Water and Waste Water Treatment

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Lecture - 35
Coagulation - I

Hello everyone, welcome back to the latest lecture session. In the last session, we looked at coagulation and the relevant principles involved and destabilising the particles or the solution. Let us get into it.

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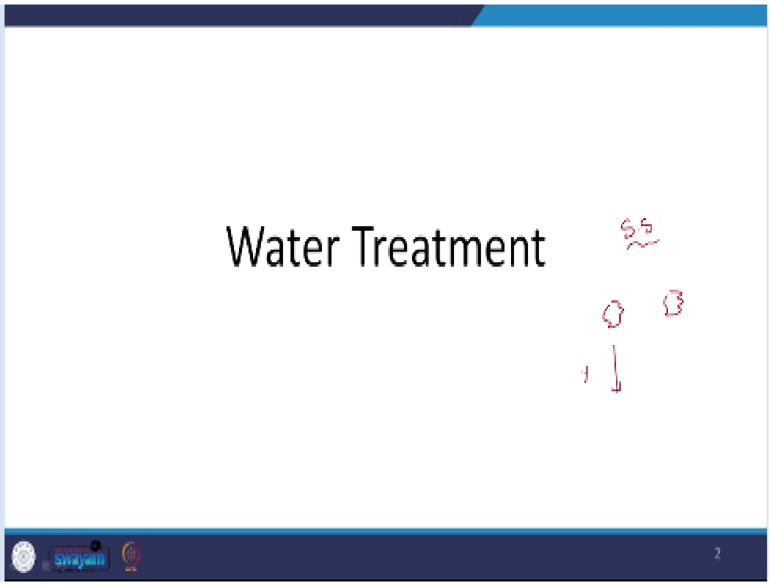

Water Treatment

So, we are in the context of water treatment, we want to remove the suspended solids, yes, some of these solids, colloids too small, they will not settle down. So, we want to bring them together, so that they form a bigger particle or a floc, so that we can settle them down. Why will not they come together?

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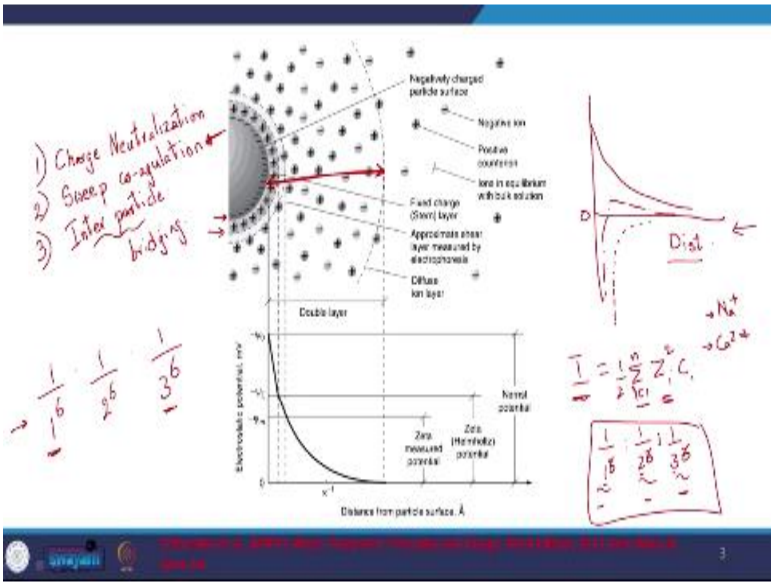

We looked at this net negative charge on the particle and it attracts counter ions, which are cations that is what we see out here. Negative charge on the particle, we looked at the relevant reasons and so on and so forth. And we know that , the repulsion is something like this. And the attractive force is something like this. And the net, , is something like this.

So, as the particle, this is distance; the x axis is distance; as another particle approaches our particle of interest, , it has to overcome this maximum. How do we, , see to it that these particles can come together? We need to suppress the repulsion forces or electrostatic force of repulsion. And how do I do it? By suppressing this electrical double layer or this or more importantly, this diffuse layer , so that is what I can do.

And how do I do that? I can increase the ionic strength. Ionic strength as we know will depend upon the charge to the power of 2 and this is how it is and , it will also have the concentration. So concentration, I will write it as the C i Z i, i equal to 1 to n.

$$I = \frac{1}{2}\sum_{I=1}^{n} z_i^2 c_i$$

So, summation of all the ions, this is i = 1, so what does this ionic strength depend upon? , the charge of the relevant ion , if it is Na^+, so +1 charge. If it is Ca^{2+}, $2^2 = 4$.

And Ci is the concentration of the relevant element , Na^+ or Ca^{2+}. So, that is how you have ionic strength. Yes, and we looked at different ways to compress this or decrease the thickness of this electrical double layer and what would the primary aspects? Let me see, where I can write that down. So, the primary ways where charge neutralisation by adding or increasing the count ionic strength.

And in that context, we saw that if we add counter ions or increase the ionic strength by adding ions that are bi-valent or trivalent. We saw that charge density is relatively higher. The effect on the ionic strength is multiplied. , we see that here also Z^2 and I think we also mentioned this 1 square is to 1 is 2; 2 square is to 1 is to 3 square. I mean charge , not square pardon me to the power of 6.
$1/1^6 = 1/2^6 = 1/3^6$

This will give you an idea about the concentration that required effects mono-valent, bi-valent, trivalent. Trivalent that is why 3, charge by that is 2, mono that is why 1, . So, you see that with respect to let me rewrite this here in a clear manner. So, if it is only one charge and if it is bi-valent and if it is tri . So, as you see with a higher charge, lesser concentrations need to be added to have the same effect as , mono-valent one at relatively high concentrations and we see the ratio that they need to be added at.

This is in theory anyway more or less what we observe well also carefully, not carefully, closely follow this relationship unless NOM there is too much NOM. , let us come back to this. So, charge utilisation, this is how we can do that by increasing the ionic strength. So, absorption and charge neutralisation go hand in hand. And in that context, we also looked at another aspect at least we looked at sweep coagulation. Sweep coagulation or at least I think we would have broached upon it.

how metal that I am adding and I have ligands which are electrons , OH^- or any other ligands. And where the critical concentration you are going to have precipitation of these metal hydroxides or what we see insoluble metals at that levels metals which are insoluble at that concentrations of the metals and ligands. You will have them precipitating. So, when you are precipitating something out from the solution, it is not dissolved anymore.

It is in a different phase. It is a solid phase. So, these can adsorb what we say, the other particles of interest or colloids or well colloids sites for adsorption and they will set out. So that is called sweep coagulation or co-precipitation. It is also called co-precipitation. In those strictly speaking, it is, you are not precipitating the other colloids out, you are just giving surface area for them to adsorb on too and the third aspect is I think, we looked at the picture inter particle bridging.

So, these are the ways you can bring about coagulation or destabilise the system. Inter particle bridging, I think it is self explanatory, you have a particle here, my polymer or such is adsorbed here and the other end or the other multiple ends, they can adsorb onto other colloids. So, I am going to form a bridge.

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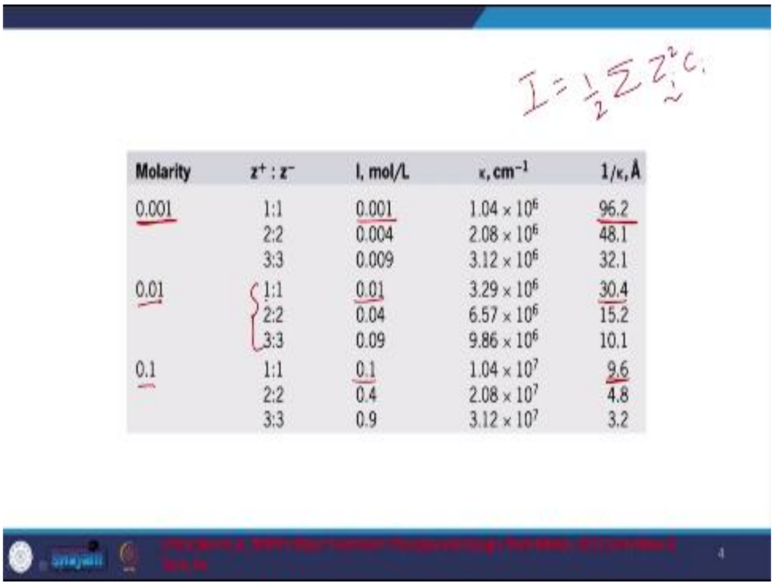

$I = \frac{1}{2} \sum z_i^2 c_i$

Molarity	$z^+ : z^-$	I, mol/L	κ, cm^{-1}	$1/\kappa$, Å
0.001	1:1	0.001	1.04×10^6	96.2
	2:2	0.004	2.08×10^6	48.1
	3:3	0.009	3.12×10^6	32.1
0.01	1:1	0.01	3.29×10^6	30.4
	2:2	0.04	6.57×10^6	15.2
	3:3	0.09	9.86×10^6	10.1
0.1	1:1	0.1	1.04×10^7	9.6
	2:2	0.4	2.08×10^7	4.8
	3:3	0.9	3.12×10^7	3.2

And in this context, we are in the context of charge neutralisation by adding the relevant or adding ions such that the ionic strength increases. So, here, first we see that with increasing concentration, , ionic strength is going to increase, yes and thus, the relevant electrical double layer is going to decrease. , ionic strength, it is going to be depends certainly on the charge and also the concentration of the relevant compound.

As you see, the charge; has a great role and that. So, compare, let us take this set, and this charge electrical double layer; 3, much lesser . So, that is something to keep in mind. Yes. So, let us move on.

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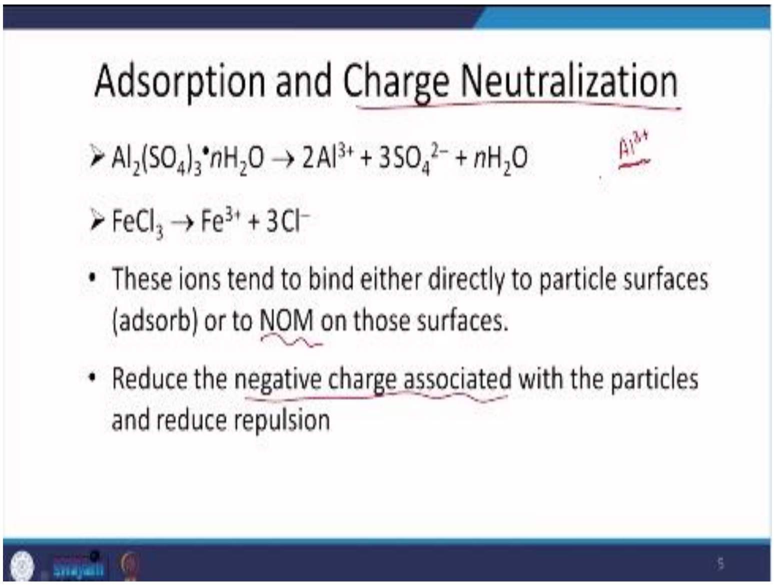

Adsorption and Charge Neutralization

- $Al_2(SO_4)_3 \cdot nH_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} + nH_2O$ Al^{3+}
- $FeCl_3 \rightarrow Fe^{3+} + 3Cl^-$
- These ions tend to bind either directly to particle surfaces (adsorb) or to NOM on those surfaces.
- Reduce the negative charge associated with the particles and reduce repulsion

And in the context of adsorption and charge neutralization, we see that , Al^{3+} and Fe^{3+} are quite commonly used. But here, it is not only charged neutralization that is something that we discussed. And I think I will come back to that later. We know that any Al^{3+} that is added will not stay only as Al^{3+} in solution that is the key aspect. So, it will not stay as a free metal, it will transform, but we will look at that later.

, even that is the same case with Fe^{3+}. So, what is it that we are discussing here, so it can reduce the negative charge associated with the particles as and we know that NOM will impart the negative charge to some of these colloids and that is why they cannot come together. And NOM being a ligand can, what we say, form a complex with this Al^{3+} or Fe^{3+}, thereby bringing down the charge on the relevant particles.

So, that is one aspect. But we will come back to this aspect of Al 3 plus, , transforming into other, what we say, compounds or forms.

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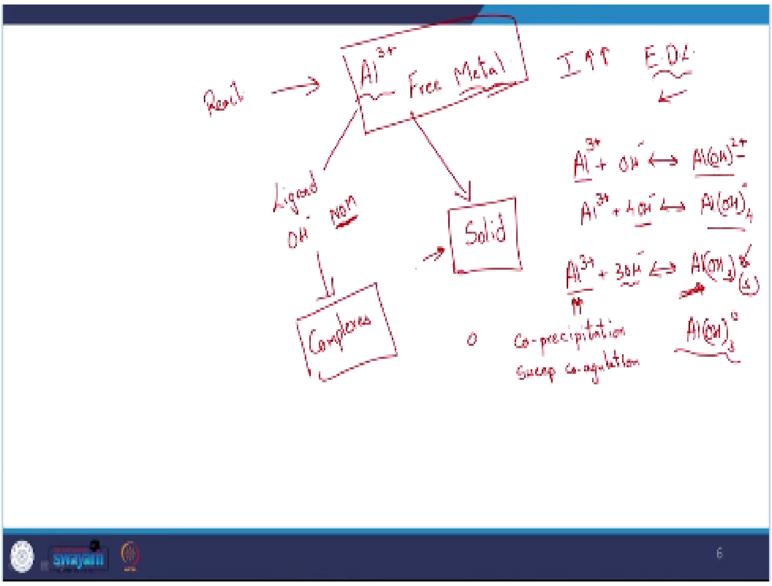

this is where I wanted to discuss this. So, whenever I add a metal, a source of Al^{3+} , alum or any other sources, what would I want it to be. I want the reactants to be such that finally I have Al^{3+}. So, that is pretty good. I increase the ionic strength and the electrical double layer thickness decreases, but it is not as straightforward as. Al^{3+} will not stay only as the free metal.

, this is what I am calling as the free metal. It will be in equilibrium. It will be in equilibrium , with different complexes. The different complexes will be formed when you have a metal and a ligand. And the most common ligand out there is OH^-. So, Al^{3+} can form ligand with OH^-. This will be in equilibrium. So, $Al(OH)^{2+}$, you see now that the charges no more 3+.

I have , depending on the concentration of OH^-, I can even have this complex being formed. And you see now, it even has a negative charge. And more importantly, as I mentioned, depending on the conditions, we will look at the graphs that will give you an idea about that. So, Al^{3+} with a ligand can form complexes. So, that is one aspect to keep in mind Al^{3+}, which is the free metal will be in equilibrium with complexes. For that, you needed ligand and the ligand is NOM also.

But that helps us in it. Another aspect is, it can even form a solid. Solid meaning, it is not dissolved in the solution anymore. So, Al^{3+}, 3 OH^- can lead to formation of $Al(OH)_3$ the solid. It can also lead to formation of $Al(OH)_3$ the complex with no charge, but it depends on the conditions . So, if Al^{3+} concentration is high enough and pH is also high enough, you will have a lot of alum precipitating out of the solution as a solid.

So, 2 ways; one can be complex formation with NOM. Al^{3+} forming a complex with NOM and neutralising the charge on the particle. But , you will also have to look at Al^{3+} forming a complex with OH^- and then charge neutralisation, the effect will decrease as you can see. And another aspect is that Al^{3+} can precipitate out as a solid. And while precipitating out as a solid, as we mentioned, it can lead to co-precipitation.

It can act as sites where the colloids can absorb or this is also called as sweep coagulation. So, this is the thing. And , please note that they are in balance. Depends on , it is like this more Al^{3+}, then , this precipitation will take place. So, it is a balance, yes. And the balances between the free metal, the complexes and also the precipitate here, . So, that is something to keep in mind.

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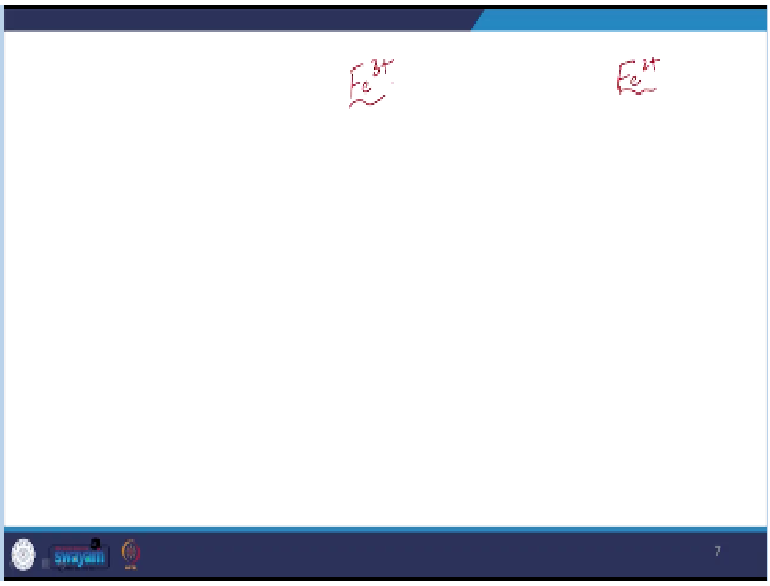

And same thing will happen with solids like not solids, metals, like Fe^{3+} ; not a lot for Fe^{2+}. Fe^{2+} is very much soluble; mostly stays as the free metal itself. But Fe^{3+} will form a lot of complexes and will also precipitate out . So, that is why you need to be careful about what you are choosing. Let us move on.

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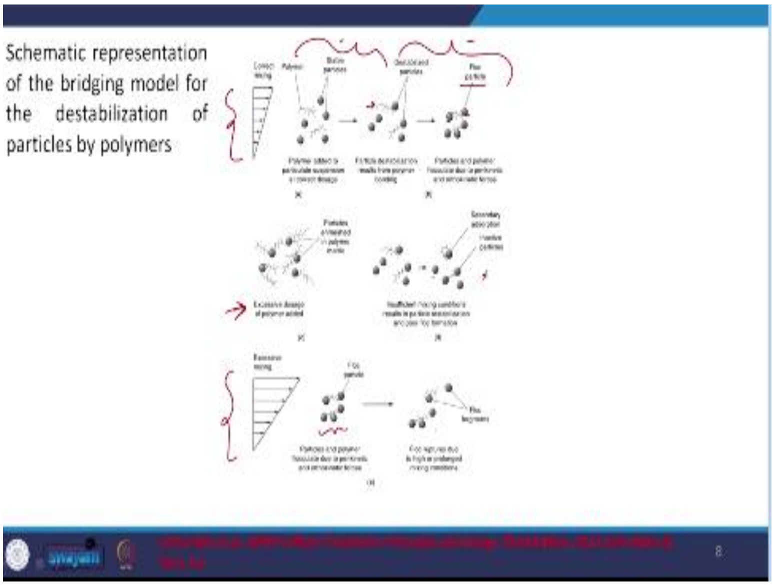

Schematic representation of the bridging model for the destabilization of particles by polymers

So, this was a good schematic, we looked at. One case was correct mixing and excessive mixing, which also plays a role. We will come back to that. So, here what do we see? We see the polymer being added in the stable particles which do not want to come together. Now, the particles are stabilised after the relevant polymer has adsorbed onto the particle and neutralise some of the charge in a way if it is cationic. If not, it has adsorbed it. Yes. And now, it is forming a bridge.

By bridging 2 or more particles, so, now you have a good floc particle. When you have excessive , that is not good. We will look at it depending on the charge that will lead to issues. It can even stabilise the system. And another aspect is due to poor mixing, , what will happen this end which should have adsorbed onto the other particle is now readsorbed onto the, not readsorbed, adsorbed onto the same particle and it has re-stabilized . , this I do not want.

And if I mix it way too much during flocculation, , this phase is coagulation maybe. And this phase here, is flocculation. So, here, I want a lot of mixing. And here I do not want a lot of mixing. If I mix it a lot here, what is going to happen? The floc which w this stage is going to break up. If I mix it way too much or I mix it for way too long, so, there are these aspects which we will look at.

So, we need to be conscious of how much energy we are imparting to the relevant solution from our paddles or such. How much mixing an important to the relevant? How much turbulence an important to the relevant solution? Let us keep that in mind and move on.

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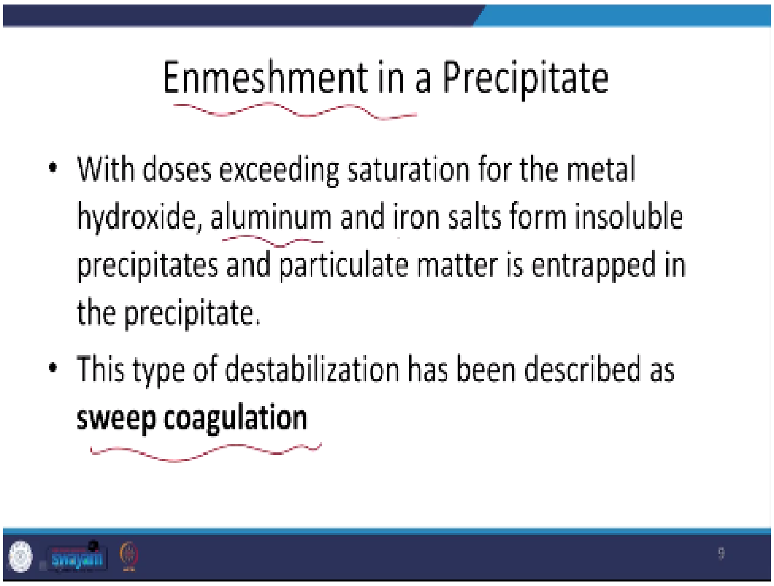

Enmeshment in a Precipitate

- With doses exceeding saturation for the metal hydroxide, aluminum and iron salts form insoluble precipitates and particulate matter is entrapped in the precipitate.
- This type of destabilization has been described as **sweep coagulation**

So, as I mentioned, it can be enmeshed in a precipitate and it is called sweep coagulation. Typically, seen with Al^{3+} and Fe^{3+}, not do with Fe^{2+} though.

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So, this is , a general schematic, you have hopefully this is the precipitate, Al^{3+} $Al(OH)_{3(s)}$; $Al(OH)_{3(s)}$ and you see the different colloids being enmeshed in that particular solid, . So, that is one aspect to consider.

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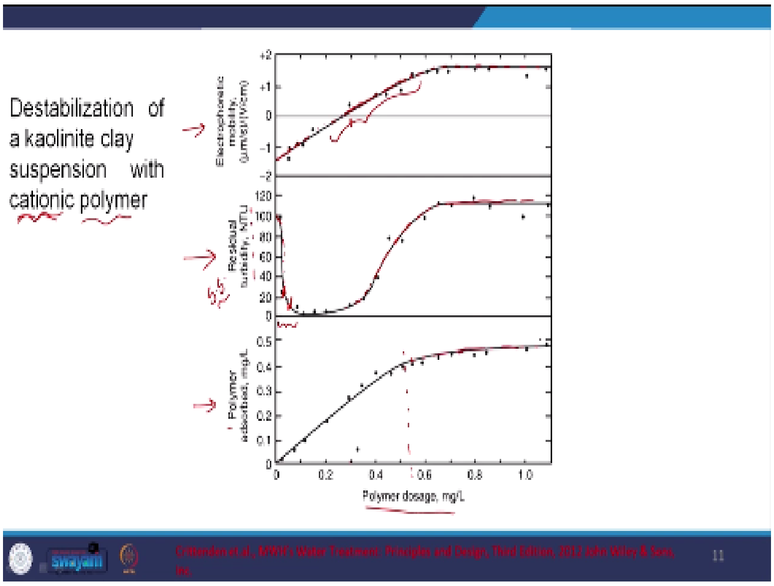

Destabilization of a kaolinite clay suspension with cationic polymer

Crittenden et.al., MWH's Water Treatment: Principles and Design, Third Edition, 2012 John Wiley & Sons, Inc.

And as I mentioned, if we add too much of the polymer, especially a charged polymer, it can lead to what we say, reverse stability, if I may say so. But that is a term that I am using. Let us look at it here. What do we have? Let us look at this graph first. Polymer adsorbed onto the particles or how much I am adding. Polymer dosage is given; polymer adsorbed is given; not all of it will be adsorbed. So, some of it will be adsorbed.

So, you see that after certain dosage, , with increasing polymer dosage, adsorption is not increasing. So, there are no more adsorbable sites or sites for adsorption. So, there is once threshold even for adsorption that is one thing to keep in mind. And the other thing, , is that let us look at this electrophoretic mobility , which was looking at or will give you an idea about the potential if I may say so, fine.

So, initially, it is negative. And I want to decrease this by adding the cationic polymer, I am decreasing it. But then due to excessive addition from 0.3 or so, I now see to it that it is positive, positive, positive. And now, what was stable because of net negative charge? I am now making them stable because of positive charge, if I may say so. And then , the relevant profile.

So, that will be very much clearly illustrated in this figure. So, in this zone, and this one, what do we see it is negative. So, if I add alum, it is going to be a sharp decrease I am going to decrease the thickness of the electrical double layer by increasing the ionic strength. So, there are the particles can come together and I see that the turbidity is decreasing a lot. Turbidity is giving me an idea about the suspended solids.

And it is decreasing, so it stays the same. So, here it looks like it is the optimum dose here or here, depending upon to which extent you want to remove the turbidity. But as I keep adding now, the particles are becoming relatively more stable or even the cations itself can act as light scattering agent. So, you see that turbidity is increasing. And you see that that mirrors considerably with respect to this profile out here.

And then you see that it results in a maximum here. So, that is one aspect to keep in mind. So, excessive addition of the polymer 2 will lead to issues. So, there is a sweep spot with respect to the amount and the costs and the turbidity that you want to capture. Let us move on.

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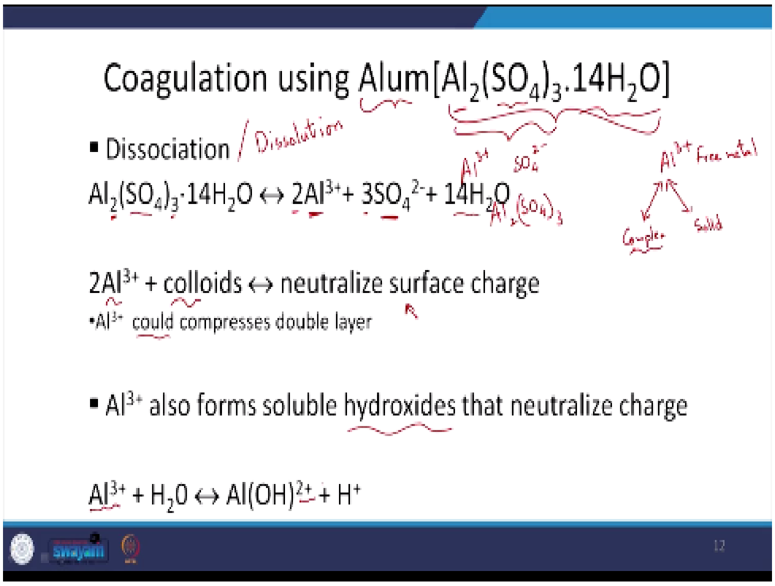

Coagulation using Alum[$Al_2(SO_4)_3.14H_2O$]

- Dissociation / Dissolution

$Al_2(SO_4)_3 \cdot 14H_2O \leftrightarrow 2Al^{3+} + 3SO_4^{2-} + 14H_2O$

$2Al^{3+}$ + colloids ↔ neutralize surface charge

•Al^{3+} could compresses double layer

- Al^{3+} also forms soluble hydroxides that neutralize charge

$Al^{3+} + H_20 \leftrightarrow Al(OH)^{2+} + H^+$

So, typical coagulant we say alum, so, looks like, this is what we have. We have a source of aluminium, so, you cannot have any solid that has charge. So, you are going to have the anion, so, that there is net zero charge and , it is hydrated . Al^{3+} and SO_4^{2-}. So, that is why it is $Al_2(SO_4)_3$. So, 6 charge that is fine, but we know that Al^{3+} does not stay once we add this what happens to the solution.

It will dissociate once you add it to the water or dissolution if I may say so; maybe dissolution, dissociation or dissolution. So, what is it going to dissociate into? So, , Al^{3+} and SO_4^{2-}, my stoichiometric coefficients Al is 2, So 2 Al^{3+} ; So $3SO_4$ and charges 2^- and water, . So, this is what we have, but we know more as an Al^{3+} will not stay; only as Al^{3+}; it will be in equilibrium with the complex. This is the free metal and also as a solid, .

It will be in equilibrium with these 3 between these 3 forms. So, what else we have here. Al^{3+} itself can neutralise the charge on colloids. But we know that might not happen depending upon the level of complexes and type of complexes being formed. And if this happens or part of it or some of it will happen, it will or could rather complex the double layer.

But as we discussed, it can form complexes. And even these complexes can neutralise some charge, . But if primary motivation is only charged utilisation, you see that if I see if I add Al^{3+}, the charge that I am getting, , it is not going to be 3^+ anymore, because I have OH^- that is forming a complex with my metal , that is one thing to keep in mind. But what else happens?

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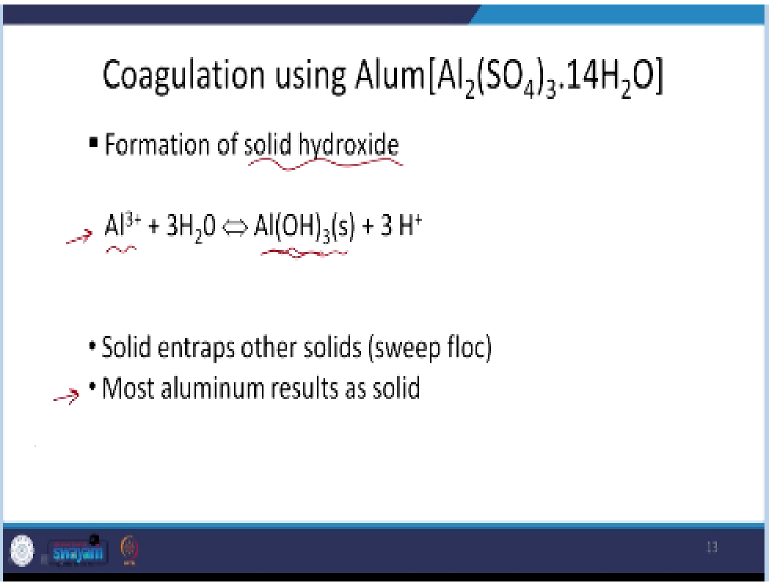

Coagulation using Alum[$Al_2(SO_4)_3.14H_2O$]

- Formation of solid hydroxide

$Al^{3+} + 3H_2O \Leftrightarrow Al(OH)_3(s) + 3H^+$

- Solid entraps other solids (sweep floc)
- Most aluminum results as solid

You have the solid being formed formation of solid hydroxide. So, this is what happens. So, this will precipitate out and we know that sweep coagulation or co-precipitation occur. So, though we discussed it earlier, we just want to mention the relevant equations . In general, you do not need to muck them up. But , standard equations or simple equations like this, one would expect you to be able to come up with it.

I want a lower thrice solid from Al^{3+}, I know, I need to add water or you can see to it that rather than releasing H^+, you can add OH^- it depends, but in the exam, some of these equations you should be able to come up with them. Depending on the OH^- and Al^{3+} concentration, most of the aluminium or Al^{3+} can form a solid or can precipitate out that is something to keep in mind.

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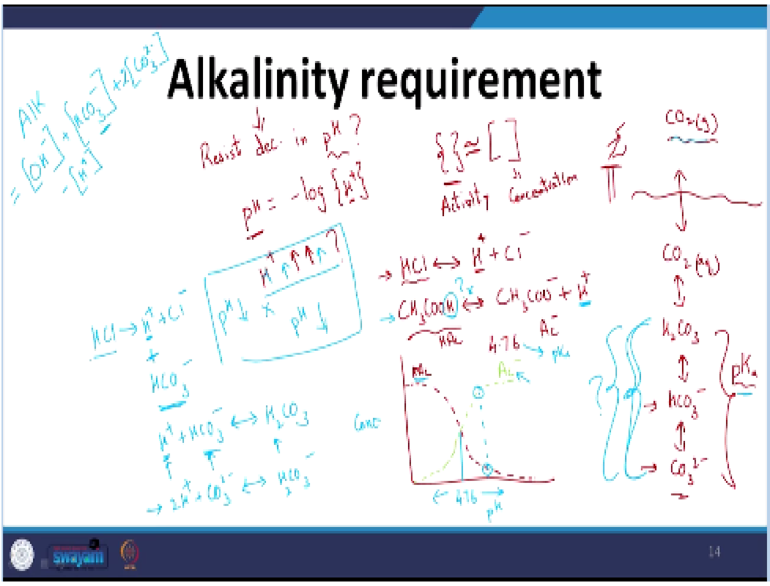

Alkalinity requirement

Alkalinity requirement: First, what is this alkalinity about? Let us just understand one aspect. So, with increasing carbon dioxide emissions, you have a lot of carbon dioxide in the gaseous phase but if we are able to capture all the emissions and measure or quantify them and look at the carbon dioxide concentration in the gaseous phase, you will get a relatively lower value than expected.

Why is that? Because, you have these ozones vast area and considerable mass of water is there. So, carbon dioxide in the gaseous phase will be in equilibrium with or it will dissolve into carbon dioxide in the aqueous phase or water. It will dissolve and this will then further transform into H_2CO_3 the acid which will be in equilibrium with the other de-protonated forms which are HCO_3^- and CO_3^{2-}.

So, you see it is an equilibrium and in this context, we looked at pH, pKa. We looked at that earlier. We might look at . So, why I mentioned this is; as you see, in general in the water we will have HCO_3^- and CO_3^{2-}. And also due to the lime deposits , you will have CO_3^{2-} or lime that is in the deposits will act as a source of CO_3^{2-}.

So, you will have carbonates in our water a lot of carbonates in our water. Why are they important? Well one aspect is as you add an acid to water or any natural water, you do not want the pH to drop. Why? pH will affect life, , we cannot drink pH or water that said 6 or such for a prolonged period of time. Please do note that, the carbonated drinks like Pepsi, Coca-Cola have remarkably low pH, I think 3, maybe 4, and , , you cannot keep drinking them for a prolonged period.

First, you will have the issues with teeth and then with respect to your system. , human body, yes issues and life in general to it will not survive when the pH is low. So, this alkalinity offer a solution will prevent decrease in pH or will resist the decrease in pH. What will it do? It will resist decrease in pH; decrease in pH and how will it do that? Let us understand that when we say decrease in pH, what do we mean?

We know that pH is equal to minus log activity or concentration of H plus and this class, we are going to assume activity is equal to or approximately equal to concentration. This is the what we say, these brackets curve brackets, we use for activity but discussion about activities beyond the scores and these brackets, we use to denote concentration. Anyway, so, how is it that pH will decrease? The pH will decrease when we increase the H plus. You can see that from this relationship.

So, how will H^+ increase or when will it increase? It will increase when I am adding a source of H^+. What are the typical sources of H plus? It can be an acid. I know that HCl strong acid because pKa is very low. At most pH ranges, it will go to H^+ and Cl^- or there are other acids too, which are relatively weaker acetic acid . Acetate and H plus, so, when I add acids depending on how strong for example, this is strong acid.

$$HCl = H^+ + Cl^-$$

pKa is zero or less than zero. So, it will always release H^+ at almost all the pH ranges. This is not such a strong acid. The pKa is 4.76. So, we looked at this graph, if you remember and this is acetic acid, I will say it is HAC. This, I am representing by HAC; this by AC minus and let me just change the colour here and the other one will be AC minus. I am just reviewing the acid base relevant aspects and this one the point at which HAC and the AC minus will be the same is the pKa 4.76 that is the pKa.

Why is this relevant? As you can see, when the pH; this x axis is pH; y axis is well to concentration of the relevant acid or the base. As you see, when the pH is less than pKa which form is predominant? The protonated form HAC. This is predominant but when this is predominant, will it be able to release the H plus? No, it cannot. So, it will not affect the pH but if the pH of the solution is greater than 4.76 and then if I add acetic acid, you see that acetic acid will dissociate and form AC^- that is what we see.

, for example, at this case. Any acetic acid that I add mostly will dissociate to AC minus and only some will stay as HAC. So, most of it will dissociate and considerable H plus will be given out and thus, you can change the pH or affect the pH. So, that is what we need to be concerned about the pKa and pH of the solution. So, coming back to where we were. So, in such a way, different acids or process can lead to increase in H^+.

When H^+ increases, pH will decrease. This, I do not want, but nature our friend always tries to help us out. So, how it does. So, either with equilibrium with carbon dioxide gas and then the; relevant compounds which we call the carbonate system or more importantly the limestone deposits in the land or subsurface, they are going to see to it that you have considerable carbonates in the system. Carbonates, yes, inorganic forms of carbon. Why are they important? .

For example, how HCO_3^- remains in my solution? Fine. And if I add the H^+ from any other acid , I add HCl to water and that goes to H^+ and Cl^-. If there is nothing else, this H plus will then add to the other H^+ that is already there; H^+ concentration will increase, then pH will decrease. That is the usual way, but if I have a HCO_3^-, what will it do?

After this addition of HCl, H plus is fine but that H plus, now will be taken up by this HCO_3^-. H^+ , HCO_3^- will go to H_2CO_3. So, you see, this H^+ is taken up by this base and this H^+ does not exist as free H^+. So, it cannot affect the pH but that depends upon how much H plus is being added and how much HCO_3^- is there. And what is the pH? And thus, the pKa relevant aspects come into play.

Same case, if I have CO_3^{2-} in my solution, it can take up H^+ and go to HCO_3^- or it can even take 2 H^+ and go to H_2CO_3 . So, these aspects are, these carbonate system play a life sustaining role. They act as agents that will resist the decrease in pH. So, that is what it is. So, what this equation for alkalinity is.

Let me write it here. Equation for alkalinity in general, there will be other variations, but in general so, what is it going to be depend upon? It is going to be depend upon the basis that are usually present in water. What are the basis present in water? , always OH^- and depending on the system in nature, you will always have HCO_3^- and CO_3^{2-}.

Since, CO_3^{2-} can neutralize 2 H^+. You see this here. You will have 2 that is the equivalence, and , OH^-, so, how to subtract H^+. So, this is the theoretical definition of alkalinity. So, without alkalinity in general, if pH is near about 6 or 7, OH^- in H^+ will cancel out. CO_3^{2-} will be negligible and mostly we are concerned with HCO_3^-. But if there is little to know alkalinity and any acid is added, because as you see, when you are adding alum, acid was being released.

So, 3 H^+ is being given out. Let me see if even the other reactions, even when the complexes are being formed H^+ is being released. So, you see that H^+ is being released into the solution. So, without medium, not medium, basis to neutralise or take up this H^+, what will happen? The H^+ will affect the or add to the H^+ already there, it will increase the H^+, decrease the pH which you do not want.

It will affect our engineering aspects the pipes and also affect life. So, you do not want that. So, in general, you want to maintain sufficient alkalinity . So, that is the background. But I am out of time we will continue this in the next session. Thank you.