Water and Waste Water Treatment
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Module No # 10
Lecture No # 46
Hardness – II

Hello everyone, welcome back to the latest lecture session. We started discussing about hard water; Water that cause issue when we were trying to use it. Boilers; Scaling is the primary issue, when we are taking about scaling, we are talking about precipitation of calcium carbonate or magnesium. When I am concerned about removing these aspects, we are typically going to add lime or soda, so I am going to soften the water by adding lime or soda.

That is why we refer to the process as Lime-Soda softening. In this aspect, we looked at some basics because we are going to use them later.

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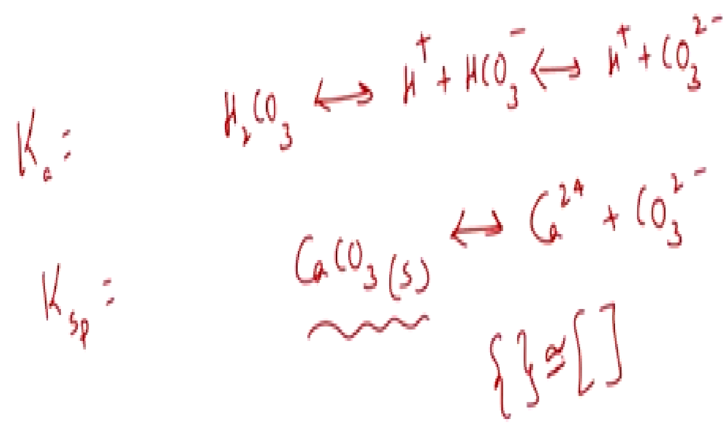

Fig 1

We know that acids can dissociate to form bases there by releasing H+ and we know that the systems can be in equilibrium. And we also know that different products or different solids can be formed. And we also saw how to write the equilibrium constant for different equations. For example, in this context (calcium carbonate equation), we saw that activity of the relevant solid is 1 assuming that it is a pure solid and that is why we do not use that in the equilibrium constant.

And in this class, we are also going to use concentration instead of activity assuming that the ionic strength is relatively less, this is what we covered in the previous session. What else we are going to look at?

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Description	Hardness range (mg/L as $CaCO_3$)
Extremely soft	0 - 50
Very soft	50 100
Moderately hard	100 – 150
Hard	150 - 300
Very hard	> 300

Fig 2

What class is it when we consider the water has hard? When the water is 100 to 150 milligram per liter that is when we are concerned with hardness. And in general, I think in Roorkee, we looked at the relevant values, it was 250. It is typically hard and different deposits upstream above Haridwar or extreme of Haridwar compared to the flow of the Ganga canal, the water can be extremely or very hard.

We see that hardness is an issue in most places and I think in the south, that at least depend upon where you are, the hardness is remarkably high.

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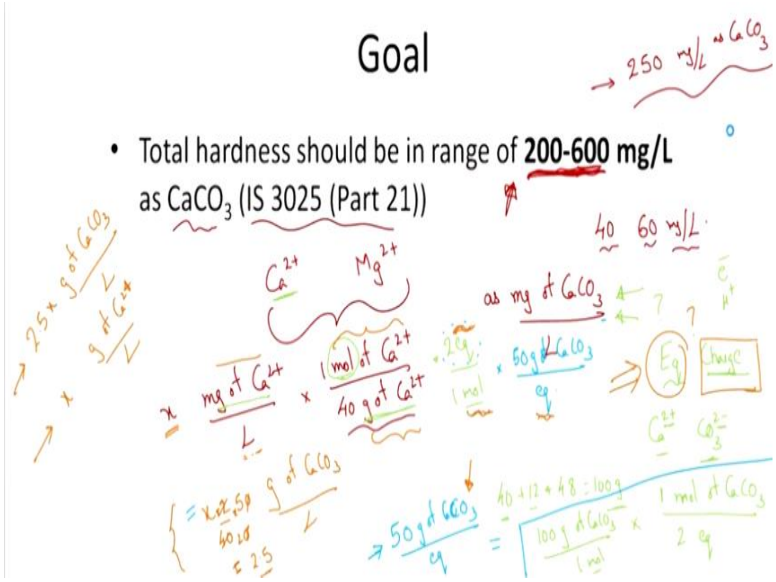

Fig 3

With respect to drinking water what does it say? At least the Indian standard says that 200 to 600 milligram per liter expressed as $CaCO_3$. Even here note that the units are expressed as $CaCO_3$, so this is one aspect I will discuss, let me come back to that. Here we see that first our Indian standards pretty lacks in this case but in general if water hardness is greater than 250 milligram per liter as $CaCO_3$,

You are going to have issues, so maybe for drinking too it is not good, looking at this 600 tedious too. In general, 250 is what you should aim for but this is what the law says that is acceptable. But that is some background for you, for example in the US I think it is around 40 or 60 mg/L typically, that will give an idea about the hardness that people try to achieve in different countries.

In this context, we started coming across some terms, what is this? Hardness or this unit milligram per liter as $CaCO_3$, I am assuming we might have discussed this in this course elsewhere but nowhere it is more relevant than when we discuss hardness. Here I am talking about hardness due to calcium, hardness due to magnesium. I cannot always keep talking about what is the concentration of calcium, magnesium when I talk to some person about the hardness of water.

There has to be some metric or some equivalents which will let me capture the hardness that will be caused by these 2 particular bivalent cations. That which is often used as expressing in the units as milligrams of $CaCO_3$ per liter, milligram per liter as CaCO3. What is the approach here? In general, I have x milligrams of Ca^{2+} per liter.

If I divide by the molecular weight, what will I get? I will get the moles, I know for one mole of Ca^{2+}, I think 40 grams of Ca^{2+} that is the relationship, 40 grams per 1 mole, so why did I write this here? In general, I am not great at dividing multiplying. But I always look at the units if I want the units of moles per liter, I need to remove this mass of calcium.

For that I need to have mass of calcium in the denominator so that is how I write it in this way. Now I have the units in terms of moles per liter of calcium but I am not concerned about having or understanding just moles of calcium and moles of magnesium. I want to have some equivalent which will give me an idea about all the calcium and magnesium present there.

That is as I mentioned typically you express in terms of $CaCO_3$, so how do I go from moles of calcium to milligram per liter of $CaCO_3$? Here the key is to understand that equivalents in this context are with respect to this charge, equivalents can be with respect to the electrons being transferred and H^+ being transferred or with respect to charge or the valency. In this case it is the charge, so Ca^{2+} as you can see it will have 2 equivalents per 1 mole.

For 1 mole of Ca^{2+}, 2+ charge so 2 equivalents will be contributed, so now I have the units in terms of equivalents. It is no more in terms of Ca^{2+} or any such aspects it is just 2 equivalents per liter, why? These moles per liter and moles per liter will cancel out. But still how do I come to as $CaCO_3$? Here the aspect to notice is that when I add CaCO3 to water it will become either Ca^{2+} or CO_3^{2-}.

If I am concerned with positive charge, 2 equivalents. If I am concerned with negative charge, 2 equivalents. Even here for 1 mole of $CaCO_3$, 2 equivalents will be given out. Here we are talking about the charge and 1 mole, looking at $CaCO_3$, 40 + 12 C calcium and carbon and 16 into 3 is 48, so that is 100 g, that is the molecular weight, so for 100 grams of $CaCO_3$ it is 1 mole.

This is where we are so if I look at this what will this turn out to be? I am going to cancel out moles and moles so I will have 50 grams of $CaCO_3$ per equivalent, so this is called the equivalent weight. that is something you have to keep in mind. Now I have this in equivalents and I want the units in terms of $CaCO_3$ from here or using this information I can now transform this equivalent and get 2 grams of $CaCO_3$.

What do I need to do? I will need to multiply by 50 grams of CaCO3 per equivalent. Now what are the units in terms of? Let us just check so as we see this mass term and this mass term cancel out and then this mole term this mole term cancels out, equivalents cancel out the mass of calcium you can only cancel out with mass of calcium. And moles of calcium only for moles of calcium but equivalents here it is with respect to charge so equivalents and you can cancel out here.

And then here what are the units finally it is as grams of $CaCO_3$ or mass of $CaCO_3$ per liter which is always here. Now we see how we can transform the units from 1 particular mass units of calcium to express them in terms of $CaCO_3$ let us just see what it entails. We started with X so it is 2 by 40 into 2 by 40 into 50. This is for calcium though keep that in mind. What do we have here? This is 20, so 2.5. hopefully I made it.

For x grams of Ca^{2+} per liter, it will turn to be that I need to add 2.5 times x grams of $CaCO_3$. Or when I add 2.5 x grams of $CaCO_3$ per liter, I will end up getting x grams of Ca^{2+} per liter. In essence I am expressing the units of Ca^{2+} in how much $CaCO_3$ equivalents it is going to be. That is the relevant aspect, so if I made any calculation errors here that you can look it up but you see the approach same case you do that for magnesium.

2 or 3 aspects to take away, here the equivalent weight of $CaCO_3$ is 50 grams so, that is something to keep in mind. The equivalents we are talking about are with respect to the charge. That is something that you will always have to keep in mind so we are going to look at this or use this quite often as you can see everything in this context of hardness or such is expressed as $CaCO_3$, that is something to keep in mind. That is enough discussion about changing from 1 unit to the other.

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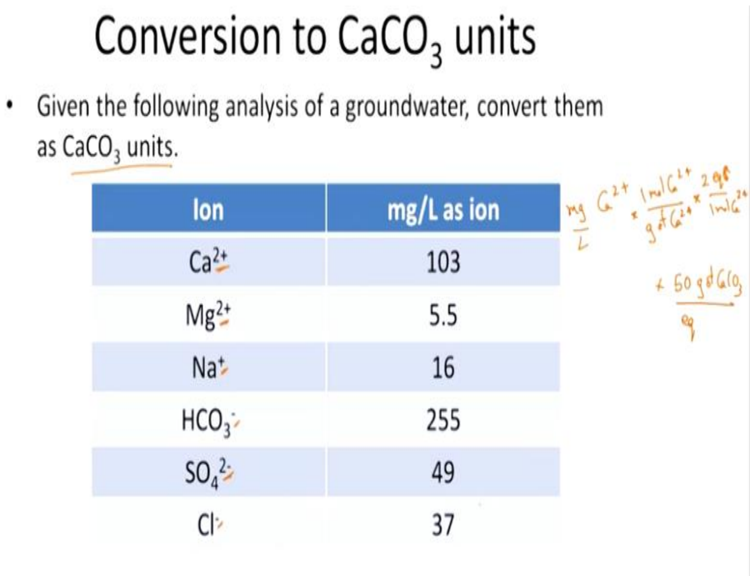

Fig 4

Conversion to $CaCO_3$ units, we have an example here. We have different ions here and we want to convert them to as $CaCO_3$ units. What is the approach everywhere? We just looked at that so if we have milligram per liter of a particular compound Ca^{2+}, first I am going to divide it by the molecular weight, 1 mole of Ca^{2+} and per grams of Ca^{2+}, then I will get it in moles and then I know that it is 2 equivalents per 1 mole of Ca^{2+}, why is that?

Because it is the charge here it is 2+. Now I have it in terms of equivalents then if I multiply that by 50 which is equivalent weight 50 grams of $CaCO_3$ per equivalent. That is when I will get the units in terms of as $CaCO_3$ it will be the same case with everything else or all the other ions. Only thing we are concerned about is charge, here it is 2+ and here it is 1+ (Na).

This means 1 equivalent per 1 mole and here it is negative, only one so 1 equivalent per mole here it is, 2 equivalents per mole, 1 equivalent per mole and also the relevant mass is given out here. What we have?

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- $\text{number of milli moles} = \frac{\text{given concentration}}{\text{molar mass}}$
- $\text{number of milli equivalents} = \text{number of milli moles} \times \text{valency}$
- $\frac{mg}{L} \text{ as } CaCO_3 = \text{number of milli equivalents} \times \text{equivalent weight of } CaCO_3$
- $\text{equivalent weight of } CaCO_3 = \frac{\text{molecular weight of } CaCO_3}{\text{valency}} = \frac{100}{2} = 50\text{ g}$

Fig 5

We understood in detail but so that it is presented in a better manner we are going to look at it. Number of milli moles equal to given concentration by molar mass but I am not always comfortable writing in this way and understanding it, I at least have learnt that the way that I write here is easier for me at least because then I can see what to cancel out or what to divide or multiple with.

That is something for you to consider if you are more comfortable with this approach that is fine. Number of millimoles; Given mass concentration by molar mass given concentration if it is in mass. Number of milli equivalents is equal to number of millimoles into valency. Milligram per liter as CaCO3 will be equal to milli equivalents into equivalent weight of $CaCO_3$.

And equivalent weight of the $CaCO_3$ is the molecular weight which is 100 divided by the valency depending on the charge whether it is positive or negative Ca^{2+} and CO_3^{2-} both 2, so that is why 2 here. That is 50 grams. 50 grams is the equivalents or the way I write it is 50 grams of $CaCO_3$, always write the compound per equivalent, that is something to keep in mind.

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Conversion to $CaCO_3$ units

Ion	mg/L as ion	Molar mass (g)	valency	milli Molar units	milli equivalent units	mg/L as $CaCO_3$
Ca^{2+}	103	40	2	2.575	5.15	257.5
Mg^{2+}	5.5	24	2	0.229	0.458	23
Na^{+}	16	23	1	0.695	0.695	34.78
HCO_3^{-}	255	61	1	4.180	4.180	209
SO_4^{2-}	49	96	2	0.510	1.02	51
Cl^{-}	37	35.5	1	1.042	1.042	52.1

$$103 \frac{mg\ of\ Ca^{2+}}{L} \times \frac{1\ mol\ of\ Ca^{2+}}{40\ g\ of\ Ca^{2+}} \times \frac{2\ eq}{1\ mol\ of\ Ca^{2+}} \times \frac{50\ g\ of\ CaCO_3}{eq} =$$

Fig 6

What do we see? Here we have the molar mass 40, 24, 23, 61, 96 and 35.5 then the valency 2 charge thus 2, 1 charge thus 1 and so on. Here we are concerned with the magnitude not the positive or negative. Milli molar units, we know how to do that, divided by the molecular weight. You can get the units in terms of moles per liter.

That is something that we have and we already have the equivalents you will have to multiply that; This is the approach that we talked about earlier and then you have it in equivalents. And equivalents, you know that the equivalent weight of $CaCO_3$ is 50 grams per equivalent so I will have to multiply it with 50 and what do I get? I will get this. Let me write it down at the bottom for calcium.

I have milligram of Ca^{2+} per liter, how many milligrams? 103. First I will need to convert into moles. If I want moles in the numerator, moles of Ca^{2+}, I will write that so I see I need to cancel out the mass. I will have to write the mass so mass will have to be the molecular weight which will give me the relationship between moles and the mass. I see that it is 40 grams of Ca^{2+} will be required to give 1 mole of Ca^{2+}.

And I know that I need to convert it into equivalents, so how do I do that? I see that Ca^{2+} has a charge of 2 so for 1 mole of Ca^{2+}, I know that I will have 2 equivalents, here obviously even though I do not write it down it is equivalents with respect to charge. And then I already know that 50 grams of CaCO3 will be required for 1 equivalent in terms of charge. And then I will get my answer so I think last time we saw that was around 2.5 times.

I think 103 to 2.5 so that is more or less it. In the same way you can calculate it for the different other compounds and you will get the relevant units expressed as $CaCO_3$. In general, may be SO_4^{2-}, for Cl^-, it does not make much sense to express them as CaCO3 but there is a reason why we do that? We can look at that later but for calcium magnesium and HCO_3^-, it makes much sense to express them as $CaCO_3$ or in equivalents of $CaCO_3$, so let us move on.

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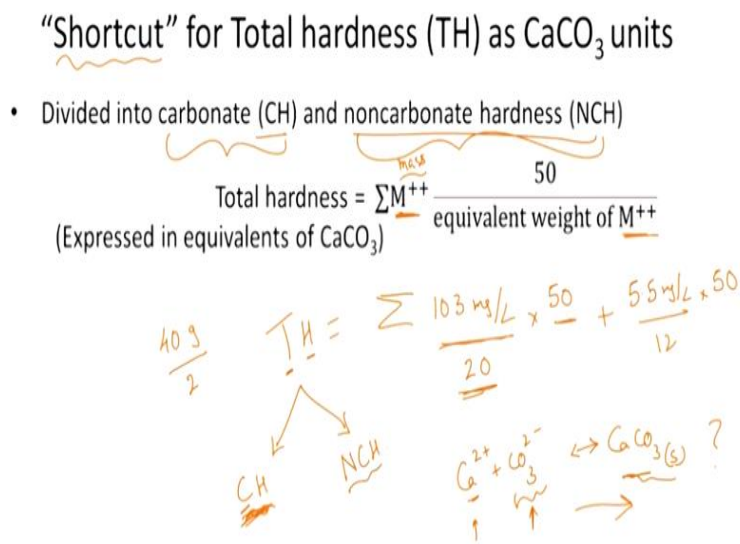

Fig 7

This is the shortcut, I typically do not like this because shortcuts, you need to mug stuff up. For total hardness as CaCO3, divided into the carbonate and hardness non-carbonate hardness, we will come back to that later. But what is the total hardness? It is equal to the sum of the bivalent concentration, this (M++) is the concentration of the bivalent cations into 50 which is the equivalent weight by equivalent weight of this bivalent cation.

For example, for Ca^{2+}, earlier equation, what it the hardness here? They want it in terms of as $CaCO_3$, how do I do that? Sum of Ca^{2+} concentration, I think 103 milligram per liter and equivalent weight of this Ca^{2+}, 40 grams is the molecular weight by 2 is with the valency that is going to be equal to by 20 into 50 is the equivalent weight of $CaCO_3$. It is more or less like for 103 milligram per liter, 20 equivalents for 50 equivalents how much?

That is how you do it. This is for calcium and for magnesium what is it like? We see it is 5.5 milligrams per liter by 24 by 2 that is 12 into 50 that will give us an idea about the relevant hardness. Here the units are in mass units, this is one reason why I do not like this way but that is something to keep in mind. This is the total hardness and what is this new term total hardness?

And why am I having to classify it further into this carbonate hardness and non-carbonate hardness? It depends on how easily you can remove it, so carbonate hardness, typically you can remove it or it is the hardness that can be removed if you are going to be able to heat of the system. This is just for classification purposes but we will see why it is relevant later. That which cannot be removed when you heat up the water you are going to call non-carbonate hardness.

This carbonate hardness is typically the one associated with magnesium typically and calcium too some of it. But we are saying carbonate hardness, I should explain it now. The carbonate hardness the concern is that as you saw earlier, one of the forms calcium precipitates out is $CaCO_3$. And what is this going to be dependent upon? If I have Ca^{2+}, how can I go from Ca^{2+} to $CaCO_3$?

What is the other compound that is missing? I need to add CO_3^{2-} or need to have CO_3^{2-}. if I have enough CO_3^{2-} or Ca^{2+} concentration, I can go to the right and precipitate out the solid. If I have enough carbonates, that is relatively easier to remove maybe that is one reason why they call it as carbonate hardness.

But in general, the textbook definition is that if you heat up the water and you can precipitate out certain forms of carbonate or magnesium that which precipitates out is called carbonate hardness. That which does not precipitate out is called non-carbonate hardness that is the relevant definition or understanding.

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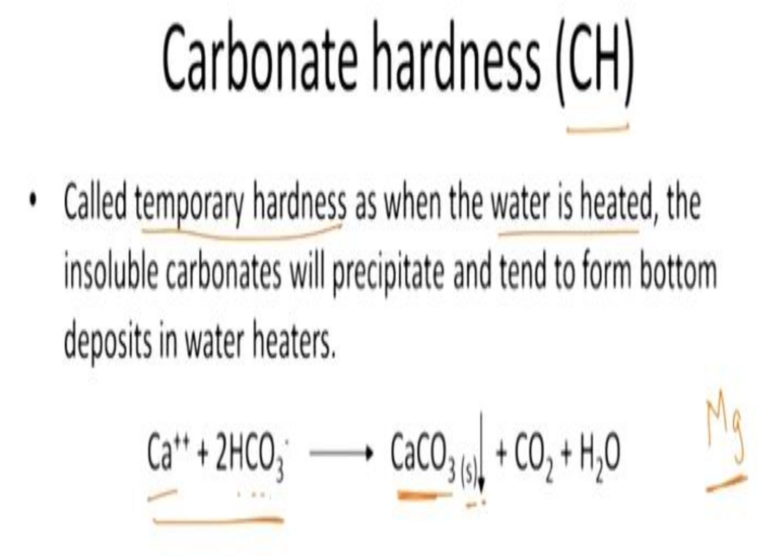

Fig 8

Carbonate hardness which is also called temporary hardness because when the water is heated the insoluble carbonates will precipitates and tend to form deposits in the water heaters this is one particular way that it occurs. But Ca^{2+} + HCO_3^-, but in effect it will have to be CO_3^{2-}, will go to $CaCO_3$ the solid, this is indicating that the solid is precipitating, that is something to keep in mind so this is for carbonate hardness but in general also you will have some due to magnesium.

Especially when you are concerned about precipitation in boilers, this is the carbonate hardness.

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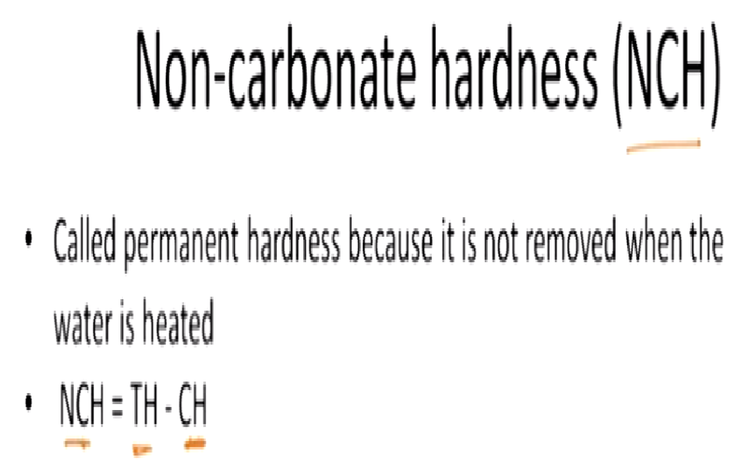

Fig 9

Non-carbonate hardness, if there is a total hardness and if you can measure what is carbonate hardness, the non-carbonate hardness is going to be the remaining part, so that is pretty much it.

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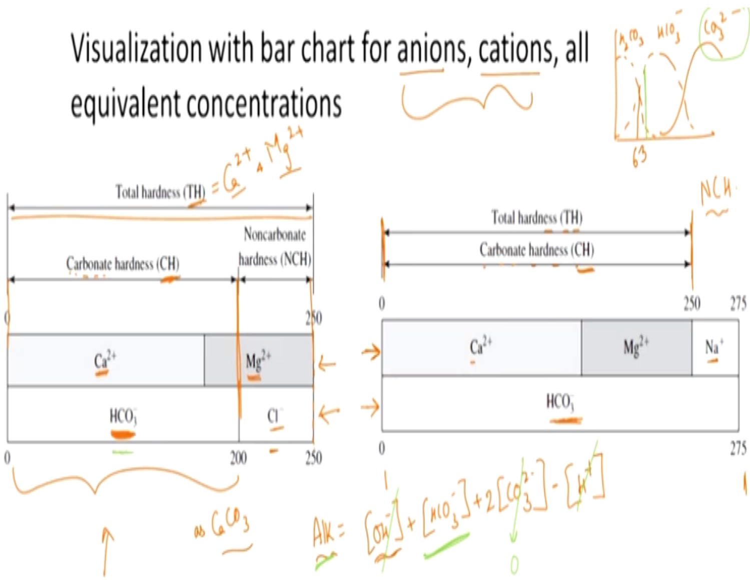

Fig 10

Let us visualize it and understand, this is the key aspect so I have different anions and cations. In this aspect if I want to use or present them in bar chart, I cannot just have milligrams of calcium, milligrams of Cl-, then there is no way to compare the equivalents so here we are talking about charge and in water always you are going to have charge neutrality. As in all the cations present are going to be equal to the equivalent concentrations of all the anions present, equivalents of all the cations equal to the equivalents of all the anions.

That is the charge balance, there will never be charge imbalance. Here we are going to have to look at equivalent units and that is one reason to why we will express units in terms of as $CaCO_3$. Now you understand why even Cl- we express as $CaCO_3$, that is a different aspect. In this figure, what do we see? We see that the relevant cations or positively charged anions are only due to calcium and magnesium.

And relevant anions or the negative charge is due to bicarbonate and Cl-. Obviously as I mentioned charge balance has to exist that is why the sum of the cations is equal to the sum of the anions. That is something to keep in mind and next aspect what do we know the total hardness to be? It is equal to the sum of all the bivalent cations. In general, we are concerned about calcium and magnesium so Ca^{2+} + Mg^{2+}.

That is why we have total hardness and compassing the concentration of Ca^{2+} and Mg^{2+}. Next what is this carbonate hardness about? In general, it will depend upon the amount of CO_3^{2-} present because I told you about form it will precipitate out when it is heated. In general, carbonate hardness it depends upon the amount of carbonate present.

Carbonate hardness will be equal to HCO_3^- present. That is what you see here carbonate hardness and the remaining part is going to be the one associated with non-carbonate hardness. Carbonate hardness, when we are measuring, we are going to see to it that we look at the carbonates that are present typically or the alkalinity at pH 7. We will come back to the alkalinity. In the second figure for a different water here we have other cations and but only one anion.

Rarely the case, these are all hypothetical cases and one aspect to keep in mind that in general in water you will never have the data for all the cations and anions that is going to be impossible to measure, that is something I wanted to mention. Here we have charge neutrality in this hypothetical water, we have all the cation equivalent concentration being equal to the sum of the equivalent anion concentrations.

Total hardness is now the sum of calcium and magnesium, so that is why you see this and carbonate hardness is the one associated with HCO_3^-. But the carbonate hardness cannot be higher than total hardness it cannot just blindly be HCO_3^-. Here because alkalinity or the carbonates are higher than the total hardness.

The concentration of the carbonates or the bicarbonates are higher than the total hardness we are going to say that carbonate hardness is equal to total hardness and there is no non-carbonate hardness, that is something to keep in mind so here when understanding the amount of carbonate hardness what am I concerned with I am concerned with the amount of carbonates present in the form of HCO_3- or CO_3^{2-}.

That is something to keep in mind, if it is less than then carbonate hardness will be equal to the alkalinity or the bicarbonate. Here I am using the term alkalinity I know we discussed this earlier, alkalinity is the acid neutralizing capacity. If we look at standard methods it will tell you about the amount of acid required to bring down the pH to around 4.3 or 4.5. I will have to add acid and see how much acid the system or the water will consume before the pH comes to 4.3 or 4.5.

What will it consume? it will consume H+, what can it be neutralized by? It can be neutralized by those bases that are in the particular system. Typically, we have only the carbonate system so the other bases are OH-, carbonate system bases HCO_3^- and CO_3^{2-}. Since CO_3^{2-} can neutralize 2H+, we will have 2 equivalents here and minus H+, so this is the equation for alkalinity but knowing that your particular system for carbonate alkalinity, I think we discussed this earlier, it is going to be something like this.

This is H_2CO_3, this is HCO_3^- and this is CO_3^{2-}, as you can see at around pH7 as I told you pKa is 6.3 and at around or near the neutral pH of water which is pH7, you can see that there is no CO_3^2, it is almost 0. And at pH7 OH- and H+ cancel out, in effect almost all the alkalinity when the pH is near neutral is equivalent to the concentration HCO 3-, that is why I was using the terms interchangeably when I talked about HCO_3^- or alkalinity, this is something we will look at in the next slide.

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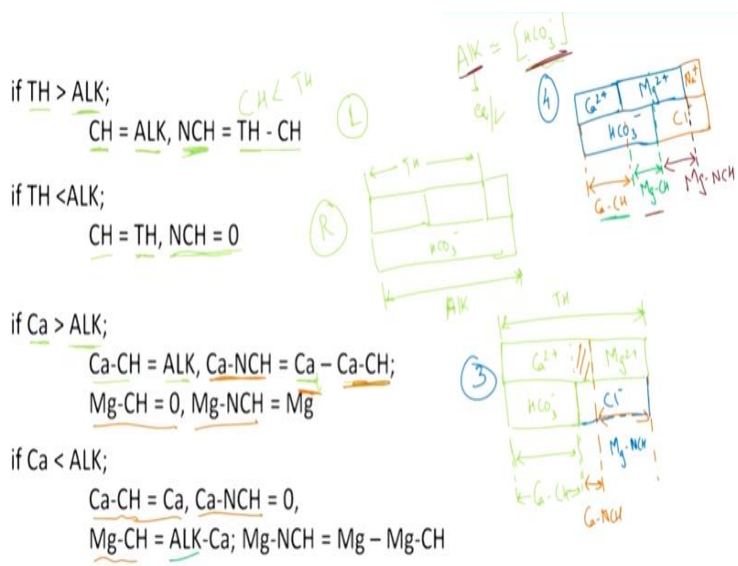

Fig 11

Let us just understand the relevant aspect if total hardness calcium and magnesium is greater than alkalinity. In general, you know the alkalinity equation but you also know that at natural pH for general water systems, alkalinity and concentration or alkalinity which is in equivalents per liter will equal to the concentration of HCO_3^-. We saw that why that is the case in the previous slide.

If total hardness is greater than alkalinity then carbonate hardness will come into the picture and that is going to be less than the total hardness. what I have? Carbonate hardness will be equal to the alkalinity. And non-carbonate hardness will be equal to the difference between total hardness and carbonate hardness and that is the same thing that we saw out here.

And let us move on and if total hardness is less than alkalinity, this is relevant to the second picture that we saw there. We see that carbonate hardness will be equal to total hardness and non-carbonate hardness will be equal to 0. This was the picture where we had some Ca 2+ some Mg 2+ some Na+ and everything else was HCO_3^-, total hardness is this and alkalinity which is in effect HCO_3^- concentration which was given in the previous slide was equal to this.

Obviously carbonate hardness cannot be greater than your total hardness, so that is why total hardness equal to the carbonate hardness and non-carbonate hardness is 0. That is something to keep in mind and what is the case if calcium is greater than alkalinity. We have HCO_3^- then here now we were looking at carbonate hardness and non-carbonate hardness. Now we are going to start looking at calcium due to carbonate hardness or calcium non-carbonate hardness, magnesium carbonate hardness, magnesium non-carbonate hardness.

First why do I need to understand this or even the previous aspects? Because the way that I am going to remove calcium or magnesium depends upon the type of ion that it is associated with when we talk about hardness. Is it carbonate or non-carbonate hardness that is why I need to be able to understand whether it is carbonate or non-carbonate hardness.

If calcium is greater than alkalinity, what will we have? Calcium carbonate hardness will be equal to alkalinity and calcium non-carbonate hardness will be equal to the total calcium concentration let me say Ca total minus the calcium carbonate hardness. Let me draw a figure that maybe will help in this manner, so the Ca^{2+} itself is greater than and this is Ca^{2+} and this is Mg^{2+}.

For this the picture, you can look at the previous slide, picture one on the left and this is the picture on the right. For this I am just trying to draw an approximate figure and here we know that calcium itself is greater than alkalinity, alkalinity I am assuming is equal to HCO_3^-. Here this is the total hardness that is something that we know but here we see that calcium itself is greater than alkalinity.

What is the calcium carbonate hardness? That is this part. That is the calcium carbonate hardness so that is this part and what else is left. this other part of the calcium will be calcium due to the non-carbonate hardness, that is what we have. Calcium due to non-carbonate hardness is the total calcium minus calcium due to the carbonate hardness. And is magnesium associated with any carbonate or bicarbonate? Nothing, so magnesium carbonate hardness is 0.

And magnesium non-carbonate hardness will be all equal to the magnesium non-carbonate hardness. This can be due to maybe Cl^-, for ease I am just going to use Cl^- here. That is magnesium non-carbonate hardness so that is the relevant figure here and what is the other figure that we have? If calcium is less than alkalinity, so this is the third case.

This is calcium and this is magnesium, Ca^{2+} and Mg^{2+}. A lot of questions with respect to stoichiometry, but we are just understanding the system. And what do we have here? Calcium concentration is itself is less than alkalinity. HCO_3^- is here and maybe let me just for the sake of it add here Na+ and the other part for charge neutrality, it is Cl^-.

What is this case? Calcium is less than alkalinity so the calcium carbonate hardness will be equal to the total calcium concentration, that is what you see. And do we presume that there is any calcium non-carbonate hardness? No, it is all used up. It is only due to carbonate hardness and then we come to magnesium carbonate hardness. What is this magnesium carbonate hardness? This is this other part that is left out here.

This is this part we still have some alkalinity left or carbonate bicarbonate left, here I have magnesium due to the carbonate hardness that is equal to the what now? Alkalinity minus the calcium or the calcium carbonate hardness, so that is what we have. And the other part is going to be equal to magnesium non-carbonate hardness, how do I get that?

This is equal to the magnesium non-carbonate hardness how do I get that? Magnesium concentration minus magnesium carbonate hardness, I will get the magnesium non-carbonate hardness. This is how you associate it, typically you associate calcium with the bi-carbonate or the alkalinity and then if anything is left over from alkalinity or the bicarbonate that you are going to use to assign to magnesium.

First calcium and then magnesium, so HCO_3^- and then the relevant anions but typically when we are talking about alkalinity, we saw why we typically refer to it as HCO_3^-. With that I will end this session and in the next session we will look at the relevant aspects about how to remove this calcium and magnesium. But at least now that you have calcium with respect to carbonate hardness and non-carbonate.

And same case with magnesium with respect to carbonate and non-carbonate and we saw the scenarios. Without extending it further, I am going to end this session.