Water and Waste Water Treatment
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Module No # 09
Lecture No # 45
Hardness – I

Hello everyone, welcome back to the latest lecture session. We are going to talk about a new aspect today. It is about lime soda softening, so let us dig in.

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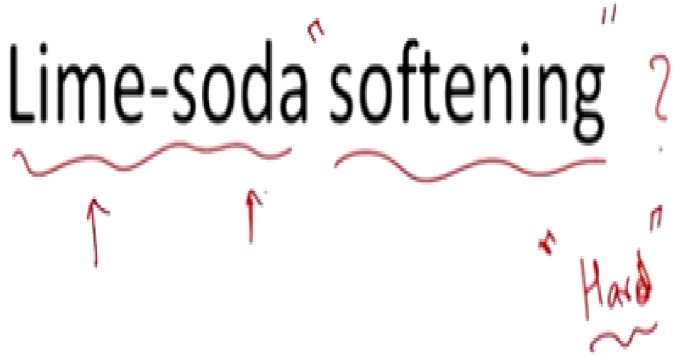

Lime-soda softening

Fig 1

I am assuming most people would have had at least some inkling about what we are going to talk about today; lime-soda. And then we are going to use that to soften the water. First what is this softening the water about? That means the water is classified as hard for some reason. When do we classify this water as hard? And how do we soften it using lime and soda? That is the primary aspect we are going to look at in this session.

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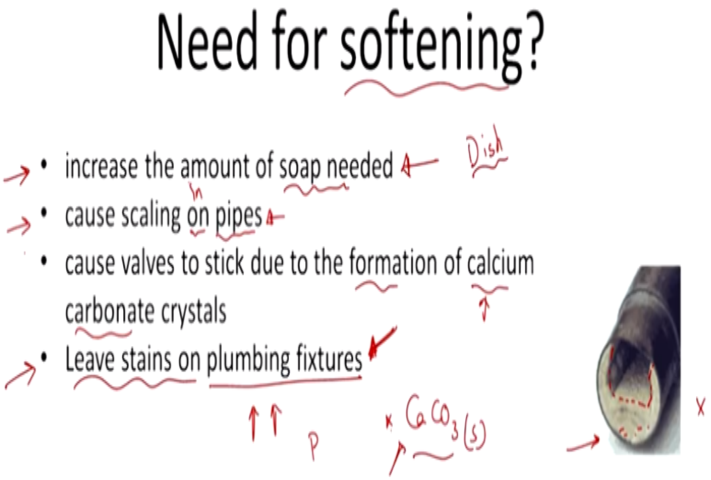

Need for softening?

- increase the amount of soap needed
- cause scaling on pipes
- cause valves to stick due to the formation of calcium carbonate crystals
- Leave stains on plumbing fixtures

Fig 2

Why do we need softening, what is this issue with this so-called hard water? If I have hard water, it increases the amount of soap needed. Those who are regularly using hard water will not be able to see this difference. But in general, you have soap (negative charge), the kind of ions that create hardness (positively charged) typically bivalent and they form what is called scum, so whenever you use soap,

Enough lather does not form, that is one thing and this is seen quite often in Indian bathrooms. You see scaling on pipes, sometimes the pipes or even the taps they break off especially the cast iron or metal pipes, something that you see, causes walls to stick and walls that are not often used or maintained, they harden up and you cannot really use them, why is that?

You have calcium carbonate crystals preventing free moment of that particular wall. And this is pretty common in India; Staining of plumbing fixtures, in bathrooms especially we see at least in from where I come from, used to see this, not in Roorkee though. Water there is relatively hard compared to the water in Roorkee. And I used to see this kind of scale that is formed on the taps or along the walls where the water used to drip.

This is due to precipitation of calcium carbonate $CaCO_3$, the solid. I have a picture here, so here you see what happens to scaling inside pipes. This is the pipe and you see calcium carbonate over time precipitating out and you see the cross-section area available is remarkably less right now. This is something you do not want, now your pipes cannot carry water that it was designed to carry, the distribution network is going to fail.

Other than that, depending upon relevant hardening you can even have cracks in the relevant pipes. This is what you see, so I should have also had a picture about stains on the plumbing fixtures. But for quite a few people in India that is something they would have seen. I do not want to this to happen, either this (precipitation) to happen or not do I want these aspects to happen (points on Fig.1); Soap and also leave stains on plumbing fixtures.

For example, people with dishwashers would notice this acutely. Because you can measure the amount of anti-hardness or water softening agent you had. In dishwasher, typically you have a detergent that is added, you are trying to form some lather decrease the surface tension between your oily particles that are on your dirty plates.

But if you have water that has high hardness, for this action to occur you are going have requirement for a lot more detergent. To prevent that and also to prevent scaling within the dishwasher, what do you need to add? You need to add, sometimes they call this anti-scaling agent or softening agent, why is this? They do not want to have this precipitation of calcium carbonate occurring on or within the relevant dishwasher.

And also, they do not want this soap to be consumed. This is one major reason why we want to have softening.

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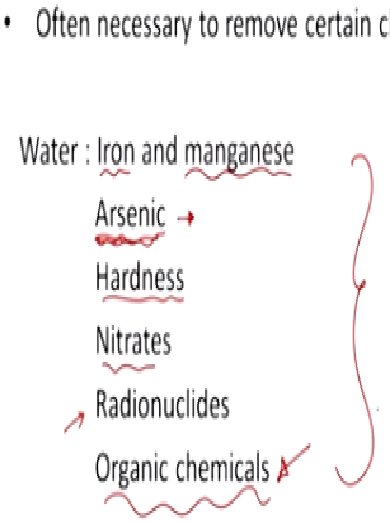

- Often necessary to remove certain chemicals form water and wastewater

Water : Iron and manganese

Arsenic

Hardness

Nitrates

Radionuclides

Organic chemicals

Fig 3

In general, in water and also waste water we need to remove certain chemicals, we looked at the general aspect. In water depending on where you are, you might need to typically remove these in India depending on where you are living, iron and magnesium will have to be removed that is relatively easily done with aeration step or an oxidation step. Arsenic carcinogenic and also non-carcinogenic adverse effects so the need for removal depends upon where you are living in India.

Hardness, quite a few places in India affected, nitrates too, radionuclides not very much, organic chemicals nowadays we see that the requirement to remove that is increasing day by day with different kinds of stresses on the surface water bodies.

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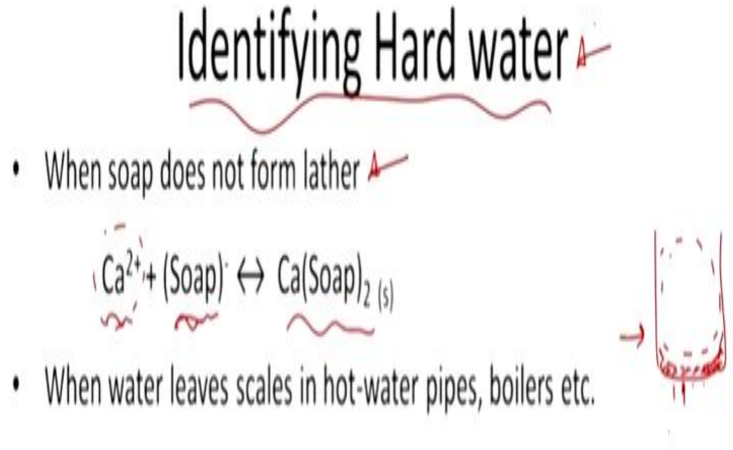

Identifying Hard water

- When soap does not form lather

$Ca^{2+} + (Soap)^{-} \leftrightarrow Ca(Soap)_{2\,(s)}$

- When water leaves scales in hot-water pipes, boilers etc.

Fig 4

And waste water, it can be any chemical especially if it is from an industry. But in general, we are concerned with metals and organic chemicals. For example, we have Patanjali nearby here and they have a thriving FMCG business out here and they are going to have organic chemicals in their waste waters, they need to be degraded. It depends upon the kind of waste water but in this course, we were looking at sewage water beds not industrial waste water.

That is something I wanted to point out. Hardness; If I want to identify hard water what are the 2 ways that we can typically do or understand? Soap you need a lot of soap to form lather, why is that? Calcium and soap you have this scum being formed (formula on Fig.4). And thus, enough soap is not available for use for decreasing the surface tension or such if I may say so.

Thus, you have to be able to add more soap than is necessary when there is little to no calcium or the relevant cation present. And another aspect that you would have seen is, I think I mentioned this earlier, we used to boil or maybe I am sure even now people boil it. Boil water in their homes for various reasons sizes either for bathing or for drinking water related disinfection. Then after sometime you would have seen scales being formed along the sides of the relevant container.

And you would see that over time a lot of energy has to be put in or lot relatively more energy has to be put into be able to cause the water to eat up by the same amount of temperature. For the same temperature change, you need to heat it up for a lot more times. You are putting in more energy per change in temperature, why is that? Because now you have these scales which are not great conducting agent of heat or not good conductors.

The water here experiences inefficient heating so that is something most people in India would have seen. Then you can say that your water is hard. As you can see in house hold applications and in industries too, you are going to see scaling and relevant issues or adverse effects in boilers, that is something to keep in mind. This is from just looking at the relevant surroundings where the water is used.

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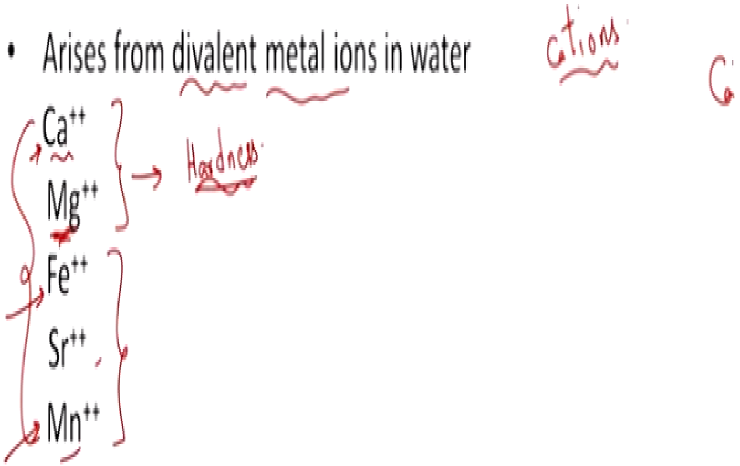

- Arises from divalent metal ions in water

Ca^{++}
Mg^{++}
Fe^{++}
Sr^{++}
Mn^{++}

Fig 5

As can be seen from the equation previously, typically we are talking about cations. And in general, we are concerned with the bivalent or divalent cations, typically they are the metal ions. And what are some of the probable metal ions? Calcium, magnesium, iron, manganese and maybe the strontium. But in general, not present a lot or at least iron and manganese are removed pretty well or in a different way by aeration.

But what is usually present because of the calcite or dolomite deposits in the ground water is calcium and magnesium. When I am talking about hardness I talk about calcium and magnesium that is something to keep in mind. It can be trivalent cations too but they rarely exist in our waters of interest if any, if they exist. And calcium and magnesium are the usually found bivalent cations that contribute to hardness in our water.

And where do they come from? They come from calcite and dolomite deposits in the subsurface. For example, I think I remember reading that calcite source of calcium accounts for almost 4% of the earth crusted. And dolomite maybe 2%, so you get an idea about the relative abundance, so ground water or water which has been in contact with these deposits will have considerable calcium being formed.

But if the relevant calcite is a solid, why will it dissolve and become or release these calcium ions or magnesium in the case of dolomite into the water, why or what happens? Let us look at that.

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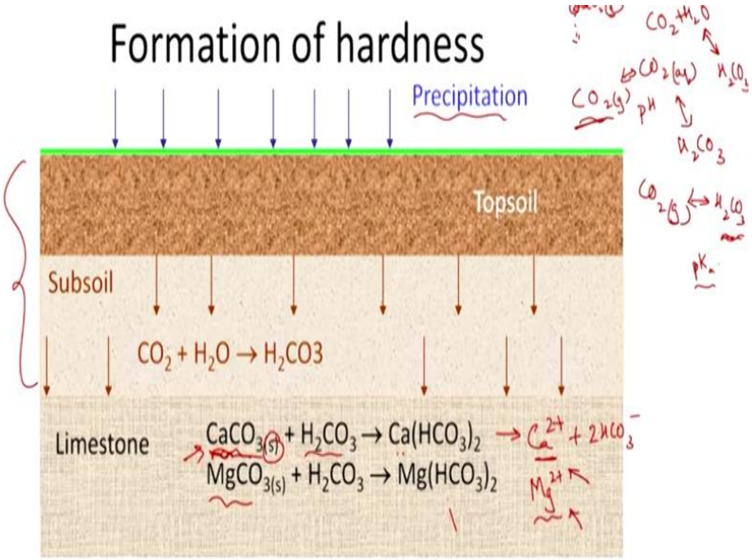

Formation of hardness

$CO_2 + H_2O \rightarrow H_2CO3$

$CaCO_{3(s)} + H_2CO_3 \rightarrow Ca(HCO_3)_2$

$MgCO_{3(s)} + H_2CO_3 \rightarrow Mg(HCO_3)_2$

Fig 6

I have precipitation and this is in contact with maybe carbon dioxide or any other gases in the atmosphere that can lead to decrease in pH. For example, carbon dioxide when it dissolves this is in the gaseous phase as rainwater droplet comes down carbon dioxide in the gaseous phase will dissolve. Carbon dioxide in the aqueous phase will be in equilibrium with H_2CO_3.

Or you can directly say that carbon dioxide in the gaseous phase will be in equilibrium with H_2CO_3. As you can see $CO_2 + H_2O \rightarrow H_2CO_3$, so this is what it typically exists as. H_2CO_3, an acid not a strong acid but the pKa is less than 7 and depending on the concentration, the pH of your rain water will be relatively less.

This is relatively acidified rain water will permeate through the soil. Some of it can be neutralized based on the different bases or such but some of it will react with these deposits, so if it reacts with calcite, it will see to it that the calcite dissolves. Earlier it is in the solid phase as these evident by this particular subscript, S for solid.

But after addition of this or coming in contact with slightly acidic water, it forms this particular compound meaning in effect it will say it will come to this (written along calcium equation on Fig.6) as you can see what was earlier as solid is now dissolved into the water. Thus, you can see that the relevant compounds calcium and magnesium are released into the, sub surface or ground water. You can see how that comes about, so here we talked about carbon dioxide as one aspect.

But there will be other gases that can decrease your particular pH of the rainwater droplet leading to dissolution of your particular deposits, that is one aspect so here we see calcium and magnesium being released into the subsurface and increasing the hardness.

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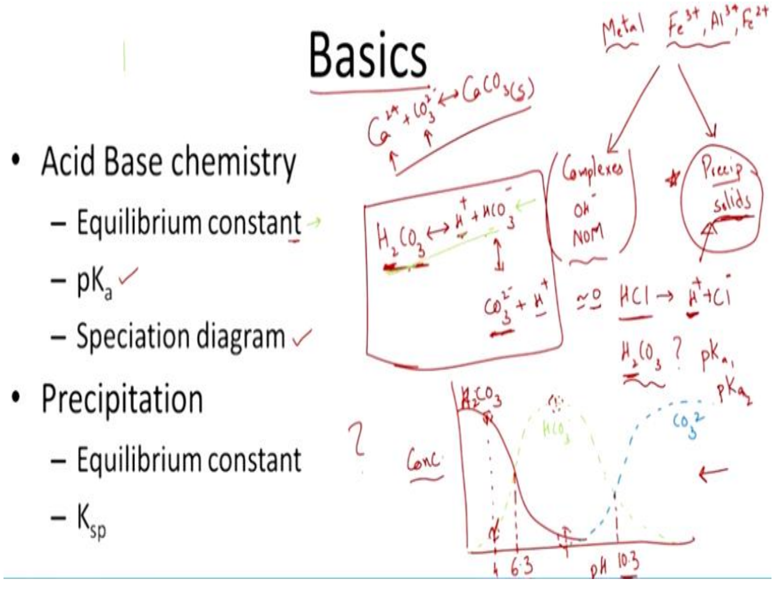

Basics

- Acid Base chemistry
  - Equilibrium constant
  - pK_a
  - Speciation diagram
- Precipitation
  - Equilibrium constant
  - K_{sp}

Fig 7

Some basics before I go further, maybe I should have even discussed this earlier but I would have assumed that about this earlier. But as a refresher we will just talk about some of the basics which we have some understanding when we look at these Lime-Soda based softening of hard water. I think some of these aspects we did discuss earlier. For example, if there is a metal.

And I think we talked about this in the context of coagulation. We were talking about Fe^{3+}, Al^{3+}, Fe^{2+}, electron deficient. Metals, when I put them into water, they are not going to be present only as water they will form complexes. And complexes can be OH^- electron rich, NOM electron rich and other ligands that are present in water or some of them will also precipitate out into different solids.

But for precipitation to occur a threshold has to be reached the solution has to be supersaturated just being saturated does not lead to precipitation. I have compounds Ca^{2+} and CO_3^{2-} in water and I know that the compounds can precipitate out as $CaCO_3$. For example, this (equation written for Ca and CO_3^{2-}) can be in equilibrium but for this to occur, either of these (reactants) should be relatively high, the system should be super saturated.

We are not going into that right here but you can look at the other NPTEL courses about environmental chemistry, that is one aspect, so we have metals that are soluble as free metals themselves and exist as free metals. We have complexes which are soluble but keep that in mind, maybe not greatly relevant in this process, but another aspect that is relevant is that you have precipitation in the form of solid state.

The solid is not in the aqueous phase so you can remove it either by sedimentation filtration or different means, typically sedimentation is practiced after coagulation and flocculation to remove the solids in the context of lime and soda softening. Here I want to talk about acid base chemistry. I think the best one to talk about is the acid of relevance here. Let me see if I have another picture there, I will come back to that.

I have H_2CO_3, this is an acid as you can see it can be a proton donor, different definitions but here we will stick with the one that talks about proton donor. This can be in equilibrium with H^+ and HCO^{3-} and HCO^{3-} can be in equilibrium with CO_3^{2-}, H_2CO_3- carbonic acid, bicarbonate and carbonate. You do not need to look at the names.

What do you see is H_2CO_3 can dissociate into HCO^{3-} and give out H^+, HCO^{3-} can further dissociate into CO_3^{2-} and give out H^+. Let us say there is a system or water where these 3 compounds H_2CO_3, HCO^{3-} and CO_3^{2-} which I refer to as the carbonate system are at equilibrium. There are 3 particular aspects here and if I remove one of them by different means then the equilibrium is disturbed and then there is going to be rearrangement of the concentrations or the H+ such that

You have a new equilibrium that exists between these 3 compounds, so that is one thing to keep in mind. But when I say acid, what is it doing? It is releasing H+ but you would have heard about strong acids like HCl going to H+ and Cl-. Why is that HCl is referred to as strong acid but maybe not H_2CO_3, why is that? Well, it depends upon the pKa and it is ability to release the H+.

For example, for H_2CO_3 I think we looked at this graph, this is called the specification diagram. Here (on y-axis) I will have the relative concentration or concentrations, on the x-axis, I will have the pH. And what else will I have here? And here I will have HCO^{3-} (green dashed curve on Fig.7) profile and here I will have CO_3^{2-} (blue dashed curve on Fig.7) profile. Let me write them down so this is CO_3^{2-} and the other one that is predominant in this region is HCO^{3-}.

The one that predominates out here (red curve on Fig.7) is H_2CO_3, so as we discussed earlier this point where both the protonated and deprotonated forms of the acid are at the same concentration is called the pKa1 for this case because there are 2 pKa's, this H_2CO_3 can give out 2 H+, so it is pKa1 and pKa2. The name is self-explanatory or the term is self-explanatory pK1 is the acid dissociation constant, acid dissociating, H_2CO_3 dissociating into H^+ and HCO^{3-}.

This is 6.3 (pKa1) and this is 10.3 (pKa2), you do not need to mug these up, these will be given if and when required, this is what I have. As you can see if the pH is around 4 somewhere out here, If I add H_2CO_3 when the pH is at 4 as you can see most of it will stay as H_2CO_3 and very little will dissociate to form HCO^{3-}, why is that relevant?

Because as you can see here, only when it dissociates, will H+ be given out. At pH 4 very little will dissociate. You can look at that, I think 6.3, 5.3 so less than 1% will dissociate. When I add H_2CO_3 at maybe 5.3 or less than pH of 5.3 as can be seen from here, Most of it will stay as

H_2CO_3, it would not affect the pH of the system because H^+ cannot be released or enough H+ cannot be released.

But if the pH is around 8 or so in this region, as you can see any H_2CO_3 that is added will mostly stay as HCO^{3-} and very little stay as H_2CO_3 so that can bring down the pH, why? In the process of H_2CO_3 dissociating into H+ and HCO^{3-}, you are going to release the H^+ and thus bring down the pH. Same case here at different pHs and pKa values. Whenever we are talking about strong acid or weak acid, what am I concerned about? I am concerned about this acid dissociation constant for the relevant acids.

For HCl it is 0, what does that mean? It is less than 0 but for practical or for illustration purposes I am asking to assume that it is 0. What does that mean? At almost all pH ranges, HCl will always give out H+ into the solution meaning it will be able to affect the pH of the solution, that is something to keep in mind. This is called the speciation diagram (refer Fig.7) where we look at the concentration of the relevant acid base species and their change with the pH.

That is something you will have to keep in mind because we will use this later. What is this other aspect, we talked about pKa and we talked about speciation diagram? But looks like I should have talked about another aspect before I skip to pKa. Let me talk about the equation that i have here. I identified the equation that I want to talk about. This is the equation that i want to talk about.

You have a reactant that is in equilibrium with products, the key is at equilibrium. There is a relationship or a constant that depends upon temperature and pressure which can give me an idea about the relative concentrations of the products to the reactants if the system is at equilibrium, so for this equation I will have something called an; Equilibrium constant (K).

What is the equilibrium constant for this equation I will write that out here.

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Fig 8

We are talking about equilibrium constant, so what do I have? The equation I am considering is H_2CO_3 in equilibrium with H+ and HCO^{3-}. Equilibrium constant Ka, I will call it Ka1, typically it is written as K that is enough. But because it is for acid dissociation, I am using the subscript Ka and 1 because it is the first one. But for now, we will just suffice ourselves to limit ourselves to K.

K is nothing but the concentration of the products as you can see the products are H^+ and HCO^{3-} raised to the stoichiometric coefficients. But you see stoichiometric coefficients here are one H^+ and one HCO^{3-} divided by the concentrations or activates rather which we are assuming to be concentrations here. This is key will take about that later, actually it has to be activity divided by the concentration of the reactants raised to their stoichiometric coefficients.

K is; On the top you are going to have the product of the concentrations of the products raise to their stoichiometric coefficients in the denominator you are going to have the product of the concentrations of the reactants raise to their stoichiometric coefficients, more or less products by reactants that is the equilibrium constant, so this is applicable as can be seen when the system is at equilibrium.

As in when the system has been given enough time to go to the furthest extent possible under those temperature and pressure conditions, that is the equilibrium constant. For this, these constants are measured, you can get them to from delta G values and most of these constants are measured or almost all of them that are known to the usual world are measured. You can use these constants and play around to get your relevant values.

The pKa2, it is similar to pH. We know is

$pH = -\log[H^+]$

In this class, we are always assuming activity of the compound is equal to concentration. And the

$pKa = -\log[K_a]$

that is something that gives you an idea about the relationship between the products and the reactants.

That is something for you to keep in mind for the other aspects we are going to discuss. And what else did I want to discuss? Acid base, we looked at that. Acid can give out a H+, base can take up a H+, so in this case HCO^{3-} can act as a base by taking H+ and going to H_2CO_3 or HCO^{3-} can act as a acid and go to CO_3^{2-} by releasing H+. It all depends upon what pH is prevailing, that is what we see here.

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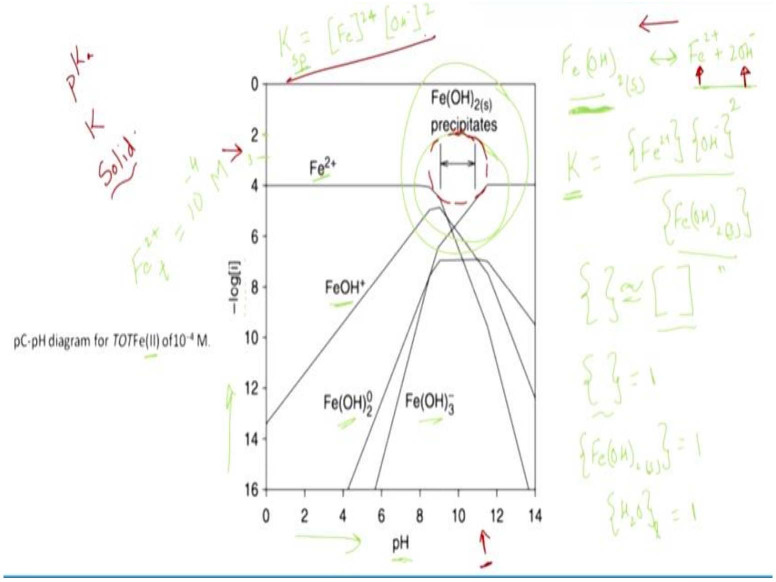

Fig 9

And precipitation; This is the figure that I wanted to have, so here we are talking about Fe^{2+} total, it is not free metal, Fe^{2+} total = 10^{-4} molar, this is a logC-pH diagram, here we have log and here we have pH. When we say log, so if it is 2 and 3 we can more or less forget or assume that whatever is at 3 is much smaller than the one at 2. log C pH diagram, so what does this tell you?

It tells you that a different particular pH and different concentration, different pH different concentrations, Fe2+ can stay as metal or it can stay as a complex or it can also precipitate, so it is range it can also precipitate. This is called for precipitation; We write it has solubility product $Fe(OH)_2$ solid will be in equilibrium with Fe^{2+} and $2OH^-$.

For this equilibrium constant, what is that equal to? Equal to activity of Fe^{2+} into the activity of OH^-, It is always products by reactants, stoichiometry coefficient by activity of the solid $Fe(OH)_2$. But as I mentioned in general in this class assuming that these solutions are low ionic strength, we are assuming that activity can be represented by concentration.

Here one aspect to keep in mind is the activity of solids, we look at as mole fraction it is going to be equal to 1 assuming it is a pure solid. Whenever you have solid in this equation constant you can think of that as being equal to 1. Activity of this is $Fe(OH)_2$ solid is equal to 1, same case with water if you ever see water in either the reactants or the products H_2O,

And because everything is in water and we are talking about mole fractions, infinite dilution, it is also equal to 1, you can neglect them, so in essence this equilibrium constant equation for the equation above will just be activity of Fe^{2+} which I am representing by concentration into this is OH^- raise to the power of 2, this is called the solubility product as you can see the solid is dissociating and becoming soluble.

This is called a solubility product when we write it in the form of the solid dissociating or dissolving. That is why we have K_{sp}, K solubility product. This is same as the equilibrium constant we discussed. For acids we call it as acid dissociation constant, for solid dissolving we call it the solubility product. These are aspects that you just need to be aware of.

And in general, as you can see when will this particular solid be formed as you can see here. You can also see that in the relevant graph. When will the reaction go from right to the left? That will happen when Fe^{2+} or OH^- are high or both are high. That is what you see in this graph also when pH is high meaning OH^- is high and also when Fe^{2+} concentration is high that is when this solid will precipitate out.

As you can see that there are certain thresholds that depends upon the relevant solubility products beyond which the metals or the relevant cations or the bivalent cations will start precipitating out. This is the background that you need to be aware of, what is it? We know the pKa, we know the speciation diagram and we looked at equilibrium constant.

We looked at solid precipitating out and for solid how to write this equilibrium constant related equation. With that I will end this session and in the next session using these particular basics, let us see how we are going to apply them to be able to remove this calcium and magnesium which are in water and which are causing relevant issues to my engineered distribution networks or whenever I use water. Thanking you for your patience I am going to end this session