

Water and Waste Water Management
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Module No # 10
Lecture No # 47
Lime Soda Softening-1

Hello everyone, welcome back to the latest lecture session. In the last couple of sessions, we started discussing about how to remove those bivalent cations which lead to hardness; Calcium and magnesium. And in that context, we looked at some acid base related background, acid base chemistry and understood that we have equilibrium between the acid and the base.

And the key aspects which decide the ratio of the acid to the base or the pH and the pKa is the acid dissociation constant and pKa which is minus log Ka, what is Ka? Ka is that equilibrium constant for that acid dissociation reaction. We also looked at equilibrium constants and how to write that so, quick recap. And then let us go forth.

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Carbonate hardness (CH)

- Called temporary hardness as when the water is heated, the insoluble carbonates will precipitate and tend to form bottom deposits in water heaters.

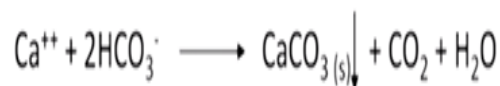


Fig 1

After discussing these aspects, we started discussing about carbonate hardness, this is referred to as temporary hardness and the insoluble hard when heated they tend to form deposits but temporary hardness, those that are associated with carbonates, that is something we discussed.

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Non-carbonate hardness (NCH)

- Called permanent hardness because it is not removed when the water is heated
- $NCH = TH - CH$

Fig 2

Non-carbonate, we call that as permanent hardness this is a working understanding, it is not removed when the water is heated. Non-carbonate hardness is total hardness minus the carbonate hardness. This non-carbonate hardness, as the name indicates non carbonate, this is one where the relevant ions calcium or magnesium are associated with ligands other than HCO_3^- or CO_3^{2-} , so non-carbonate hardness.

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Visualization with bar chart for anions, cations, all equivalent concentrations

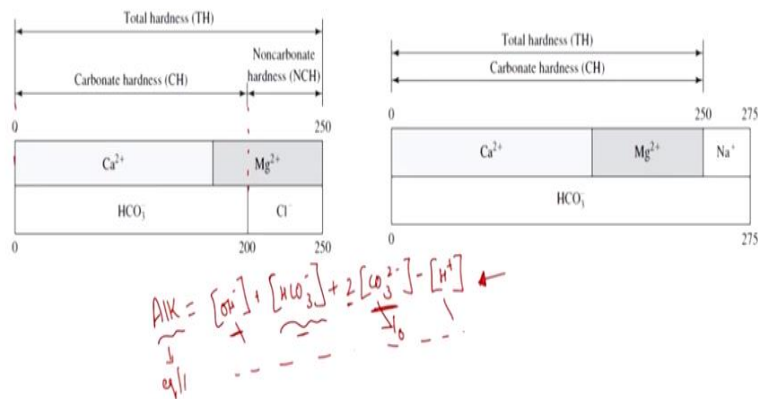


Fig 3

In that context, we looked at the figure, here we looked at different permutations and combinations. Carbonate hardness, it is equal to the alkalinity and this case because alkalinity is less than the total hardness, what do we see here? We came across this aspect; alkalinity is equal to the acid that is required to bring down the pH to 4.5 or 4.3.

That is the actual practical definition that is given the standard methods when we try to find the alkalinity by titration considering that the bicarbonates or the carbonate system is the only system that is prevalent here in this water. We list all the basis that can neutralize the acid + $\text{HCO}_3^- + 2 \text{ times } \text{CO}_3^{2-}$. Why 2? Because as you can see, CO_3^{2-} can neutralize 2H^+ .

And $-\text{H}^+$, we are adding the acid H^+ . As we see from earlier about pH 7 and looking at the speciation diagram, we see that there will be little to no CO_3^{2-} present, OH^- and H^+ will cancel each other out when the pH is near neutral. When we talk about alkalinity it is typically HCO_3^- especially when the pH is near neutral.

But be careful when making this assumption. Because if people want to ask questions and throw you off track, this is one particular case where people try to throw you off track. That alkalinity is not equal to HCO_3^- but it depends upon the relevant scenario. If not, you will have to calculate the alkalinity like this. And alkalinity here the units of the relevant compounds are moles per litre. And the units will be in terms of equivalents per litre for alkalinity.

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$$\begin{aligned}
 &\text{if } \text{TH} > \text{ALK}; \\
 &\quad \underline{\text{CH}} = \underline{\text{ALK}}, \quad \underline{\text{NCH}} = \text{TH} - \text{CH} \\
 \\
 &\text{if } \text{TH} < \text{ALK}; \\
 &\quad \underline{\text{CH}} = \underline{\text{TH}}, \quad \text{NCH} = 0 \\
 \\
 &\text{if } \text{Ca} > \text{ALK}; \\
 &\quad \underline{\text{Ca-CH}} = \text{ALK}, \quad \underline{\text{Ca-NCH}} = \text{Ca} - \text{Ca-CH}; \\
 &\quad \text{Mg-CH} = 0, \quad \text{Mg-NCH} = \text{Mg} \\
 \\
 &\text{if } \text{Ca} < \text{ALK}; \\
 &\quad \text{Ca-CH} = \text{Ca}, \quad \text{Ca-NCH} = 0, \\
 &\quad \text{Mg-CH} = \text{ALK} - \text{Ca}; \quad \text{Mg-NCH} = \text{Mg} - \text{Mg-CH}
 \end{aligned}$$

Fig 4

And then we move on to looking at different permutations and combinations, if total hardness is greater than alkalinity and then carbonate hardness will be defined by the one's associated with the carbonates meaning alkalinity and non-carbonate hardness will be the difference and for the total hardness being less than alkalinity, than all the hardness will be only carbonate

hardness. Same case we looked at differentiation with respect to calcium carbonate hardness, calcium non-carbonate hardness and so forth. This we all did discuss so I will move on.

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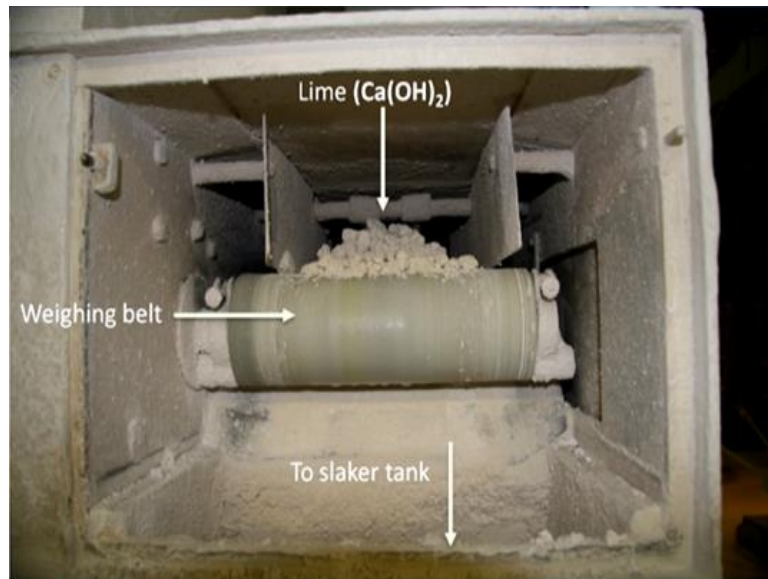


Fig 5

Here you see lime being added or slaked lime anyway or hydrated lime. As you see this is the weighing belt and depending on the mass required, you are going to add it to the slaker tank. It is a mass balance which we will look at later.

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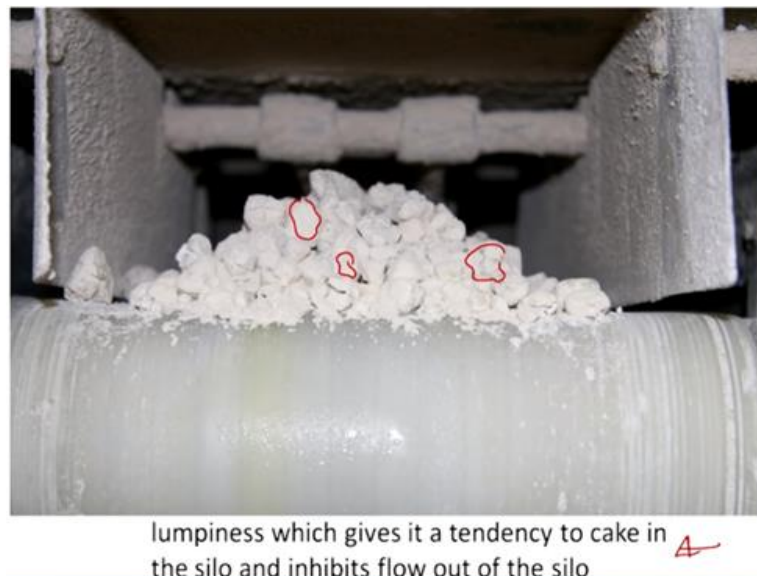


Fig 6

And here the lumpiness, you see the lumps that is why the cakes form even when you are trying to measure something with a spoon or such if it forms cakes or lumps, it is difficult to

measure so, that is what they are trying to say. And it inhibits the flow out of the silo, that is something to keep in mind. But this is for lime or hydrated lime.

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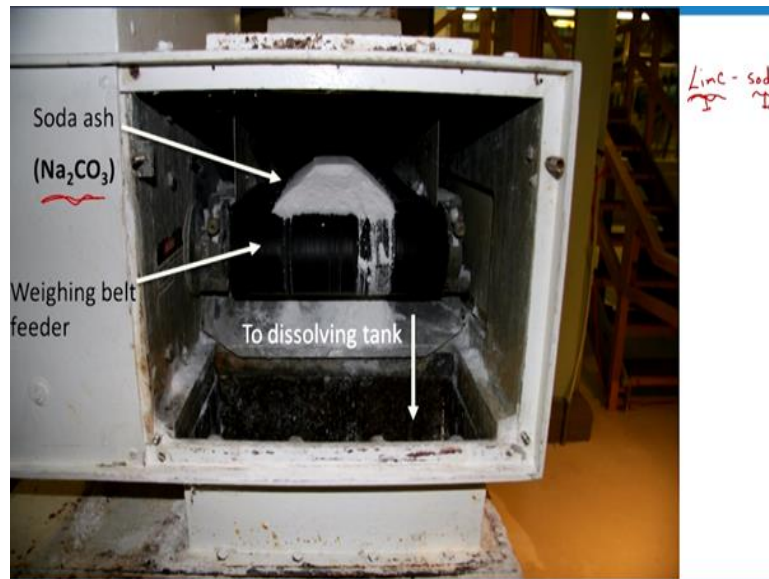


Fig 7

And with soda ash, which we will also look at later, we are always talk about lime soda softening. Lime is typically hydrated lime, $\text{Ca OH } 2$, and when we say soda, you are talking about Na_2CO_3 or soda ash, but soda ash unlike lime, you can see the texture. And it is relatively powdered and it is thus easy to dissolve or weigh and, that is something to keep in mind.

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Unlike lime, soda ash is granular. It does not cake and flows easily from the storage silo

Fig 8

Here, it is granular and thus flows easily. That is one thing to keep in mind, just a practical aspect I wanted to mention based on the information that Mackenzie Davis's student presentations gave. These student presentations are accessible to YouTube. You can just look up the link from the McKenzie water and wastewater book and access a variety of such pictures which convey practical information, Lets me move on.

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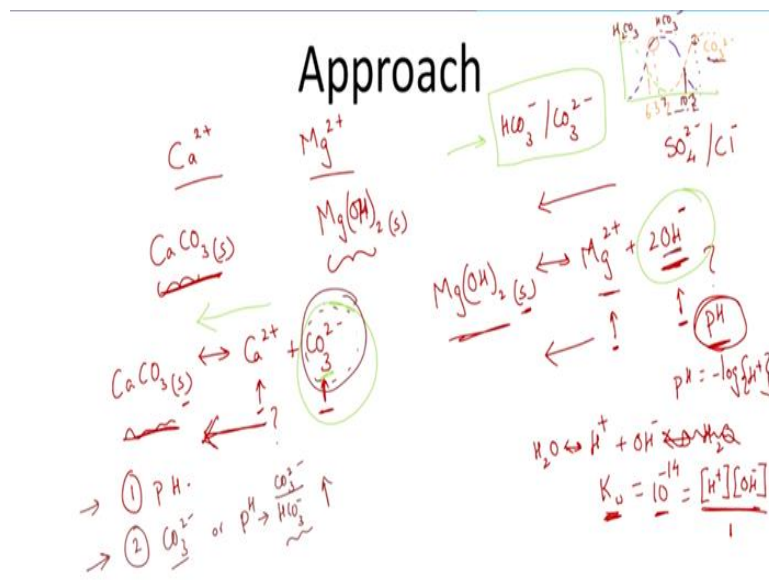


Fig 9

What is the approach here as in that how Ca^{2+} , Mg^{2+} and some of these will be associated with HCO_3^- or CO_3^{2-} based on the pH of the system and some will be associated with those that we refer to as permanent hardness. let us see how do I get these out of my relevant system. We will look at other ways, but here we are talking about precipitation and then removing the precipitate from the relevant solution.

Precipitation, what is it that we are trying to do? These compounds are now dissolved; calcium and magnesium are dissolved in water. Depending on the conditions that you create, depending on the ligand that you add, ligand is electron rich metal, calcium magnesium or electron poor, depending on the pH conditions and the relevant compounds you can see to it that the solution is super saturated with respect to a certain kind of solid.

And then you can see to it that your solid precipitates out. When the solid precipitate out it is not dissolved anymore, size is bigger and then you can look at coagulation and flocculation and then sedimentation or such to remove these suspended matters from your water. The

approach here is; We have something dissolved, we want to precipitate it out so that they are not dissolved anymore

But become suspended solids or can that can be settled out, that is the approach. Here, I have to precipitate them out. Typically, I will try to precipitate calcium out in the form of calcium carbonate the solid and magnesium hydroxide the solid. Different forms of calcium are different other compounds are feasible, but based on what is typically available in water and what is easy to dissolve.

This is what people have been using this meaning these are the solids that people prefer to precipitate out; CaCO_3 and magnesium hydroxide. One aspect I wanted to mention here is what is the solubility product related equation here or dissolution CaCO_3 ? If I write the equation as dissolution, $\text{Ca}^{2+} + \text{CO}_3^{2-}$ and for this and goes to it can dissolve into Mg^{2+} and 2OH^- .

S is for the solid, other compounds are dissolved now, they are in equilibrium in general saturation, super saturation, nucleation, agglomeration but, we will not go into that, there are more aspects to understand. But here let us just look at the bigger picture you need to saturate it or supersaturated rather. For the reaction to go from the to the left,

What do I need to do? Le chatelier's principle or in general what do I need to do? If the system is at equilibrium and I want to trigger precipitation, what do I want to do? I want to saturate or supersaturate the solution with Ca^{2+} or and CO_3^{2-} , when I want to increase the concentration of these particular calcium and CO_3^{2-} the reaction as returned will then try to shift towards the left and the solid will precipitate out.

Same case here, if I increase the magnesium concentration, or increase the OH^- concentration, meaning increase the pH, then the system will try to go left so that it will achieve a new equilibrium and then this solid can precipitate out. Here we can either increase calcium or magnesium, that is one thing. But here we are talking about removing the calcium or magnesium that is already in solution.

Adding more calcium does not really come into the picture here. But we will look at that is an internal aspect here, what else can I do? I can increase the CO_3^{2-} or increase the OH^- . How do I increase OH^- ? For that, I can increase the pH. pH is negative log H^+ . And $\text{H}^+ + \text{OH}^-$, they will be in equilibrium with water.

And water dissociation constant K_w is equal to 10^{-14} . This is like the equilibrium constant. I will have the activities which I am assuming to be the relevant concentrations of H^+ , concentration of OH^- by activity of water. Activity of water, we are going to assume it is a dilute solution, it is going to be 1. K_w which is 10^{-14} is concentration of H^+ into OH^- . If I decrease the H^+ concentration, OH^- will increase or such, you can see the relationship here.

I am going to have to increase the pH if I want to increase the OH^- concentration, that is something to keep in mind. Approach one is to increase the pH. That is for magnesium hydroxide precipitation, I want the system to go in this direction, what about the other aspect if I want this reaction to go in this direction, what do I do? One approach as we discussed was increasing OH^- , here we are trying to increase CO_3^{2-} .

If the water does not have any CO_3^{2-} or HCO_3^- , then I will think of adding bicarbonate or carbonate. But in general water will have some bicarbonate or carbonate, why is that in general? Water is in equilibrium with carbon dioxide typically or has been in contact with some deposits earlier and you are typically going to have some CO_3^{2-} and HCO_3^- .

This you are going to typically have but from the speciation diagram, this is for HCO_3^- the green one was for H_2CO_3 and this is for CO_3^{2-} . But the pK_a is 6.3, at around neutral pH, what is predominating? Mostly it is HCO_3^- .

The middle one corresponds to HCO_3^- the one on the far left corresponds H_2CO_3 , the acid. As you can see at around pH7, which is represented by this line, we see that it is mostly going to be present as HCO_3^- But I need CO_3^{2-} , so how do I see to it more of CO_3^{2-} is present. If I just add some CO_3^{2-} , it itself can lead to increase in pH but as you see if I increase the pH by different means

At higher pH, CO_3^{2-} will predominate and what is this pK_a ? This pK_a is 10.3 near about 10.3 or such, you can see you will have well to the significant amount of CO_3^{2-} , so by increasing the pH or by adding CO_3^{2-} , the second approach or the other approach for calcium removal is to add CO_3^{2-} or if there is already enough HCO_3^- then increase the pH such that the ratio of CO_3^{2-} to HCO_3^- increases.

Increase the pH such that ratio of CO_3^{2-} to HCO_3^- increases, this is the approach one for magnesium one for calcium. But what are the key aspects here we need? OH^- which is

typically present in water and we will also need CO_3^{2-} , what are the different ways you can raise the pH? We will look at that later. I want you to look at one figure for now.

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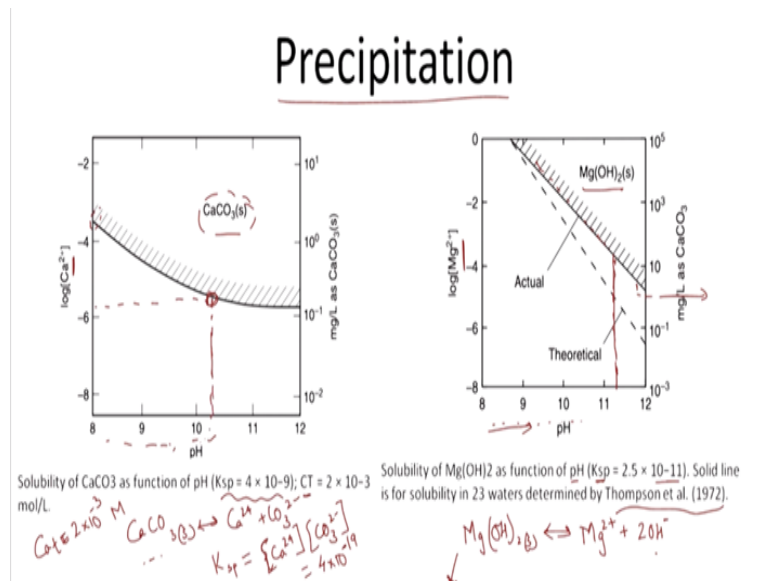


Fig 10

Here we are trying to achieve precipitation and let us look at it. pH is on the x axis and on the y axis, we have log of calcium. This is a log-C pH diagram, solubility of CaCO_3 as a function of pH is given and looks like the solubility product K_{sp} for CaCO_3 , which we discussed earlier, CaCO_3 the solid going or being equilibrium with Ca^{2+} and CO_3^{2-} .

The K_{sp} or equilibrium constant for this which I am mentioning as solubility product, why solubility? As you can see the solid is dissolving. Solubility product will be equal to activity or concentration of Ca^{2+} into concentration of CO_3^{2-} and that they are saying is equal to 4×10^{-9} . And the total calcium, calcium total is equal to 2×10^{-3} moles or 2 milli moles.

That is the information that we have, I am just writing it down so that you understand the background. With increase in pH, here they are talking about calcium, the free metal. Let us see at relatively low pH, you need to have relatively high calcium free metal concentration. But as I keep increasing the pH, I see that even at relatively low calcium concentration

Or I will be able to achieve relatively low concentration. Maybe at around this pH or as such, I can see that, I will start forming the relevant solid. You understand the pH level that is required. And also you saw that pK_{a2} for the H_2CO_3 system is 10.3. You can also understand why this is the case? Because at this case too, you will have CO_3^{2-} being predominant so that is one aspect to keep in mind.

Same case here. Well, let us move on to the hand side. And let us look at this log-C pH diagram for magnesium. And here solubility of magnesium hydroxide, the solid as a function of pH and the Ksp is given. Please note that Ksp is much lesser here. The solid line is for solubility in 23 waters, designed by Thomson et al. and we have it from Crittenden et al.

The solid line looks like the average, let us have a few sets of data. What do we see here? As we increase the pH, let me write down the equation, magnesium hydroxide the solid it will be in equilibrium with Mg²⁺ and OH⁻. As I increase the pH, what is happening? I am increasing the OH⁻ concentration. As I increase the pH, then you can see that magnesium hydroxide concentration starts or magnesium hydroxide, the solid, starts precipitating out.

And theoretical and actual seems to be lesser. In general, for this removal to take place, typical pH you want is around 11.5 or so even done at 10 point something but in general at around 11.5. And for calcium carbonate removal, let us see our calcium removal in the form of CaCO₃, typical pH is around 10.5, typical, keep that in mind, this is where it comes from. Now that we have the information, let us see how we are going to go about it.

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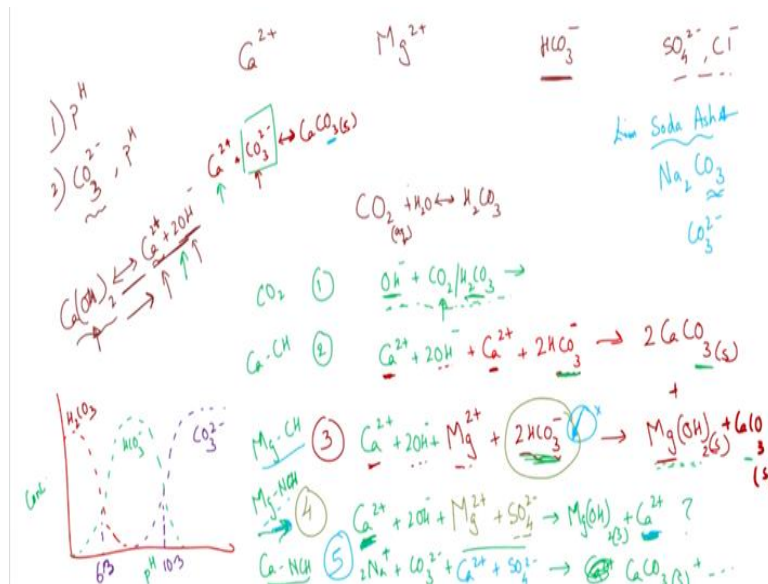


Fig 11

I have calcium, I have magnesium and I have HCO₃⁻ at around pH assuming in the water is around 7 or 8 and all the CO₃²⁻ is present as HCO₃⁻ and then I will have other ions which are of not great interest for me here. But I am mentioning that because that indicates that some of the calcium and magnesium is or can be associated with non-carbonate hardness.

I might not have enough carbonate for everything. Let us see how to go about it? Different ways to raise the pH as in we mentioned that we can either raise the pH or for calcium increase the CO_3^{2-} concentration and even for this rather than adding CO_3^{2-} , if there is already enough HCO_3^- , we can increase the pH. Approach results around adding a compound that will increase the pH and if required add CO_3^{2-} to the system.

That is something to keep in mind. Typically, we can add lime CaOH twice well to the cheap and this as you can see, it will immediately dissolve to Ca^{2+} and 2OH^- though I write this equation it is typically an irreversible one. If not irreversible mostly in this direction it will dissociate into Ca^{2+} and 2OH^- . But here the question that should arise is fine I am increasing the pH by adding this OH^- but seems like I am also adding a source of calcium.

And that seems to be counter intuitive, is not it? I mean, I want to remove calcium and magnesium, but I am adding a source of OH^- to increase the pH that also has calcium. Well, that seems counter intuitive. But if you look at this documentary it is not as difficult or as counter intuitive as we would expect. First aspect to increase the pH, we are going to add the $\text{Ca}(\text{OH})_2$, let us see, which I am going to refer to as lime.

From this I am going to get Ca^{2+} and OH^- . First thing is if there is any acid present in the relevant system, that will consume the relevant OH^- that I am putting it. Whatever I have, typical acid can be CO_2 in equilibrium with water. When we say CO_2 , it is almost always present as H_2CO_3 in the water. But if I add any OH^- , the consumption of OH^- will be by CO_2 .

That is something to keep in mind. OH^- will be consumed by the CO_2 or H_2CO_3 as you write it. whatever I add OH or lime, if there is any carbon dioxide or H_2CO_3 present or if there is any dissolved carbon dioxide present, it will consume the OH^- first that is one thing to keep in mind. Once I have seen to it that all the acid this is an acid H_2CO_3 and that I am quenching by adding OH^- from my lime.

The additional lime that I am going to add, let us see what that is going to happen. That by adding lime what am I getting? $\text{Ca}^{2+} + 2\text{OH}^-$ but in the water, what is already present? I already have some lime. And let us have some HCO_3^- , let us see write. And if you look at the stoichiometry, this OH^- I am increasing the pH. When I increase the pH of the water, they said HCO_3^- is going to convert to CO_3^{2-} .

We know this speciation diagram; We already have that but I will just write that here for the sake of understanding so let me find this is for HCO_3^- , x axis is pH y axis is the relative concentration of species and the last one will be first CO_3^{2-} . And this is going to be the pK_a2 is around 10.3. And the pK_a1 is 6.3, around that

As the pH is around 7 as you can see most of the CO_3^{2-} is present as HCO_3^- , but by adding OH^- , the equilibrium is going to shift between HCO_3^- and CO_3^{2-} and go towards CO_3^{2-} and once you have enough CaCO_3 , we know that we have this equation; $\text{Ca}^{2+} + \text{CO}_3^{2-}$ can precipitate out as CaCO_3 dissolved. This reaction will be favoured, especially when you have higher CO_3^{2-} , so you will have 2CaCO_3 being formed.

In effect even though I am adding some calcium from the lime, I am still removing one mole of calcium along with the mole of calcium that I am adding that is not balanced. But we will look at the balanced equation later, this is one aspect. But key aspect to note is that this will occur only if there is already some HCO_3^- present in the water. If not, we have to add the HCO_3^- , that is one aspect.

What about magnesium? I know that magnesium will precipitate out as magnesium hydroxide. How will this come into the picture? How will this be done? I already have magnesium and if I am adding the relevant calcium hydroxide, what am I adding? Lime. What will I get? Ca^{2+} and 2OH^- , this is what I have, what is that? I will end up removing this particular magnesium hydroxide. I should have written $\text{Mg}(\text{OH})_2$ the solid there.

Let me just write that down. Magnesium hydroxide twice Or $\text{Mg}(\text{OH})_2$. For this to occur, Mg^{2+} is there to OH^- but as we know and we looked at from this previous equation for this to occur we have to increase the pH such that the pH comes to almost around 11 or above 11 that is something to keep in mind. But if you look at the documentary, it will come to that more or less in general.

But what else will happen here if there is no alkalinity or no carbonate left? The Ca^{2+} will now be introduced in the system. In effect, you are removing magnesium, but adding calcium but if there is alkalinity present or carbonate present already in the solution, then this calcium will combine with that and be precipitated out as CaCO_3 , the solid. What happens will depend upon the amount of carbonate that is initially present.

If you have enough carbonate and this is magnesium carbonate hardness then this is going to take place and not this, so that is something to keep in mind. What about other aspect? What about magnesium that is not associated with carbonate hardness? Then you are going to see to it that the other reaction occurs. If it is Mg^{2+} ,

And it is associated with other compounds which are not carbonates, what will happen here? When I add lime $Ca^{2+} + 2OH^- + Mg^{2+} + SO_4^{2-}$ gives magnesium hydroxide the solid precipitating out but you will now have calcium.

It all depends upon whether it is magnesium carbonate hardness or magnesium non carbonate hardness. Here at the end of this picture, you see that I still have some calcium in effect I am introducing some calcium, how do I remove this calcium? We know that calcium will be removed only when there is enough CO_3^{2-} here?

But I have already used up all the CO_3^{2-} looks like in the system to either remove it in the form to precipitate $CaCO_3$, the solid. But for magnesium non carbonate hardness, I am adding calcium in the source of I mean from lime and that is still there, how do I remove this or even if there is any calcium that is present as non-carbonate hardness? What have you removed until now the CO_2 , the calcium carbonate hardness and magnesium carbonate hardness.

And here we have removed magnesium non carbonate hardness., this is what we have. But how do I remove calcium non carbonate hardness and also the calcium that I have added during this particular stage? How do I remove that? I will remove that by adding a source of CO_3^{2-} and what is that source of CO_3^{2-} ? That is going to be my soda ash, this will have to be added either here or if there is enough alkalinity, if not I will have to add it here.

Depending on where we add it or such, the stoichiometry will change if you are assuming that this is magnesium with carbon hardness. I do not need to add it here. But magnesium due to non-carbonate hardness and if I want to remove calcium here, some people will add lime here itself not lime soda ash. What is soda ash? Soda ash is nothing but Na_2CO_3 .

This will have to be added when I want a source of CO_3^{2-} , so soda ash is typically added here. Why? Because I do not want this free calcium to stay in this solution. I added soda ash here, along with lime, I would have precipitated out this calcium same case with calcium non-carbonate hardness. I have calcium that is associated with non-carbonate hardness and what

will I do? I will add soda ash. Let me add the soda ash that is 2Na^+ and CO_3^{2-} , so I am adding the soda ash and then

I am going to have CaCO_3 solid precipitating out and the other ions. Why am I adding soda ash to remove calcium non carbonate hardness and also in this magnesium non-carbonate hardness? To remove the calcium that's coming from the lime. in 2 aspects, I am typically adding the soda ash, so that is the relevant aspect. These are the 5 or so steps that you can think of if I missed anything in general.

We will look at them later. But that is the approach and we will now look at how to be able to calculate different variables or the dose of lime from an example. But we look at that later on. Thanking you for your patience. That is it from me for now.