

Water and Waste Water Management
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Module No # 09
Lecture No # 48
Lime-Soda softening-II

Hello everyone, welcome back to the latest lecture session. We are discussing about lime soda softening. We now have enough background in the relevant aspects so let us dig in the last one we were trying to look at the removal CO₂.

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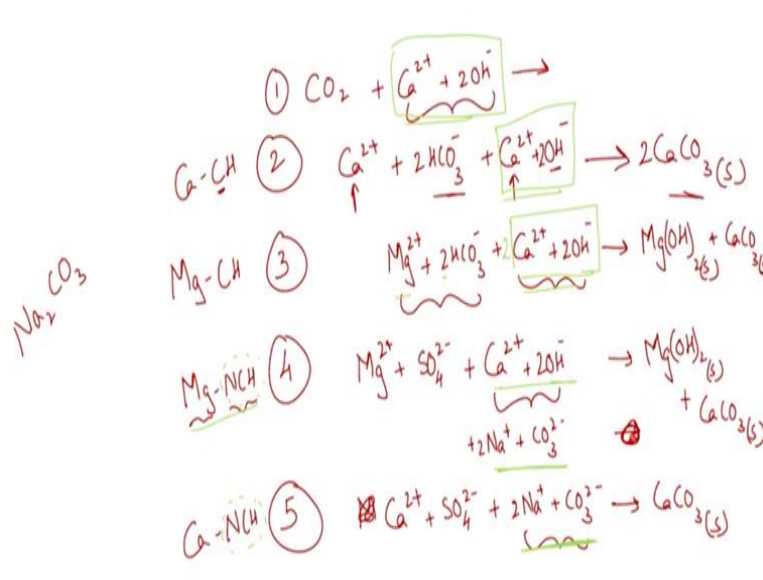


Fig 1

First the acid if that is present, I will have to remove that by adding lime Ca²⁺ and 2OH⁻ and the relevant products. And in the second one, we looked at removing calcium that is associated with carbonate hardness thus there is already enough carbonate. What does it mean? I have Ca²⁺ and I have some HCO₃⁻ but I do not have enough CO₃²⁻ which I want because the solid that will precipitate out is CaCO₃ the solid.

If I add this Ca²⁺ and OH⁻ will increase the pH and thus change HCO₃⁻ to CO₃²⁻ and thus CaCO₃ the solid will be precipitated out in that manner both the calcium that is initially present in the water and the calcium I am adding the along with lime are being precipitated out and the next one will be magnesium associated with carbonate hardness.

I have Mg^{2+} in my solution and I also have the relevant carbonate and so if I am adding relevant lime, it will see to it that assuming that the pH has been raised to the high enough value, magnesium hydroxide will precipitate out and also conversion of this bicarbonate to carbonate will take place.

And also, $CaCO_3$ will precipitate out and the fourth one is magnesium due to non-carbonate hardness. Here I have magnesium associated with ions other than carbonates. How do I remove them? Here I am adding Ca^{2+} and OH^- , so I am increasing the pH by adding lime. And thus, I will have magnesium being removed in the form of magnesium hydroxide.

But what about the calcium that I added here? For that I will have to add a source of CO_3^{2-} . What is the source of CO_3^{2-} ? That is the soda ash, Na_2CO_3 . If I add that, I will then also have source of CO_3^{2-} and then the calcium that comes with the lime will also precipitated out. This is because the magnesium is associated with non-carbonate hardness and then what about the calcium that is associated with non-carbonate hardness?

Same case here I have calcium associated with other ions, ions other than carbonates and bicarbonates. To remove this, adding the relevant sort of ash this is the soda ash. And then I am going to have relevant removal of solid, these reactions are not balanced but I am just looking at the relevant solids that are being formed. What are we adding here at different stages?

Here we are adding lime (Reaction-1), here (Reaction-2) also we are adding lime, one mole of lime per one mole of calcium that is present. And here (Reaction-3) also for one mole of magnesium carbonate hardness present, I am adding one mole of lime in the case of magnesium carbonate hardness. What is it that I seem to be doing anyway if this stoichiometry does not add up we will look at it and change it later. Here, I will have to add 2.

Because of this stoichiometric. Here if I want $CaCO_3$, what needs to be formed? Maybe rather than looking at the unbalanced equation, it will be better to look at the balanced equation later but here we are adding lime. Here (Reaction-4) also lime here in the case of Magnesium non carbonate hardness, I am adding both lime and soda ash in the case of calcium non-carbonate hardness, I am adding soda ash. Soda ash comes into picture when we

are dealing with the non-carbonate hardness related aspect that is something to keep in mind. Let us move on.

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Summary of chemical additions to soften water		
Step	Chemical addition ^d	Reason
Carbonate hardness		
1.	Lime = CO ₂	Neutralize H ₂ CO ₃
2.	Lime = HCO ₃ ⁻	Raise pH; convert HCO ₃ ⁻ to CO ₃ ²⁻
3.	Lime = Mg ²⁺ to be removed	Raise pH; precipitate Mg(OH) ₂
4.	Lime = required excess	Drive reaction
Noncarbonate hardness		
5.	Soda = noncarbonate hardness to be removed	Provide CO ₃ ²⁻

^dThe terms "Lime" and "Soda" refer to mg/L of Ca(OH)₂ and Na₂CO₃ respectively, as CaCO₃ equal to mg/L of ion (or gas in the case of CO₂) as CaCO₃.

Fig 2

What is it we are adding? We are adding lime, this is from McKenzie et. All, so lime we are adding it to neutralize CO₂, neutralize H₂CO₃ the dissolved CO₂ and lime enough to alkalinity or HCO₃⁻. Why I want to raise the pH and convert HCO₃⁻ to CO₃²⁻? Then CaCO₃ will precipitate out and then lime equivalent to magnesium to be removed. Why I want to raise the pH such that magnesium hydroxide precipitates out and this we have not mentioned earlier.

But typically, lime is required in excess because just if it is stoichiometrically relevant, the reaction will not take place, you want the solution to be super saturated for that precipitation reaction to be driven for that you are typically going to add an excess. This depends from one particular case to the other. But there are thumb rules in general, this is added to drive the reaction for non-carbonate hardness what is it we want.

We want CO₃²⁻ source. Soda ash or soda because non carbonate hardness has to be removed. We are providing CO₃²⁻. This is why we are adding it. In general, this is called lime addition. And this is called excess lime addition. Let us see when I am also adding lime to remove magnesium. I am going to refer to it as excess lime addition. And then from removing non-carbonate hardness, this is the soda of ash, this is a good overview. Let us see what else we have.

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Reactions and stoichiometric ratios ??

- CO₂ (neutralize acid so pH can be raised)

- Reaction:



- Stoichiometric ratios:

- Lime: $\frac{1 \text{ mole Ca(OH)}_2}{1 \text{ mole CO}_2} = \frac{2 \text{ eq}}{2 \text{ eq}} = 1 \text{ mg CaCO}_3 / \text{mg CaCO}_3$
- Soda ash: none required

Fig 3

And more importantly stoichiometric ratios, why? Well whatever questions people ask are typically going to be based on stoichiometry. And depending on how well they think they can look at the fundamental assumptions and chain them around. Let us look at the stoichiometric ratios and relevant reactions which I did not balance earlier. The first one should be with respect to the carbon dioxide.

We have carbon dioxide and it is an acid. This carbon dioxide will typically be in equilibrium with H₂CO₃. If it is there, it has to be neutralized so that the pH can be raised. Whatever lime that I add, I am assuming that it is initially going to be taken up by carbon oxide and CaCO₃ is going to precipitate out, S is for precipitate. Let us see if it is balanced, Co₂, CaOH twice and CaCO₃ and H₂O, looks like it is pretty well balanced.

What is it stoichiometric ratio? I need to understand for how many moles of carbon dioxide present, how many moles of lime I need to add. Then I can easily calculate it. Let us see that. One mole of lime you see here stoichiometric quotient here is one has to be added for one mole of carbon dioxide. Here, if we look at it with respect to charge, CaOH twice.

It is either Ca²⁺ +2 charge 2 equivalents, or 2 OH⁻ to charge equivalents. Here it is two equivalents with respect CaOH twice and also CO₂, I know is H₂CO₃ in solution. It is either 2H⁺ to charge or equivalents or CO₃²⁻ or to charge or to equal. It is equal and to 2 equivalents per 2 equivalents. And then, if it is equal and equivalent if I want to convert it

into units of CaCO₃, so it is 1 milligram of CaCO₃ equivalent per milligram of CaCO₃ equivalent.

That is one thing to keep in mind. Let us go further soda ash, do we add any carbonate here? No so soda ash non-required.

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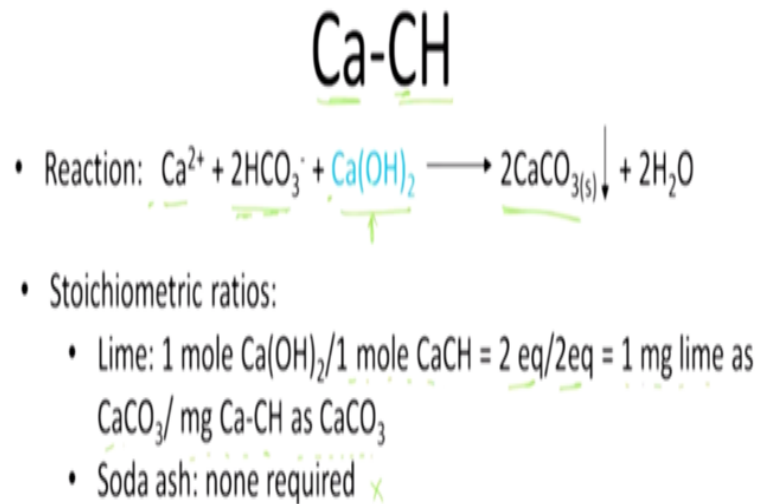


Fig 4

Next aspect the reaction is with respect to removal of calcium associated with carbonate hardness. Calcium that is associated with carbonate hardness, what are we adding? We are adding lime and you can look at the stoichiometric ratios but you see that 2 moles of CaCO₃, the solid will precipitate out. Let us look at the ratios that are required. I am having to add one mole of calcium hydroxide per mole of calcium.

That is associated with carbonate hardness, 1 mole of calcium hydroxide per one mole of calcium carbonate, not calcium associated with carbonate hardness. 2 equivalents per 2 equivalents, that is that is something to keep in mind. One milligram lime as CaCO₃ per milligram of Ca-CH as expressed as CaCO₃ but once we get it in terms of equivalents, it is pretty easy.

Let us move on. We are done with calcium carbonate hardness. We will look at magnesium. Is it am I adding any soda of ash here, is any HCO₃ or CO₃ 2-required? No, why is that? Because already we are dealing with the carbonate hardness part. Does there is enough bicarbonate or carbonate present, we just need to increase the pH. What are we doing in this reaction? We are adding lime and increasing the pH.

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Mg-CH

- Reaction: $\text{Mg}^{2+} + 2\text{HCO}_3^- + 2\text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCO}_3(s) \downarrow + \text{Mg}(\text{OH})_2(s) \downarrow + 2\text{H}_2\text{O}$
- Stoichiometric ratios:
 - Lime: $2 \text{ mol} / 1 \text{ mol Mg-CH} = 4 \text{ eq} / 2 \text{ eq} = 2 \text{ mg lime as CaCO}_3 / \text{mg Mg-CH as CaCO}_3$
 - Soda ash: none required

Fig 5

Next one magnesium associated with the carbonate. What is the reaction here? I have magnesium associated with the carbonates and here I know that magnesium will precipitate as magnesium hydroxide, so I want to increase the pH by adding lime so, that is why we have magnesium hydroxide being precipitated out but why am I adding 2 moles?

Because here my role is not just to remove the magnesium that is present, I also want to remove the calcium that I am adding here. If I add it here you see that I have to increase the pH and that HCO_3^- in the solution will be transformed into CO_3^{2-} so for that I also need to add enough OH^- and then the calcium will be precipitate out as CaCO_3 .

For that I am adding 2 moles. Am I adding any soda ash? None here. Take home message is for 1 mole of magnesium, 2 moles of calcium hydroxide will be added so stoichiometry ratios what we just mentioned, 2 moles of calcium hydroxide per 1 mole of magnesium associated with carbonate hardness so that is why it is 4 equivalents per 2 equivalents meaning 2 milligrams per lime

As CaCO_3 for one milligram of magnesium associated with carbonates expressed as CaCO_3 but why is this two? You can see that one is for precipitating out magnesium hydroxide, the other is for transforming HCO_3^- to CO_3^{2-} , that is why we have 2 moles here in this reaction, are we adding any soda ash? None, why? Because it is already carbonate hardness, we are assuming that there is already enough bicarbonate present there.

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Mg-NCH

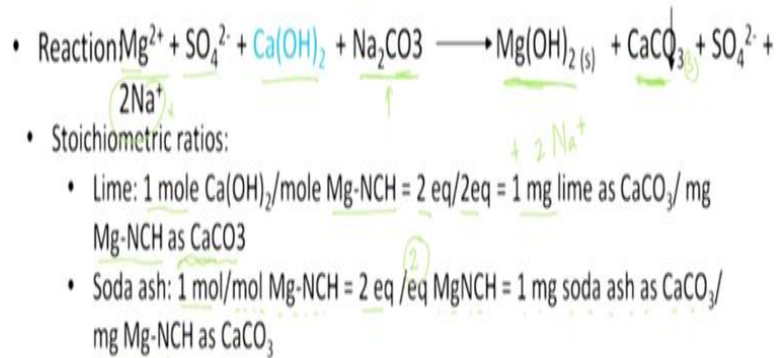


Fig 6

What about the magnesium now that is associated with the non-carbonate hardness? Let us look at that. Here are two aspects magnesium has to be precipitated out as magnesium hydroxide, so I need to add lime because I need source OH^- to increase the pH. The second one is I also need to be able to remove the calcium if not, that will add to the hardness so to remove that calcium.

I will also need to add a source of carbonate. Why here it is the one associated with non-carbonate hardness meaning. No more carbonates or bicarbonates present here just raising the pH is not good enough. I will also have to add a source of carbonates which is soda or soda ash let us so let us look at that magnesium associated with other ions, non-carbonate hardness, so I am adding lime, and then the soda ash.

When I add lime, this OH^- will lead to increase in pH and precipitate out the relevant magnesium hydroxide. And what about this particular Na_2CO_3 , what will that do? It will do the source of CO_3^{2-} , so that calcium that comes in with lime is going to be precipitated out so you can just understand the equations. There is Na^+ is out here on this hand side.

Stoichiometric ratios, let us see. For one mole of magnesium associated with non-carbonate hardness, I need to add one mole of calcium hydroxide, 2 equivalents per 2 equivalents and thus one milligram per lime as $CaCO_3$ per one milligram of non-carbonate hardness, magnesium non carbonate hardness expressed as $CaCO_3$ but what about soda ash? I am adding one mole of soda ash per mole of magnesium, same case here.

One mole of soda ash, Na₂CO₃ is added per mole one mole of magnesium non-carbonate hardness. It is 2 equivalents with respect to magnesium non-carbonate hardness, one milligram of soda ash as thus CaCO₃ per milligram of non-carbonate hardness, magnesium non carbonate hardness expressed as CaCO₃.

One correction here that is something to keep in mind and let us move forward. I am done with removing calcium due to carbonate magnesium due to carbonate and non-carbonate. I am still left with calcium due to non-carbonate hardness.

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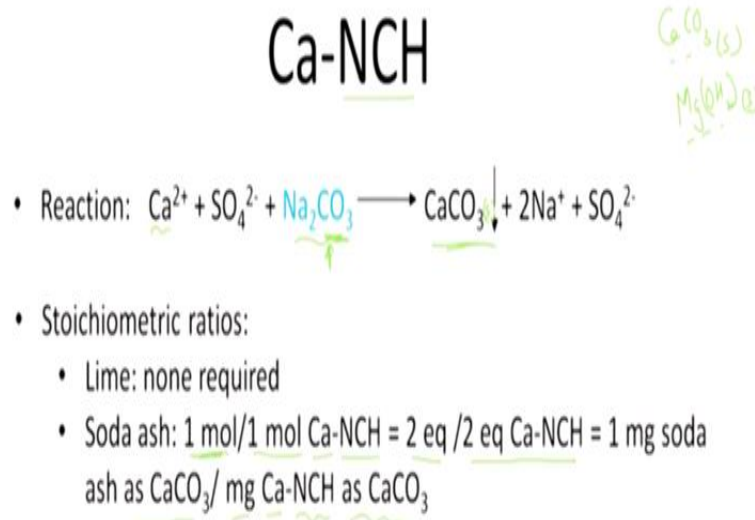


Fig 7

For that what is the approach? There is no carbonate so CaCO₃ cannot precipitate out. I will have to add CO₃²⁻, why is it that we are looking at this at the end? Well because what two ways; One is we are adding lime to increase the pH. Only if I increase the pH and add the relevant soda ash well CO₃²⁻ stay as CO₃²⁻. If not, if I keep the pH around 7 and then add Na₂CO₃, pH will rise a bit but not enough for the CO₃²⁻ that.

I am adding in the form of Na₂CO₃ to stay as CO₃²⁻, it will instead maybe stay as HCO₃⁻. That is one reason here, what is the reaction? Calcium, that's why we are looking at this part at the end assuming that we have raised the pH high enough whatever Na₂CO₃ that I add will see to it that the CO₃²⁻ from here will stay as CO₃²⁻ mostly. We are adding soda ash because we want to add a source of CO₃²⁻ and that is precipitating it out as CaCO₃ the solid and we are done with it.

Am I adding any lime not necessarily here at the stage. Lime is not required and we have one mole of soda being added for one mole of calcium associated with the non-carbonate hardness. 2 equivalents per 2 equivalents and 31 milligram of soda ash expressed as CaCO_3 per 1 milligrams of calcium associated with non-carbonate hardness expressed as CaCO_3 .

Typically, note that we add units in terms of CaCO_3 in general if you are not able to remember just understand that we are trying to remove CaCO_3 solid and magnesium hydroxide solid. And then you can just try to see how much of soda ash or how much of your lime has to be added to be able to precipitate this out and then you will get the relevant equivalents.

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Excess Dose ?

- Excess lime to raise pH to help drive reactions (range from 20 to 40 mg/L as CaCO_3)

Fig 8

Let us see if we can summarize that. Another aspect in general we have to add an excess dose, why is that required? Because we want to keep the solution supersaturated, just saturation or adding the amount just stoichiometrically enough for triggering the relevant precipitation will not be good enough. That is why you need to add an excess dose to drive the relevant reaction.

Here they are saying that it is from 20 to 40 milligrams per litre expressed as CaCO_3 this is a with respect to lime expressed in the units of CaCO_3 you need to add almost 20 to 40 milligram per litre.

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Summary of chemical dose calculations

	Stoichiometric Coefficients (mg as CaCO ₃ /mg as CaCO ₃)		
	Lime Ca(OH) ₂	Soda Ash Na ₂ CO ₃	
→ CO ₂ /H ₂ CO ₃	1.0	0	CaCO ₃ (s)
Ca-CH	1.0	0	2 CaCO ₃ (s)
Ca-NCH	0	1.0	CaCO ₃ (s)
Mg-CH	2.0	0	Mg(OH) ₂ (s) + 2 CaCO ₃ (s)
Mg-NCH	1.0	1.0	Mg(OH) ₂ (s) + CaCO ₃ (s)
	Dose (mg/L as CaCO ₃) ←		
→ Excess	35 mg/L	35 mg/L	

Fig 9

Here is a summary of what we looked at if there are any errors you can change that. When we let us just go through that when we are adding carbon di oxide meaning H₂CO₃ so there is already enough CO₃²⁻ present there so if I just add lime. It is going to precipitate out as CaCO₃ that is why one mole of CaOH twice. Lime soda ash is Na₂CO₃.

And let me write out here what is going to precipitate out so here one mole of CaCO₃ will precipitate out so, calcium due to carbonate hardness, I am adding lime CaOH twice, 1, calcium is already here and 1, calcium is coming from here. If I add one, what is it CaOH twice that should be enough to increase the pH such that HCO₃⁻ is converted to CO₃²⁻.

And then I am going to have presentation of this and then what about calcium non-carbonate hardness? Non carbonate hardness, what do I need to add? I need a source of CO₃²⁻, so that's why I'm adding soda ash. And I am not adding any relevant lime. What is it that will precipitate out? CaCO₃ the relevant solid. What about magnesium the carbonate hardness? Here we have 2 aspects for increasing pH, one is to precipitate out in the form of magnesium hydroxide.

That is why we already have one or requirement for one mole of lime. And why do we need the second mole of lime? Because we already have 1 calcium that is coming into the solution when we added lime for increasing the pH. For precipitating out that lime, we will have to add this particular lime to CaCO₃. You can understand why we are adding 2 moles; The one associated with magnesium non carbonate hardness, what is it that we are doing.

We are adding one mole of lime to increase the pH, so magnesium hydroxide, the solid will precipitate out and also to precipitate out the calcium that we are adding. When we added lime here, we will have to add Na_2CO_3 so I am going to remove CaCO_3 . What are the solid? These are this is what we have and from that you can understand this and what is the dose here excess?

Why am I adding this to keep it supersaturated? Typically, I am going to add this excess dose expressed as CaCO_3 . All this is a summary of what we have looked at until now, that is something to keep in mind here, let us move on.

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Approach

$$\text{CaCO}_3(s) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$$

$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \approx 10^{-9}$$


1. Allocate hardness to CaCH, CaNCH, MgCH, MgNCH
2. Calculate desired hardness removal 200 mg/L 
3. Allocate hardness removal to CaCH, MgCH, MgNCH, CaNCH

Fig 10

Approach is not typically for hardness, allocate hardness first to calcium carbonate hardness, then look at calculation of calcium non carbonate hardness. If there is ultimately left you will assign it to magnesium carbonate hardness and depending on the amount of magnesium left you will allocate it to magnesium non carbonate hardness. From this you will also look at what is the removal required.

Here I have to mention this, why am I not saying just that I need zero milligram per litre? Well 2 aspects, if I have it this way, it is going to lead to corrosive water. You do not want it to have no precipitate being formed, sometimes people want to form a thin layer of the CaCO_3 in the pipe so that that acts as a protective coating it prevents the pipe from being corroded.

Other than that, because these equations as you can see CaCO_3 , the solid will be in equilibrium with Ca^{2+} and CO_3^{2-} . And we saw that there was an equation for this, K_{sp} is equal to what Ca^{2+} into CO_3^{2-} and I think we saw this equation, something to be around 10^{-9} . We saw this in one of the earlier graphs in this session or the previous session.

As you can see you are always going to have it in equilibrium, you will never be able to reach zero. You will be able to reach very low values, you will have to keep adding more and more of this lime or the soda ash which is not feasible. And more importantly, it is always at equilibrium. How much ever you remove some calcium will always be in equilibrium with that particular solid. It is in equilibrium, so if it is like this, you can maybe bring it down here. But you will still have equilibrium.

You will always have some calcium, you with this process the way we are doing it you cannot get zero hardness and also you would not want to have everything removed? Because if this is the pipe you want to have a thin coating such that the pipe is not corroded otherwise the water is seemed to be corrosive. I think we will look at this now.

And then you allocate hardness to calcium carbonate hardness. I would then do it for magnesium carbonate, magnesium non-carbonate and calcium non carbonate hardness, but others would also say that you will have this here and in that order. But it does not make too much difference here, what is the approach? This is the aspect, first calculate the hardness and associate and give it to relevant calcium.

And then magnesium, find out what is the objective and to what level we want to remove these 200, 150, 80, 40 or such and then you will calculate the amount of lime or such required.

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Approach

4. Calculate doses using stoichiometric ratios and amounts to be removed
 - a) Must remove all CO₂ in all cases
 - b) Must add excess dose of lime when Mg is being removed (about 20-40 mg/L as CaCO₃). Davis suggests excess of 10 mg/L for removal of Ca-H.
 - c) If calculated lime dose does not exceed alkalinity + CO₂, then pH may not be high enough to drive reactions; this is particularly true when MgH Mg²⁺ should be removed. In that case, lime dose should be increased to be alkalinity + CO₂ + excess 4

Fig 11

How is it? You want to remove carbon di oxide in all the case if there is any carbon di oxide all of it will have to be removed. And then add excess dose of lime when magnesium is also being removed, that what is it. Now you have magnesium carbonate hardness being removed along with the calcium carbonate hardness. And if the calculated lime dose does not exceed alkalinity + CO₂, then pH may not be high enough to drive the reactions.

That is one thing to keep in mind if I am adding lime and all the lime is consumed by the alkalinity or the CO₂, it is not increasing the pH. That is something that you have to keep in mind then pH might not be high enough to drive the reactions. This is true when magnesium carbonate hardness should be removed. In that case lime should be increased. Lime dose should be increased to alkalinity + CO₂ + excess let us so that is something.

Keep in mind why as I told you, magnesium will be removed at relatively high pH around 11.5. The pH has to be increased considerably. That is why you are adding this excess to that is something to keep in mind so let us move on.

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$$\begin{aligned} \text{Lime dose} &= 1.0 (\Delta\text{CO}_2) + 1.0 (\Delta\text{Ca-CH}) + 2.0 (\Delta\text{Mg-CH}) + 1.0 (\Delta\text{Mg-NCH}) \\ &+ \text{excess} \\ \text{Minimum lime dose} &= \text{Alkalinity} + \text{CO}_2 + \text{excess if Mg removed (all as CaCO}_3\text{)} \\ \text{Soda ash dose} &= 1.0 (\Delta\text{Ca-NCH}) + 1.0 (\Delta\text{Mg-NCH}) + \text{excess} \end{aligned}$$

Fig12

Looking at this table or the summary earlier what is it that we have here? We have lime dose. For removing one mole of carbon di oxide, one mole of calcium associated with carbon hardness one and for magnesium associated with carbonate hardness. Two moles of lime and the one associated with non-carbonate hardness, one mole of lime and some excess has to be added to drive the relevant reaction.

That is something to keep in mind. What about soda ash? Minimum lime dose, will be alkalinity and carbon di oxide because all the OH- you are going to add will be taken up by this CO₂ or H₂CO₃ and alkalinity is nothing but acid neutralizing capacity. You have to add excess enough to be able to remove this is for the minimum lime dose and excess will have to be added especially.

If magnesium has to be removed, all the units are being expressed as CaCO₃ that is something to keep in mind, when is soda ash to be added when I have no carbonate present in my solution, I have to give the relevant CO₃²⁻ and it is added when I have to remove calcium non-carbonate hardness or magnesium non carbonate hardness and excess to drive the relevant reaction. I see that it is one for each case. Let us move on.

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Lime-Soda calculation

- Data for a water sample
- Flow rate (Q) = 50,000 Litres per day
- Purity of slaked lime (Ca(OH)₂) = 86%
- Purity of soda (Na₂CO₃) = 98%
- Calculate Daily requirement of Lime and Soda ash respectively.

Impurities	Concentration (mg/L)
→ CaCO ₃	280
→ MgCl ₂ ←	138
→ Mg(HCO ₃) ₂ ←	100
→ MgSO ₄ ←	80
NaCl	35
Fe ₂ O ₃	55
→ CaSO ₄	110
SiO ₂	40

Handwritten notes above the table:
 → Ca²⁺, Mg²⁺, HCO₃⁻ (pointing to CaCO₃, Mg(HCO₃)₂)
 ← Ca-CH, Ca-NCH, Mg-NCH (pointing to MgCl₂, MgSO₄)
 70% (written next to the purity of slaked lime)

Fig 13

We have one example here. Let us just look at that and wind up for now. And then we will have one more session probably where we will wrap up lime soda softening. We have it for a water sample. Here we have the data such that it is easy for us to understand whether it is carbonate hardness or non-carbonate hardness, flow rate is 50,000 litres per day or 50kld, this slaked lime purity is at 86%.

This is something to keep in mind. The purity here that is mentioned is actually pretty high typically it might be around 70%, that is one aspect. Purity of the soda ash and Na₂CO₃, this typically is relatively high 98%. And we are asked to calculate the daily requirement of lime and soda ash respectively. Here we have different impurities and the relevant concentrations.

First thing is to understand per litre how much lime or soda ash that I need to add, once I have that how the flow rate which is volume per time volume litres per day time and then I will be able to calculate the required lime or soda ash per day, it is pretty simple. First approach is to look at this so as I can see I have calcium here, magnesium here.

And also, calcium here so calcium is associated with carbonate hardness. Calcium is also associated with non-carbonate hardness. It is therefore making the job here easier for us. If not, you will have had to look at general understanding of this kind of chart. Where is this? But there if I had information, like this Ca²⁺, Mg²⁺ and HCO₃ independently.

Rarely will we ever have it in this manner. We would not know in what form the CaCO₃ will be, we already know calcium came and we would not know whether it came in from CaCO₃

or other form. Typically, you will only be able to measure Ca^{2+} or Mg^{2+} you cannot measure CaCO_3 directly that is dissolved in the solution. Once it is dissolved, it will be present as the relevant ions.

But in this example, we are taking a theoretical look. But if not in general, you will be able to measure calcium, so I will write calcium here. And I will be able to measure magnesium. I will be able to write magnesium here. I will be able to write alkalinity or HCO_3^- and then maybe the other anions. And then I will say, the Ca^{2+} or I have some calcium and carbonate hardness.

And as you can see, our alkalinity is less than the calcium concentration, I will also have calcium non carbonate hardness. And then I will say all the magnesium will be associated with only non-carbonate hardness. That is the typical approach. If the ions are given this is the usual way. But here people were just trying to throw it of set but you understand my issues with the questions being framed in this manner.

You cannot measure CaCO_3 directly, but you will measure the ions, That is enough. What about magnesium? It is present in the form of carbonate hardness in some cases, present in the form of non-carbonate hardness in some cases, so in a way that making the job easier. Let us move on.

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Lime-Soda calculation

- Conversion of concentrations into mg/L as CaCO_3

Impurities	Conc.(mg/L)	Equivalent weight (g)	Milliequivalents/L	As CaCO_3 (mg/L)
CaCO_3	280	50	5.6	280
MgCl_2	138	47.5	2.905	145.25
$\text{Mg}(\text{HCO}_3)_2$	100	73	1.37	68.5
MgSO_4	80	60	1.333	66.65
NaCl	35	58.5	0.598	30
Fe_2O_3	55	26.67	2.062	103
CaSO_4	110	68	1.617	80.85
SiO_2	40	29	1.379	68.95

Handwritten notes: $\frac{MW}{n} = \frac{MW}{2}$, $\frac{50}{100} = \frac{50}{100}$, $\frac{100}{50} = \frac{200}{100}$

Fig 14

We have listed them out here. Equivalent weight, equivalent weight for CaCO_3 . It is either Ca^{2+} or CO_3^{2-} each one charged 2. That is why it will be molecular weight by N and N in

this case is 2. Same case you can look at it for all the other cases here. For here it is going to be 1, here it is 2. Same case 2 here I am talking about the valency.

And here it is 3+, Not even 3+ I think it is 6+ here if I am not wrong because it is Fe^{3+} , and I have 2 of them. It is 6+ here and same case oxygen is 2-, I have 3 of them, it is 6 here. Ca^{2+} , SO_4^{2-} , so it is 2 here, as I want to it is going to be equal to 4 here, in that manner, you can get this particular equivalent with molecular weight by N.

Let us see and you can get that particular aspect here. Based on that, you have the relevant valency and from that, you can get the relevant equivalent weight here, molecular weight by the valency and you will calculate the equivalent weight. And then you will be able to calculate the equivalents per litre. How do I get that I have the concentration here, milligrams per litre and I want equivalent in the top.

I will have to have mass in the bottom here, for one equivalent what is the weight gram of that particular compound? Then grams will cancel out. I will have it in terms of equivalent. In effect I am dividing by equivalent weight, but such the approach that I prefer but here for putting all the data into one table, we trimmed some of the aspects.

If not, I would have written valency molecular weight and gone from there. Here I have it as equivalents and then I know this, that for CaCO_3 it is. But for one equivalent it is 50 grams of CaCO_3 this also we calculated earlier. If I multiply it 50 grams of CaCO_3 per equivalent then I will end up in this last column 1, 2, 3, 4, 5, fifth column. That is what I have from these two, I will get the fourth column.

Multiplying the fourth column by this I will end up with the fifth column so all the units are now expressed as CaCO_3 . CaCO_3 to 80 milligram per litre will be as CaCO_3 itself. That is something to keep in mind. Let's move on and see what else we have.

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$$\begin{aligned}
 \bullet \text{ Lime dose} &= 1.0 (\Delta\text{CO}_2) + 1.0 (\Delta\text{Ca-CH}) + 2.0 (\Delta\text{Mg-CH}) + 1.0 (\Delta\text{Mg-NCH}) + \text{Excess} \\
 &= 0 + 1 (280) + 2(68.5) + 1(66.65+145.25) \text{ as CaCO}_3 \\
 &= 628.9 \text{ mg/L as CaCO}_3 \\
 &= 628.9 \times \frac{\text{eq. weight of Ca(OH)}_2}{\text{eq. weight of CaCO}_3} \text{ mg/L as Ca(OH)}_2 \\
 &= 628.9 \times \frac{37}{50} \text{ mg/L as Ca(OH)}_2 \\
 &= 465.38 \text{ mg/L as Ca(OH)}_2
 \end{aligned}$$

$\frac{\text{mass}}{\text{Vol}} \times \frac{\text{Vol}}{\text{time}}$

$$\begin{aligned}
 \bullet \text{ Daily lime requirement} &= Q \times \text{lime dose} \\
 &= 50,000 \text{ L/day} \times 465.38 \text{ mg/L} \\
 &= 23.27 \text{ Kg / day}
 \end{aligned}$$

Fig 15

Lime dose there is no carbon di oxide present. And we already have this from earlier for now. We are not saying that there is any excess but in general always keep in mind that excess has to be added. From that we are just calculating how much Ca as CaCO₃ is required, we need equal and so why is that? Because I cannot compare concentration of carbon di oxide here.

If you want you can calculate the concentration of lime in terms of moles and then transform it into CaCO₃. But it is easier to express everything in terms of CaCO₃. Let me move on and then so this is the amount of lime that he asked to be added as CaCO₃ to remove the relevant hardness. And then we wanted in terms of CaOH twice concentration. Equivalent weight of CaOH twice concentration by equivalent weight of CaCO₃, then the units are going to be as milligram per litre as CaOH twice.

What is this 37 by 50 and this is the amount of CaOH twice, how to add in terms of mass of CaOH twice per volume. Here the units were as CaCO₃. And we just transform them into units of CaOH twice because I think the question asked for that. What about soda ash? Let me finish daily lime requirement. This is mass. Mass per volume is what I calculated. But I want daily per time or per day how much is required.

For that I will have to multiply that by volume per time, then I will get mass per time. Flow volume per time is nothing but flow rate. You just have to change the units, 1 litre the mass of water you can change that. And that seems to be saying that I need 23.27 kgs of calcium hydroxide of lime per day. But one thing to note that our source of lime is not pure I have to add that. It is 86%.

If I divide this by 0.86, this is the value that I need. I need 27 kgs per day of lime and not the 23 that I calculate earlier, why? it is only 86% pure so that is why I am dividing it by 0.86.

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$$\begin{aligned}
 \bullet \text{ Soda ash dose} &= 1.0 (\Delta \text{Ca-NCH}) + 1.0 (\Delta \text{Mg-NCH}) \\
 &= 1(80.85) + (145.25 + 66.65) \text{ as CaCO}_3 \\
 &= 292.75 \text{ mg/L as CaCO}_3 \\
 &= 292.75 \times (\text{eq. weight of Na}_2\text{CO}_3 / \text{eq. weight of CaCO}_3) \text{ mg/L as Na}_2\text{CO}_3 \\
 &= 292.75 \times 53/50 \text{ mg/L as Na}_2\text{CO}_3 \\
 &= 310.315 \text{ mg/L as Na}_2\text{CO}_3 \\
 \bullet \text{ Daily Soda ash requirement} &= Q \times \text{Soda ash dose} \\
 &= 50,000 \text{ L/day} \times 310.315 \text{ mg/L} \\
 &= 15.51 \text{ Kg / day}
 \end{aligned}$$

Fig 16

Same case with soda ash, I know this from the relevant setup that I have earlier and I will plug that in and magnesium and non-carbonate hardness we also we looked at that so I will not go back there. First as CaCO₃ and then now I wanted as Na₂CO₃ and this is what we have found. This is now as Na₂CO₃. And same case as lime here I have to calculate the dose. Here I am going to multiply that by the flow rate. I will get it mass per time.

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• Since purity of Soda ash is 98%,

$$\text{Daily requirement of Soda ash} = 15.51/0.98 \text{ Kg / day}$$

$$= 15.83 \text{ Kg / day}$$

Fig 17

And purity is 98% so I have to divide by 0.98, I will now need to add 15. Kgs or 16 Kgs per day. Let us keep in mind that in both these cases, we have not looked at adding the excess, but without adding the excess, you will never be able to get that particular precipitation going. That is something to keep in mind if the question does not ask for excess.

You can always add that excess as to be added later. With that, I will end today's session and we will look at different configurations in the next session and probably wrap up this hardness removal by lime soda softening and with that, thank you.