.22 of in terms of equivalent weight which will be required for ferrous sulphate. So, the same will be requirement for the calcium bicarbonate also so 0.22 is the requirement milligram equivalent per liter which is required for the calcium bicarbonate.

Now, going further calcium bicarbonate actually gets formed via this reaction from calcium carbonate and the equivalent weight of calcium carbonate is 50 this already we know. And so equivalent weight of calcium bicarbonate also we have we can easily find out by dividing by 2. So, alkalinity requirement will be here it is 50 so it is 0.22 into 50 so it is 11 milligram per liter as CaCo3 which is required.

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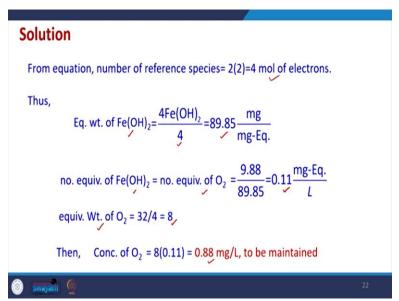


Now, this is for the first section now for the second case section it is given that if lime solution contains only 60 percent of the calcium oxide. So, how much of this line solution is required to convert the initial reactant product to FeOH2 so ferrous hydroxide so this is being asked. So, for this condition we again write the equation so we have a ferrous hydroxide to ferric hydro sorry we have to go back we have this ferrous bicarbonate reacting with this calcium hydroxide to form a ferrous hydroxide and certainly calcium carbonate goes off. And from this equation we see that equivalence of iron hydroxide are ferrous hydroxide for its equivalent weight of can be calculated to be 0.22 already we have calculated earlier.

And the reaction for formation of calcium hydroxide calcium hydroxide is given here so this is from this so from here we can calculate, the in terms of equivalent weight it is same. So, equivalent weight of calcium oxide which is required is 40 plus 16 so that is 56 milligram per milligram equivalent. And since the amount contains only 60 percent lime so we can divide 0.22 into 56 in divided by 0.6 because only 60 percent lime is there. So, overall 20.53 milligram per liter of lime requirement will be there with respect to treatment of this water with that optimum dose.

Now, third case we have to find out the oxygen which is required for converting ferrous into ferric form. So, this is the reaction we can easily write so amount of FeOH2 already we know this is 0.22 equivalent was given so we convert it into milligram per liter so it is 9.88 milligram per liter.

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And from this actually we also see that number of electron transfer which happens is 2 into 2 so 4 mole of electrons are required. So, for equivalent weight of FeOH2 so we can calculate it is 89.85 and number of equivalence of FeOH2 is equal to number of equivalent of O2 because here we have divided by 4 so we can directly write it. And we convert this into the respective form so we found out it is 0.11 milligram per equivalent per liter. And if we divide by 4 because for equivalent weight of O2 is 32 divided by four which is 8.

So, 8 into 0.11 that will give 0.88 milligram per liter of oxygen has to be maintained in the water for converting the ferrous hydroxide into ferric hydroxide. So, generally this event much amount of oxygen will be available so all the ferrous form will get converted into ferric also if it is not there it will remain as such. So, this is there so we can calculate the lime requirement we can calculate the dose requirement and through that we can calculate the cost requirement and the size of the coagulation unit requirement etcetera. So, we have performed some calculations.

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Some of the books you can refer for further enhancing your knowledge so we end this particular section will continue with the settling because once the coagulation has been done and we have bigger flock size. So, how much is the volume of the overall settling unit and how the design calculations and other essential requirements with this fixed settling are there that we will continue in the next lecture thank you.