Water and Waste Water Treatment
Prof. Bhanu Prakash
Department of Civil Engineering
Indian Institute of Technology - Roorkee

Module No # 10
Lecture No # 49
Recarbonation

Hello everyone, welcome back to the latest lecture session and in last 3 or 4 sessions we looked at different aspects pertaining to lime-soda softening. But before we go further at least in this session let us look at the bigger picture. I want to remove hardness; Calcium and magnesium, how do I remove by precipitating them? Calcium carbonate $CaCO_3$ solid or magnesium hydroxide $Mg(OH)_2$ solid.

For both these cases we typically raise the pH, in general just raising the pH is good enough if there is enough carbonate for the calcium carbonate to precipitate out. But if there is not enough carbonate then I have to add a source of carbonate. Adding a source of carbonate if required and rising the pH for all the cases. How do I raise the pH? I raise the pH by adding lime, calcium hydroxide.

And to remove the relevant non-carbonate hardness if there is the case when there is not enough bicarbonate present you are going to add a source of CO_3^{2-}, that is soda so lime and soda that is how we looked at it and we looked at the relevant reactions and we summarized them in this manner.

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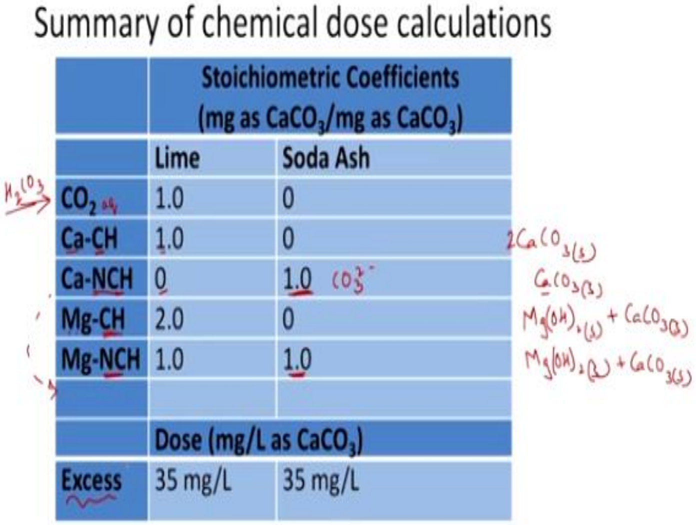

Summary of chemical dose calculations

	Stoichiometric Coefficients (mg as $CaCO_3$/mg as $CaCO_3$)	
	Lime	Soda Ash
CO_2	1.0	0
Ca-CH	1.0	0
Ca-NCH	0	1.0
Mg-CH	2.0	0
Mg-NCH	1.0	1.0
	Dose (mg/L as $CaCO_3$)	
Excess	35 mg/L	35 mg/L

Fig 1

In general, if there is carbon oxide or if there is H_2CO_3, this is carbon dioxide aqueous dissolved or H_2CO_3 then you have to remove, that this is an acid. For that you look at it these are the stoichiometric ratios we already looked at them. Carbonate hardness- Calcium, you are precipitating that as $CaCO_3$ the solid and 2 $CaCO_3$ will come out in this reaction. Here we already have enough carbonates, we are just adding lime to increase the pH.

And then calcium non-carbonate hardness but this we discussed at the end here let me come back to that. Then magnesium when we have carbonate hardness but magnesium, we know it is going to precipitate out as magnesium hydroxide. But when I add lime, there is calcium but when I add lime here to increase the pH, I still have carbonates present and thus the calcium that I add can precipitate out as calcium carbonate if there is enough carbonate.

Magnesium non-carbonate hardness here same case as above to magnesium I am going to increase the pH by adding lime. But here it is non-carbonate hardness not enough carbonate so for the reason I have to add some soda ash so that the calcium in the lime that I add it will be removed. And then we look at calcium non-carbonate hardness, here non-carbonate hardness. Adding lime here itself will make no sense but I know that calcium will precipitate out as $CaCO_3$ the relevant solid.

Here I am not adding lime, I am not increasing pH, I am directly adding a source of CO_3^{2-} so $CaCO_3$ the solid will precipitate out. That is why you can just intuitively come up with this particular table not necessary to mug it up in general. And why do we add the excess? Because we want to keep the solution super saturated to drive the reaction.

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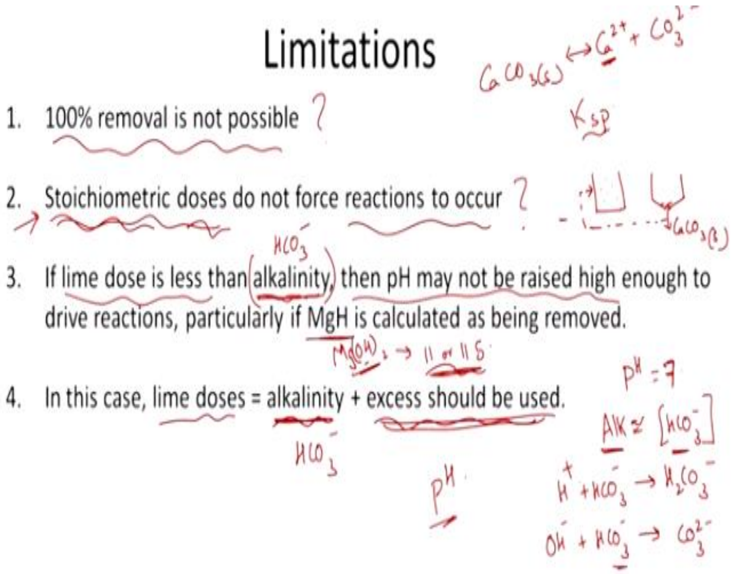

Limitations

1. 100% removal is not possible
2. Stoichiometric doses do not force reactions to occur
3. If lime dose is less than alkalinity, then pH may not be raised high enough to drive reactions, particularly if MgH is calculated as being removed.
4. In this case, lime doses = alkalinity + excess should be used.

Fig 2

What are the limitations? 100% removal is not possible, why? As we looked at it the system is in equilibrium, $CaCO_3$ the solid will always be in equilibrium with some concentration of Ca^{2+}. And we also looked at Ksp, so as you can see chemically it is not possible at least with respect to precipitation to have zero concentration, some thing or the other is always going to be in equilibrium with solid, at least feasibly.

And also, stoichiometry doses themselves do not force reactions to occur for example we looked at a particular question and then solved it. But the way the question was asked it did not talk about the excess or what is required to drive the reaction. In general, just maintaining the stoichiometry ratios would not start or trigger the precipitation. For precipitation to occur you need nucleation and then there are other steps- Agglomeration, ripening or crystal growth.

For these to occur or the rate to be high enough for these steps to occur you need high enough concentration of the relevant reactants. Meaning calcium or the carbonate so next aspect is stoichiometry doses themselves do not force reactions to occur, why is this? In general, you have different steps in precipitation. First step is nucleation which is pretty slow and for that to occur you need remarkably high concentrations of the relevant dissolved compounds.

Or supersaturated solution is required you can look at the relevant info there but here as I mentioned we needed the solution to be supersaturated. Or to bypass this nucleation step where I want to provide a surface for the relevant other crystal to precipitate on. And have a crystal being formed, what can I do or what do people do?

Typically, if this is my sedimentation tank and the sludge settles down here, the sludge is $CaCO_3$ the solid. Rather than just removing it what can I do? And if this is the tank where I am adding the lime soda such that the $CaCO_3$ is being precipitated out later, I can recycle some of it, some, why? I have some $CaCO_3$ solid here and that will give the relevant surface area, here it is an issue of both surface area and super saturation.

I can really supersaturate to high levels or also super saturate or also provide some surface area for the relevant solids to precipitate upon. There are 2 ways to go about it and one aspect is recycle, the other aspect is stoichiometric doses are not enough. That is why we need to add excess to supersaturate the relevant solution, that is something to keep in mind.

Next aspect is if lime dose is less than alkalinity then the pH may not be raised high enough. One aspect in general in this case pH = 7 or usually around 7, 6 or 8 and at that case alkalinity is equal to or almost equal to HCO_3^-, we looked at it, I am not going to go into that. But in general alkalinity is acid neutralizing capacity. If I add H+ to the relevant water, HCO_3^- will neutralize this acid.

But here it seems contradictory if lime dose is less than alkalinity then the pH might not be raised. Here when I am talking about alkalinity, I am referring to HCO_3^-. But layman’s terms in general get questions too, they confuse this or use this interchangeably. Keep in mind that here we are talking about HCO_3^-, why? Even when I add OH^- from my lime and that can be neutralized by my particular HCO_3^-.

Why? HCO_3^- can act as both an acid or a base so that is one thing to keep in mind if lime dose is less than the HCO_3^- concentration then the pH might not be raised high enough to drive the reactions and why is that critical? Typically, magnesium hydroxide $Mg(OH)_2$ we looked at the relevant figures. For this typically pH around 11 or 11.5 is required for the precipitation or to occur.

That is something to keep in mind, OH^- is reactant so when pH is high, OH- is high so thus high pH is required. That is something to keep in mind, why is this an issue? Well 2 cases lime dose, alkalinity typically water you will typically have alkalinity. You need to have considerably high lime doses and in this case lime dose is equal to alkalinity plus the excess should be used.

Excess for 2 cases because it is just not sufficient to look at the HCO_3^- concentration to increase the pH, also I will have to add excess for 2 cases, excess is for driving the stoichiometric reaction or the reaction. And then when it is just about near about alkalinity, why is this to increase the pH?

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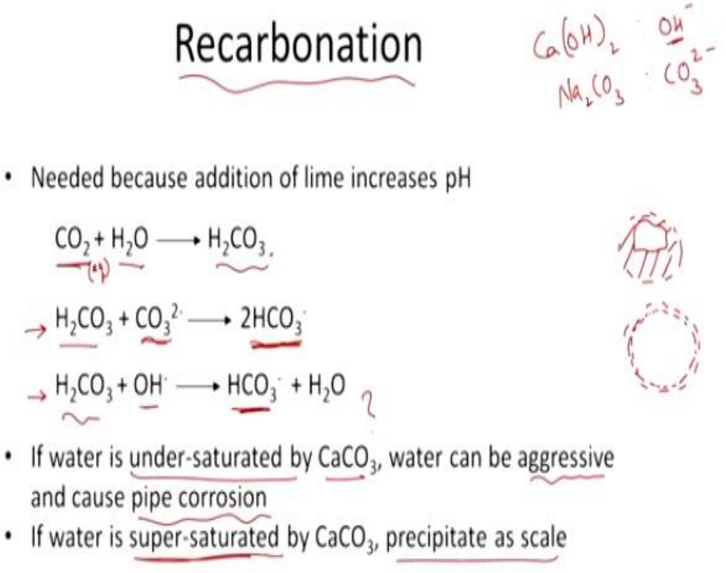

Recarbonation

$Ca(OH)_2$ OH^-
Na_2CO_3 CO_3^{2-}

- Needed because addition of lime increases pH

$CO_2 + H_2O \longrightarrow H_2CO_3$.

$\rightarrow H_2CO_3 + CO_3^{2-} \longrightarrow 2HCO_3^-$

$\rightarrow H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$

- If water is under-saturated by $CaCO_3$, water can be aggressive and cause pipe corrosion
- If water is super-saturated by $CaCO_3$, precipitate as scale

Fig 3

Let us move on recarbonation. I am done with removing calcium and magnesium by precipitating out $CaCO_3$ and magnesium hydroxide. But in all this case what I have been doing? I am adding $Ca(OH)_2$ lime, what is this? A source of it is the source of OH^- and also Na_2CO_3 soda ash or soda what is this a source of? It is a source of CO_3^{2-} so this strong base CO_3^{2-} also will increase the pH but depending on where the pH is.

At the end depending on which step you are at the pH will be very high and this very high pH cannot be supplied to relevant population. Other than that, it will leave and lead to corrosion of your relevant distribution network. You have to bring the pH down if not to 7 at least 8 or so acceptable level you have to bring the pH down. What is an easy way?

There are different ways adding acid HCl to bring it down but when I add HCl, I am also adding Cl- I am increasing the total dissolved solid and that is not something I want to do. And keep in mind that by adding lime I have removed all the HCO_3^- is a good buffer. It can act as both, an acid or a base so if there is no buffer in solution the pH can either increase of decrease or increase depending on either the acid or base coming into contact with your water.

Here I want to achieve 2 objectives one is I want to decrease the pH to acceptable levels without increasing the TDS and the second one is if possible, adding a buffer is something that will prevent excessive change in pH around that pKa value. What is good way to go about it? Looks like the carbon oxide which we removed earlier. I will bubble carbon oxide gas through water and once it becomes or dissolves with H_2O it is going to be in equilibrium with H_2CO_3.

And H_2CO_3, HCO_3^- will be formed if there is a lot of CO_3^{2-}, H_2CO_3 that we formed here will react with CO_3^{2-} or the H_2CO_3 that we add will react with OH- and again HCO_3^- is formed. I am bringing down the pH and also seeing to it that I am adding a buffer, HCO_3^- will provide a relatively decent buffer near pH 7 why? We know that pka1 is 6.3 so that is one aspect to keep in mind.

Here when we are adding this and looking at these aspects, we need to look at an aspect called under saturation or super saturation by $CaCO_3$. We look at why that is relevant? If water is under saturated, water can be aggressive. It can be corrosive and can lead to pipe corrosion. If it is remarkably under saturated, it can lead to pipe corrosion. In general, ideal case we saw some picture where precipitation was at this level.

Everything precipitated out and I think one fourth or one third of the area was available for the pipe. You do not want that but you want to something like there is a thin layer of the precipitate all around such that the pipe is not corroded. You wanted to just at that border and have some precipitation that is the ideal case. But you do not want to be under saturated neither do you want it to be super saturated.

Because then there will be too much scaling so how do we look at this or how do we understand this? There is a particular way to go about it.

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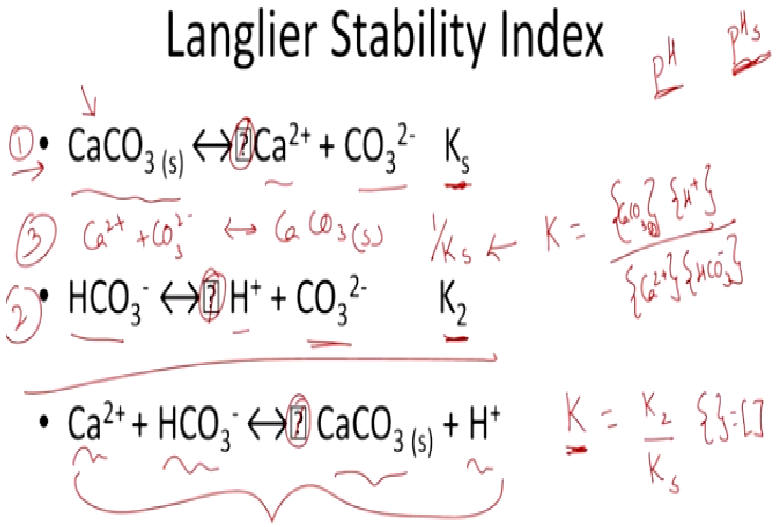

Langlier Stability Index

pH pHs

① • $CaCO_{3(s)} \leftrightarrow Ca^{2+} + CO_3^{2-}$ K_s

③ $Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_{3(s)}$ $1/K_s \leftarrow K = \frac{\{CaCO_3\}\{H^+\}}{\{Ca^{2+}\}\{HCO_3^-\}}$

② • $HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$ K_2

• $Ca^{2+} + HCO_3^- \leftrightarrow CaCO_{3(s)} + H^+$ $K = \frac{K_2}{K_s}$ $\{\}:[]$

Fig 4

It is called the Langlier stability index, so I think some type of when I change the font. We ignore this so we have some equations that we need to keep in mind here. We know that $CaCO_3$ the solid goes to this is the solubility reaction of $CaCO_3$ dissolution reaction goes to Ca^{2+} and CO_3^{2-}. For that we know that we have Ksp, the solubility product.

This is nothing but the equilibrium constant. Similarly, we know that HCO_3^- can dissociate into H^+ and CO_3^{2-}. For that we will have its own equilibrium constant which we used to form pKa but I am digressing here. From these 2 reactions depending upon changing the reactants in products in this particular first reaction, I can add them up and you see that I will get this particular reaction.

If I swap this first reaction such that Ca^{2+} + CO_3^{2-} goes to $CaCO_3$ the solid, why do we write in this way? This is the typical way for which the solubility product is being calculated. But if I swap it then it is going to become 1 by Ks, the equilibrium constant for this reaction which has been swapped will be 1 by Ks. And then if I add this new reaction 3 and 2, what will I get? CO_3^{2-} can cancel them out it looks as if Ca^{2+} + HCO_3^- goes to the $CaCO_3$ solid + H^+.

What is this new equilibrium constant for this one though? It will be K2 by Ks this into the K for this and the K for the second or the third reaction is 1 by Ks. It turns out to be the K for this composite reaction is K2 by Ks. Let us just use this so if I want to use this to develop a relationship, what am I trying to do? We are trying to see to it that we can look at the pH of the solution and then look at the pH of the saturated conditions and compare and see whether it is over saturated or under saturated.

For that I am trying to get this pH saturation or equilibrium condition. Let us just use this, so how do I write the K for this reaction? We know it is going to be the activity of the relevant products, $CaCO_3$ the solid activity of H^+ raise to the stoichiometric coefficient nothing here and what else do we have? We have Ca^{2+} and HCO_3^- as I mentioned activity of solids, we assume it to be 1 assuming it is a pure solid, mole fraction is equal to 1. And assuming that activity is equal to concentration.

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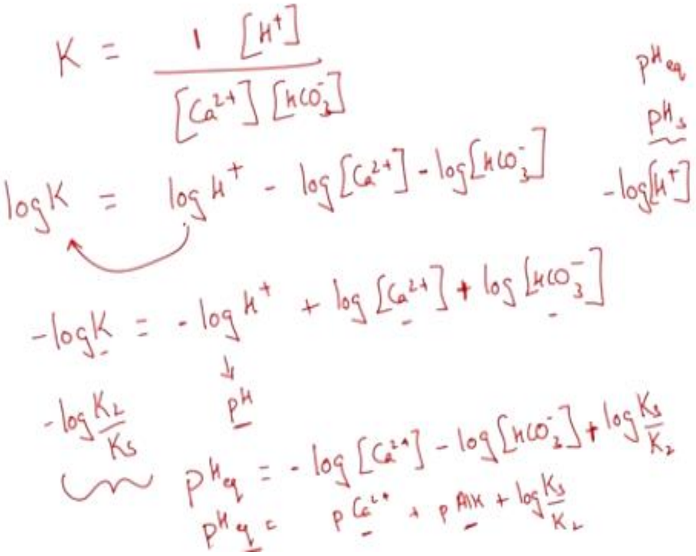

$$K = \frac{1\ [H^+]}{[Ca^{2+}][HCO_3^-]}$$

$$\log K = \log H^+ - \log[Ca^{2+}] - \log[HCO_3^-]$$

$$-\log K = -\log H^+ + \log[Ca^{2+}] + \log[HCO_3^-]$$

$$-\log \frac{K_2}{K_s} \qquad pH$$

$$pH_{eq} = -\log[Ca^{2+}] - \log[HCO_3^-] + \log\frac{K_s}{K_2}$$

$$pH_{eq} = pCa^{2+} + pAlk + \log\frac{K_s}{K_2}$$

pH_{eq}

pH_s

$-\log[H^+]$

Fig 5

I have the equilibrium constant for the relevant solid, it is one and I am now approximating the activities by concentrations. This is what we have so let me make sure I put it down. And now I just want to take the logarithm, why is it? As I mentioned at the end of the day, I want to find the pH equilibrium or pH saturation, to get the pH saturation I need to take logarithm to transform this H^+ into minus log H^+, that is the final aspect.

If I take logarithm on both sides, log K is equal to what now? log of H^+ minus log of Ca^{2+} -log of HCO_3^-. And then if I take this to the left-hand side and this to the right-hand side and multiplied by negative, what will I have? I have minus log K= minus log H+ + log of calcium minus log of HCO3-. You do not need to mug this up just try to understand the relevant process.

Here this is nothing but the pH and this too what is K minus log of K2 by Ks, so this is a constant and this is what does this give me for a given calcium concentration and given alkalinity or carbonate concentration. I will now be able to calculate the pH equilibrium so pH equilibrium will be equal to we have minus log calcium minus log HCO_3^- and minus log K2 by Ks, so if I want to make it plus.

I will see say it is Ks by K2, so this pH at equilibrium this you can write it as if it is P Ca^{2+}. Then it will be positive, P I am saying it is minus log, same case here you can say it is P of alkalinity plus log of this constant Ks by K2 so what it this equilibrium indicating? It is the equilibrium indicating the case when this solid is just precipitating. For a given system if the calcium concentration and the alkalinity or in the term of HCO_3^-, I can then calculate this pH equilibrium and what can I do from that?

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L.S.I.

$I = pH - pH_{eq}$

$I > 0$ super sat

$I = 0$ sat.

$I = 0.2$ } ideal.

$I < 0$ under...

Fig 6

This Langlier saturation index I or LSI will be equal to the actual pH minus the pH at equilibrium which we just calculated. And you see how we can calculate this, so for a given case you can see if I is greater than 0 it is super saturated. And if I is equal to 0 it is just saturated, I less than 0 it is under saturated. If it is under saturated this is the Langlier stability index.

Langlier stability index and if it is super saturated, I know depending on the level of super saturation that it can lead to lot of precipitate being formed. Under saturated, it can lead to corrosion. Typical value it seems like if I is equal to or around 0.2, this is ideal this is the condition you would typically want to look at. And people use this Langlier stability index to just have back of the page calculation or rough calculation to see.

Whether it is saturated or super saturated or under saturated, that is one way to look at your case, let me move on.

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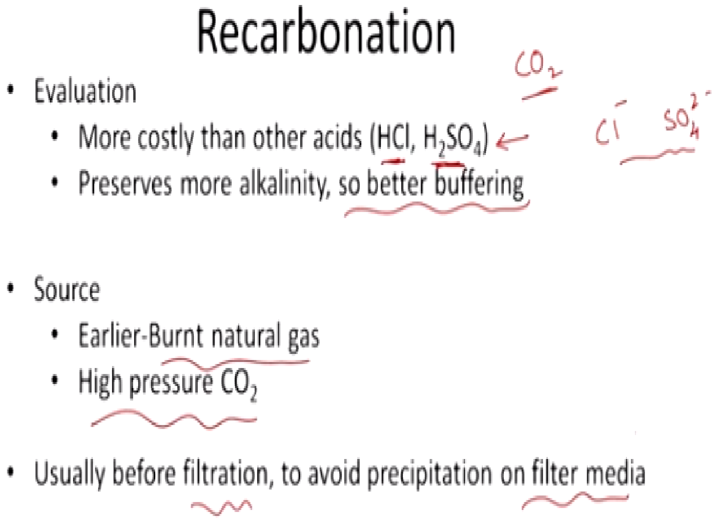

Recarbonation

- Evaluation
  - More costly than other acids (HCl, H_2SO_4)
  - Preserves more alkalinity, so better buffering
- Source
  - Earlier-Burnt natural gas
  - High pressure CO_2
- Usually before filtration, to avoid precipitation on filter media

Fig 7

Recarbonate, so we already looked at this if adding CO_2 is relatively costly then adding HCl or H_2SO_4. But I mentioned why we would not add them because one thing TDS will increase, Cl- will stay in the solution, SO4 2- will stay in solution, that is not something that I want. And also, they would not add to any buffering but by adding CO_2, we will have HCO_3^- so that is a good buffer.

That is why we add carbon dioxide even though it is slightly costlier. Earlier they used to burn gas as the source. But now you have enough different ways to have high pressure carbon dioxide systems. Usually before filtration it looks like to avoid precipitation on the filter media anyway that is one aspect that you typically use it before filtration.

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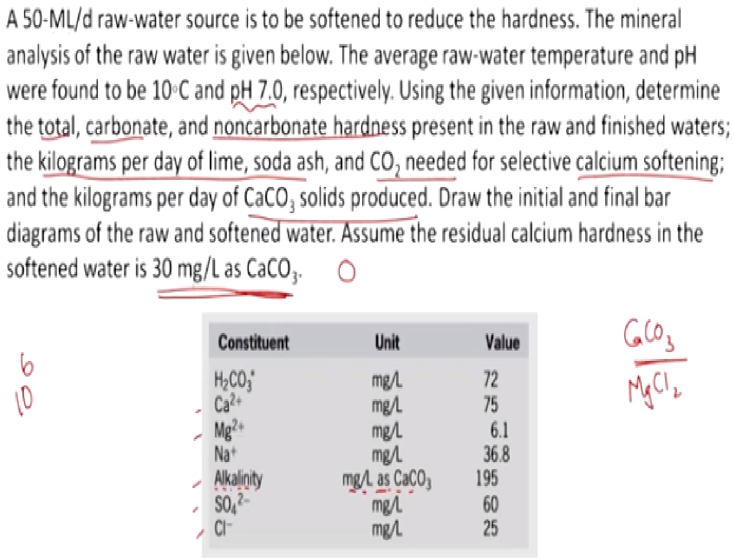

A 50-ML/d raw-water source is to be softened to reduce the hardness. The mineral analysis of the raw water is given below. The average raw-water temperature and pH were found to be 10°C and pH 7.0, respectively. Using the given information, determine the total, carbonate, and noncarbonate hardness present in the raw and finished waters; the kilograms per day of lime, soda ash, and CO_2 needed for selective calcium softening; and the kilograms per day of $CaCO_3$ solids produced. Draw the initial and final bar diagrams of the raw and softened water. Assume the residual calcium hardness in the softened water is 30 mg/L as $CaCO_3$.

Constituent	Unit	Value
$H_2CO_3^*$	mg/L	72
Ca^{2+}	mg/L	75
Mg^{2+}	mg/L	6.1
Na^+	mg/L	36.8
Alkalinity	mg/L as $CaCO_3$	195
SO_4^{2-}	mg/L	60
Cl^-	mg/L	25

Fig 8

Here we have another example let us just look at that. A 50 MLD, meaning million liters per day, 1 million is 10 to the power of 6. 1 million liters per liters MLD a 50 MLD raw water source is to be softened to reduce the hardness and the mineral analysis of the raw water is given below let us look at this. Compared to the previous example we looked at this is more realistic. Because these are the way or these are the ions you will typically be able to measure.

Earlier I think we measured something as if $CaCO_3$ was given and I think $MgCl_2$ was given and so forth. Rarely will they exist as $CaCO_3$ and rarely will we know what was put into the water, so that was just for a theoretical case. But here we see that we have H_2CO_3 or carbon dioxide and calcium magnesium alkalinity which is expressed as CaCO3. Alkalinity will always be in equivalent units or expressed as $CaCO_3$.

And SO_4^{2-} and Cl^- so, we have to relevant constituents here and what else? They say that pH is 7 that makes our job easier. Using the given information determine the total carbonate and non-carbonate hardness this is pretty standard we know how to do that? But before doing that we know we are talking about total hardness. We are using the concentrations of 2 different compounds.

And in general, we are not going to express them as moles per liter, it does not make much sense it has to be in equivalents per liter. Equivalents per liter relatively difficult for the layman to understand so, we express the units as $CaCO_3$. The first step is to convert all this into $CaCO_3$ units. We will look at that and also looks like how much lime and soda ash is needed for only removing calcium softening typically that is the one selective calcium softening means typically about removing the calcium that is associated with the carbonate hardness.

And also, what is the CO_2 needed later and the kilograms of $CaCO_3$ sludge is going to be produced. Because if I am removing calcium what is going to precipitate out? $CaCO_3$ the solid is going to precipitate out. How much is being what do we precipitated? And then just the initial and final diagrams. Assume that the residual calcium hardness in the softened water is this is my objective.

As I mentioned we can never get to 0 so this is the residual calcium hardness. Anyway, let us go ahead and look at how we go about things.

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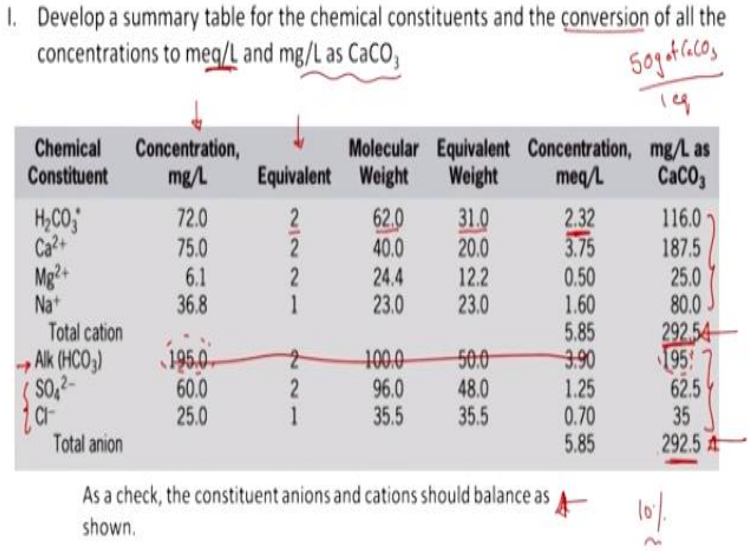

I. Develop a summary table for the chemical constituents and the conversion of all the concentrations to meq/L and mg/L as $CaCO_3$

$\frac{50\,g\text{ of }CaCO_3}{1\,eq}$

Chemical Constituent	Concentration, mg/L	Equivalent	Molecular Weight	Equivalent Weight	Concentration, meq/L	mg/L as $CaCO_3$
$H_2CO_3^*$	72.0	2	62.0	31.0	2.32	116.0
Ca^{2+}	75.0	2	40.0	20.0	3.75	187.5
Mg^{2+}	6.1	2	24.4	12.2	0.50	25.0
Na^+	36.8	1	23.0	23.0	1.60	80.0
Total cation					5.85	292.5
Alk (HCO_3)	195.0	2	100.0	50.0	3.90	195
SO_4^{2-}	60.0	2	96.0	48.0	1.25	62.5
Cl^-	25.0	1	35.5	35.5	0.70	35
Total anion					5.85	292.5

As a check, the constituent anions and cations should balance as shown.

10%

Fig 9

First thing is conversion as I mentioned we want in it equivalent units or typically we used the equivalent units expressed them in terms of $CaCO_3$. What is the aspect, here in the first column we have the chemicals or the compounds here the concentration milligram per liter which was given earlier? And then the equivalents this is with respect to charge H_2CO_3, 2 or CO_3^{2-} so equivalent is 2, Ca^{2+} too charge equivalent is 2.

Similarly, for everything out here so let us move on here so then here we get the molecular weight and so forth. For alkalinity, please remember that the units were already present as or given as milligram per liter as $CaCO_3$. All this is not required if it is 195 milligram per liter as $CaCO_3$ even if you jump over hoops, it is will going to end up as 195 milligram per liter as $CaCO_3$.

For SO4 2- too, well because we want the chart, we are putting them in. We have the molecular weight dividing the molecular weight by the equivalent will get the equivalent weight. And then dividing with that you are going to get your particular equivalent concentration expressed as equivalents. But I wanted to expressed as $CaCO_3$ I know that 50 grams of $CaCO_3$ is one equivalent.

If I multiply it with that, equivalent cancels out and the units will be in terms of as $CaCO_3$. Here well this is a theoretical exercise in general we will never have all the anion and cation information. But people typically want us to check it within a margin of 10% error. Here if I sum up all the cations and all these anions, we need to see charge balance and that is what we see. Equivalents of the cation and equivalents of the anion, positive and negative.

Both are balanced so that is what we see that is one aspect that they mentioned as an aside here.

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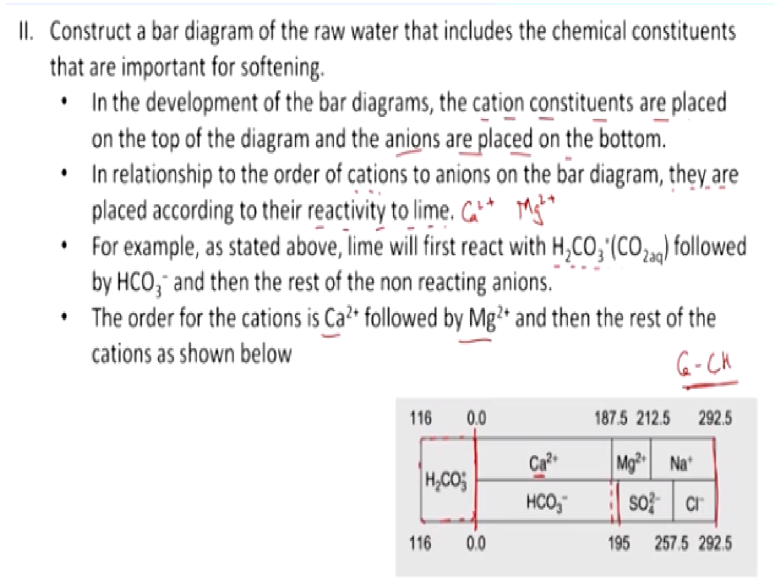

II. Construct a bar diagram of the raw water that includes the chemical constituents that are important for softening.

- In the development of the bar diagrams, the cation constituents are placed on the top of the diagram and the anions are placed on the bottom.
- In relationship to the order of cations to anions on the bar diagram, they are placed according to their reactivity to lime. Ca^{2+} Mg^{2+}
- For example, as stated above, lime will first react with $H_2CO_3^*(CO_{2aq})$ followed by HCO_3^- and then the rest of the non reacting anions.
- The order for the cations is Ca^{2+} followed by Mg^{2+} and then the rest of the cations as shown below

G - CK

Fig 10

Construct a bar diagram that includes the chemical constituents that are important for softening. Here there are some aspects we already know this, typically we are placing the cations at the top and anions at the bottom. And which cations are we having here they are typically placed according to the reactivity to lime. And with respect to lime are based on lime addition which one will typically state out if there is alkalinity.

It is the Ca^{2+} that is why we have it and then so one aspect I should have mentioned was this info I presented was with respect to the cations. But we should always have this acid if it is present if there is any dissolved acid H_2CO_3 present, that is first going to react with my lime so first I am going to have H_2CO_3 and then the relevant constituents. And here calcium followed by magnesium and then the rest of the cations.

Let us see what we have. We have some H_2CO_3, we just looked at that so H_2CO_3 equivalents is 116. Any lime I add will first react with this H_2CO_3, so that is why they have it in this manner. From here we are starting our axis or zero and then we are putting calcium 187.5 and then the relevant magnesium and sodium. Similarly, for HCO_3^-, SO_4^{2-} and Cl^- though there has to be a charge balance.

And that is why we see good agreement out here. What is the next aspect? What are the take home messages here? We see that total hardness calcium plus magnesium is greater than HCO3-

or the alkalinity as people are as laymen are calling it. But you see that for this particular example we are only concerned with removing calcium and as you can see HCO_3^- concentration is greater than calcium.

It is greater than calcium so what does that tell me? All the calcium hardness is as carbonate hardness so for that if there is enough carbonate what do I just need to do or bicarbonate, I just need to increase the pH. Such that this HCO_3^- will convert to CO_3^{2-} and it will precipitate out. We know that so it is just addition of lime that we want to look at, that is the thing that take home message we have here.

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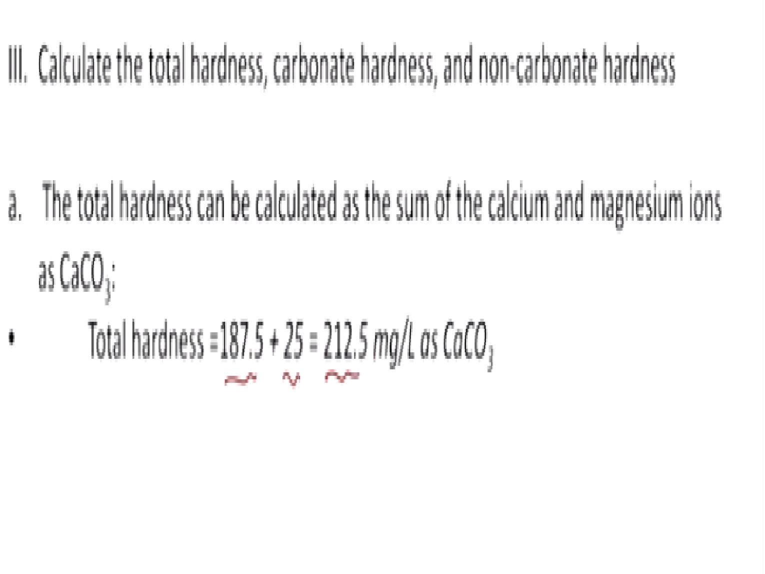

III. Calculate the total hardness, carbonate hardness, and non-carbonate hardness

a. The total hardness can be calculated as the sum of the calcium and magnesium ions as $CaCO_3$:

- Total hardness = 187.5 + 25 = 212.5 mg/L as $CaCO_3$

Fig 11

Let us see what else we have. We have the question here and total hardness it is calcium plus magnesium and this is the total hardness. And what else do we have?

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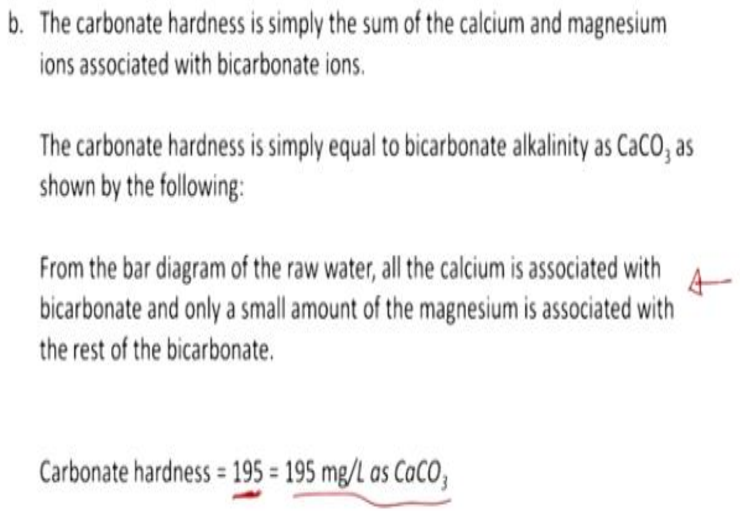

b. The carbonate hardness is simply the sum of the calcium and magnesium ions associated with bicarbonate ions.

The carbonate hardness is simply equal to bicarbonate alkalinity as $CaCO_3$ as shown by the following:

From the bar diagram of the raw water, all the calcium is associated with bicarbonate and only a small amount of the magnesium is associated with the rest of the bicarbonate.

Carbonate hardness = 195 = 195 mg/L *as* $CaCO_3$

Fig 12

Carbonate hardness is equal to just the HCO_3^- as $CaCO_3$, HCO_3^- was 195 so that is the relevant aspect and this is what I just mentioned with respect to calcium and carbonate hardness let me move on.

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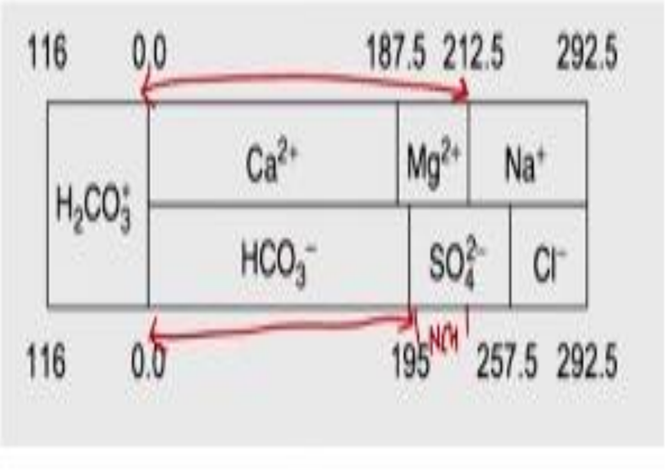

Fig 13

This is just the relevant aspect, it was HCO_3^- = 195 that is why the carbonate hardness is equal to this. That is the case because the total hardness was greater than HCO_3^-. Now what is the remaining part? That will be the non-carbonate hardness so, let us just calculate that.

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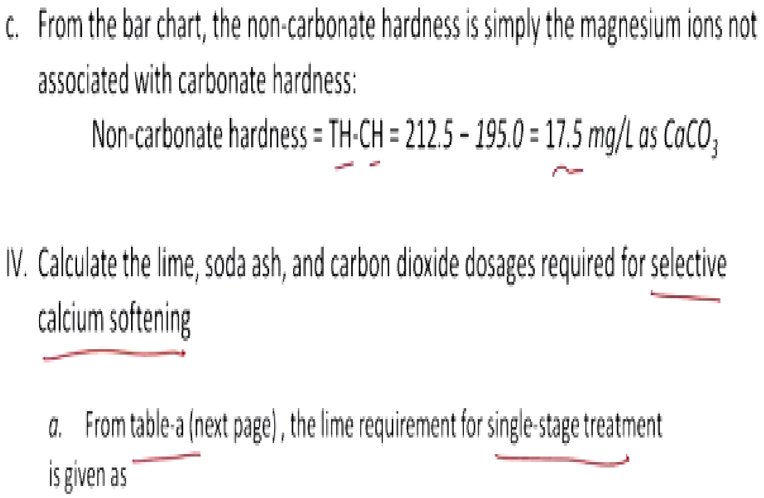

c. From the bar chart, the non-carbonate hardness is simply the magnesium ions not associated with carbonate hardness:

$$\text{Non-carbonate hardness} = TH\text{-}CH = 212.5 - 195.0 = 17.5\ mg/L\ as\ CaCO_3$$

IV. Calculate the lime, soda ash, and carbon dioxide dosages required for selective calcium softening

a. From table-a (next page) , the lime requirement for single-stage treatment is given as

Fig 14

Non-carbonate hardness is total hardness minus this so that is 17.5, that is relatively less here. And calculate the lime soda ash and carbon dioxide dosages required for selective calcium removal. Here when we are talking about selective calcium softening, we are talking about single stage removal when we say single stage we will discuss that later. But we are talking about only the calcium removal that is associated that too the calcium associated with carbonate.

We will look at this table here but we will cover this later but for now keep in mind that when we are talking about single stage.

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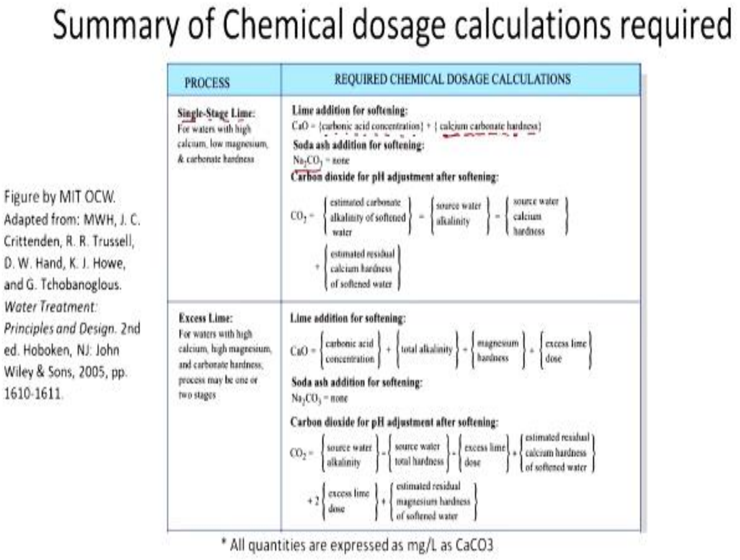

Summary of Chemical dosage calculations required

PROCESS	REQUIRED CHEMICAL DOSAGE CALCULATIONS
Single-Stage Lime: For waters with high calcium, low magnesium, & carbonate hardness	**Lime addition for softening:** $CaO = \{\text{carbonic acid concentration}\} + \{\text{calcium carbonate hardness}\}$ **Soda ash addition for softening:** $Na_2CO_3 = \text{none}$ **Carbon dioxide for pH adjustment after softening:** $CO_2 = \{\text{estimated carbonate alkalinity of softened water}\} - \{\text{source water alkalinity}\} - \{\text{source water calcium hardness}\} + \{\text{estimated residual calcium hardness of softened water}\}$
Excess Lime: For waters with high calcium, high magnesium, and carbonate hardness; process may be one or two stages	**Lime addition for softening:** $CaO = \{\text{carbonic acid concentration}\} + \{\text{total alkalinity}\} + \{\text{magnesium hardness}\} + \{\text{excess lime dose}\}$ **Soda ash addition for softening:** $Na_2CO_3 = \text{none}$ **Carbon dioxide for pH adjustment after softening:** $CO_2 = \{\text{source water alkalinity}\} - \{\text{source water total hardness}\} - \{\text{excess lime dose}\} + \{\text{estimated residual calcium hardness of softened water}\} + 2\{\text{excess lime dose}\} + \{\text{estimated residual magnesium hardness of softened water}\}$

* All quantities are expressed as mg/L as CaCO3

Figure by MIT OCW. Adapted from: MWH, J. C. Crittenden, R. R. Trussell, D. W. Hand, K. J. Howe, and G. Tchobanoglous. *Water Treatment: Principles and Design.* 2nd ed. Hoboken, NJ: John Wiley & Sons, 2005, pp. 1610-1611.

Fig 15

Single stage lime, what is it that we are adding? We are adding enough such that the H_2CO_3 is removed and then the calcium carbonate or calcium associated with the carbonate hardness. We are just adding that for just removing calcium, do I need to add Na_2CO_3? No, why is this? Because all of the calcium is associated with CO_3^{2-} or HCO_3^- so, I do not need to add any source of CO_3^{2-}. That is something to keep in mind so let me just move on, we will cover this tables later.

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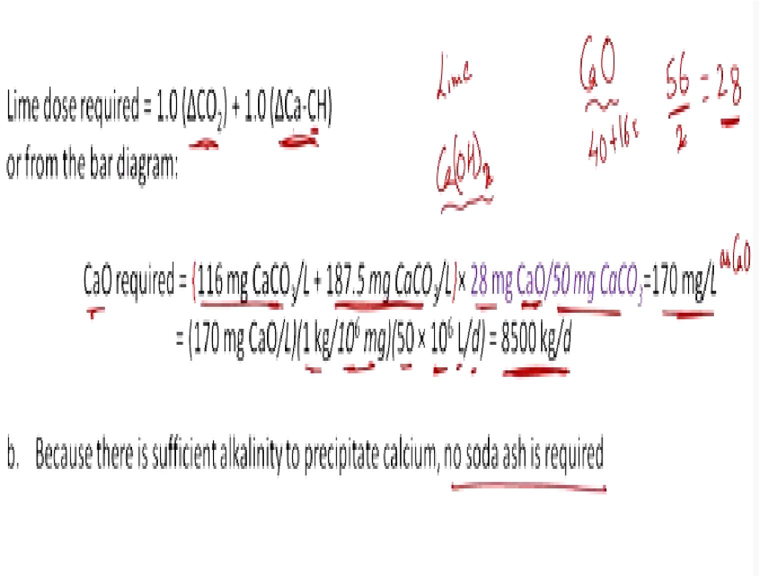

Lime dose required = 1.0 (ΔCO_2) + 1.0 (ΔCa-CH)

or from the bar diagram:

Lime

$Ca(OH)_2$

CaO

40+16

$\frac{56}{2} = 28$

CaO required = (116 mg $CaCO_3$/L + 187.5 mg $CaCO_3$/L) × 28 mg CaO/50 mg $CaCO_3$ = 170 mg/L as CaO

= (170 mg CaO/L)(1 kg/10^6 mg)(50 × 10^6 L/d) = 8500 kg/d

b. Because there is sufficient alkalinity to precipitate calcium, no soda ash is required

Fig 16

Lime dose required is carbon dioxide and one for this particular case of calcium hardness associated with the carbonate. From the diagram we can look at this so express as $CaCO_3$, we have this from the diagram carbon di oxide concentration or H_2CO_3 concentration and the calcium carbonate hardness or the calcium concentration. And then looks like in the question they were asking is about CaO not slaked lime. That is why to be relatively sure.

We are calculating it in terms of CaO. Equivalents of Ca^{2+} and O^{2-}, so 56 by 2 that will be equal to 28. Calcium is 40 oxygen is 16 so that is equal to 56, molecular weight by 2 the valency so that is why equivalent weight is 28. Equivalent weight of $CaCO_3$ is 50 milligram per liter so now I will get the units in terms of as CaO.

That is why CaO, so that is one aspect lime traditionally, slaked lime is $Ca(OH)_2$. But in India, they use it interchangeably you can look at the question in detail when you do that. If I wanted for 50 MLD though 50 million is 10 power 6 liters per day. I may also know 1 kg per 10 power 6 milligrams transforming the units. In one day, it will lead 8500 kgs per day looks like I am overshooting the time but let me finish this question and we will end it here.

Because there is sufficient alkalinity to precipitate calcium as I mentioned, no soda ash is required.

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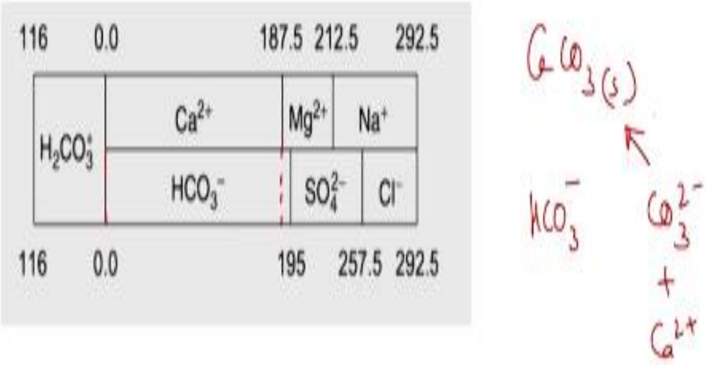

Fig 17

That is what we see here, everything is associated with HCO_3^-, only thing I need to do is to precipitate it $CaCO_3$ solid, I just need to change the pH so that HCO_3^- now becomes CO_3^{2-}. And this 2- will react with the calcium and it will form the precipitate. That is thing that is why we do not need to add soda.

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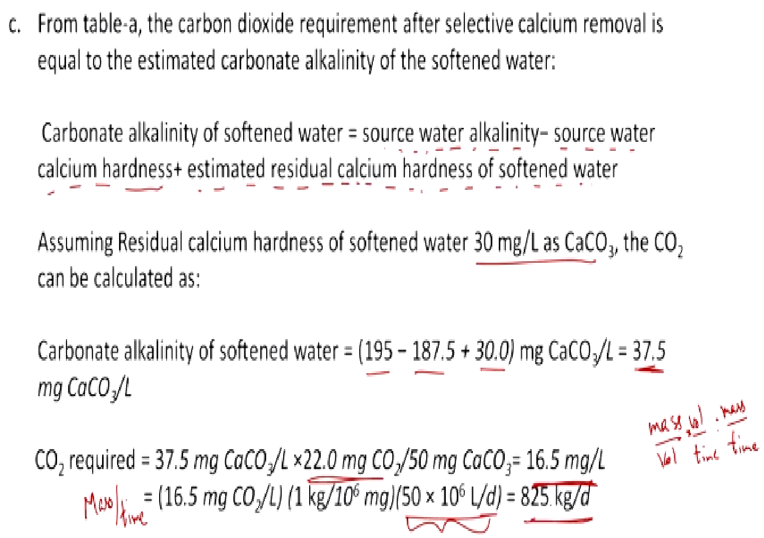

c. From table-a, the carbon dioxide requirement after selective calcium removal is equal to the estimated carbonate alkalinity of the softened water:

Carbonate alkalinity of softened water = source water alkalinity− source water calcium hardness+ estimated residual calcium hardness of softened water

Assuming Residual calcium hardness of softened water 30 mg/L as $CaCO_3$, the CO_2 can be calculated as:

Carbonate alkalinity of softened water = (195 − 187.5 + 30.0) mg $CaCO_3$/L = 37.5 mg $CaCO_3$/L

CO_2 required = 37.5 mg $CaCO_3$/L ×22.0 mg CO_2/50 mg $CaCO_3$= 16.5 mg/L

$\frac{\text{mass}}{\text{vol}} \cdot \frac{\text{vol}}{\text{time}} \cdot \frac{\text{mass}}{\text{time}}$

Mass/time = (16.5 mg CO_2/L) (1 kg/10^6 mg)(50 × 10^6 L/d) = 825 kg/d

Fig 18

What is the carbon dioxide required after certain to calcium removal? It is equal to the estimated carbon alkalinity of the carbonate alkalinity of the softened water. Simple exercise I will skim through this so carbonate alkalinity of softened to water after softening is equal to source water alkalinity minus source water calcium hardness. Because I am removing that plus estimated residual calcium hardness of softened water.

It is pretty straight forward here so it is not assuming residual calcium hardness is given as 30 milligram per liter. From that the equivalents can be straight forward calculated this is the alkalinity this is the calcium hardness that was removed, this is the excess and that is why we have the need for carbon dioxide here to be 37.5. But here the units are expressed as $CaCO_3$ here, we are going to change the unit using the equivalents.

And then we are going to get this particular case of 16 milligram per liter. Let me move on and then 50 MLD mass required will be this is the concentration, this is mass per time, how much is the mass per time? Here I have mass per volume but I need it in mass per time, how do I do that? Multiply it with volume per time. But what is volume per time, the flow rate that is what we are multiplying it with here and we are getting 825 kgs per day is required.

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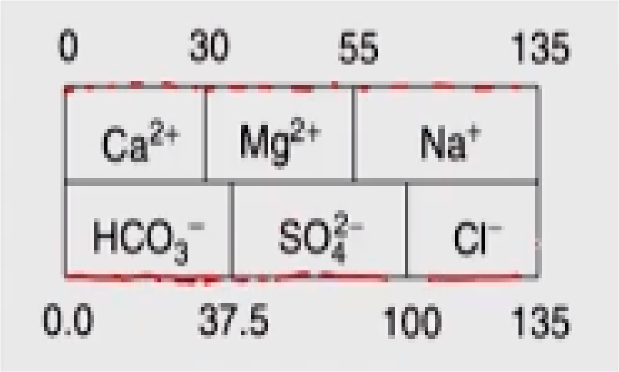

Fig 19

And the final bar chart, so this is the residual calcium, magnesium we never removed sodium too we never removed. After bubbling in your particular carbon dioxide or residual this thing carbon dioxide requirement it is 37.5. That is 37.5 and SO_4^{2-} and Cl^- we never touched and so this is the final bar chart that represents the constituents there.

With that I will end today's session, in the next session we will wrap up lime softening, there are configuration we need to look at. Then we will move on to one of the aspects that is quite regularly used which is adsorption but that I will leave for the next session, thank you.