

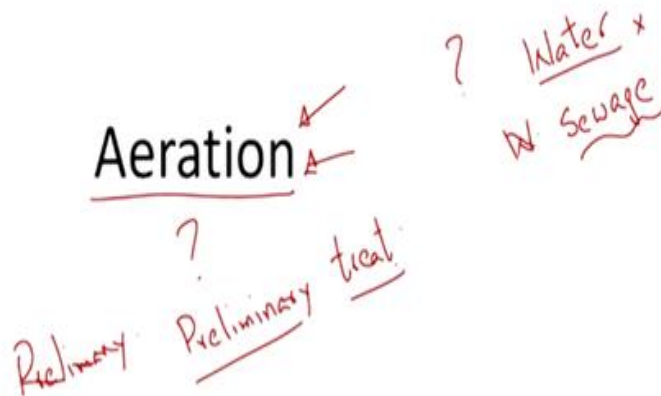
**Water and Waste Water Management**  
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**Indian Institute of Technology-Roorkee**

**Module No # 11**  
**Lecture No # 55**  
**Aeration: Removal of Fe and Mn**

Hello everyone, we are more or less at the fair end of this particular course. Initially we talked about wastewater than water, we are yet to talk about residuals but we will wrap that up after this particular session. In this session and the couple of sessions proceeding this session, we were looking at remove less specific compounds, let us see. Specific compounds like calcium, magnesium.

And if there are trace compounds with ion exchange or with respect to nanofiltration or by using reverse osmosis that is what we have discussed. In this line of understanding if I may say so or learning let us look at one more aspect.

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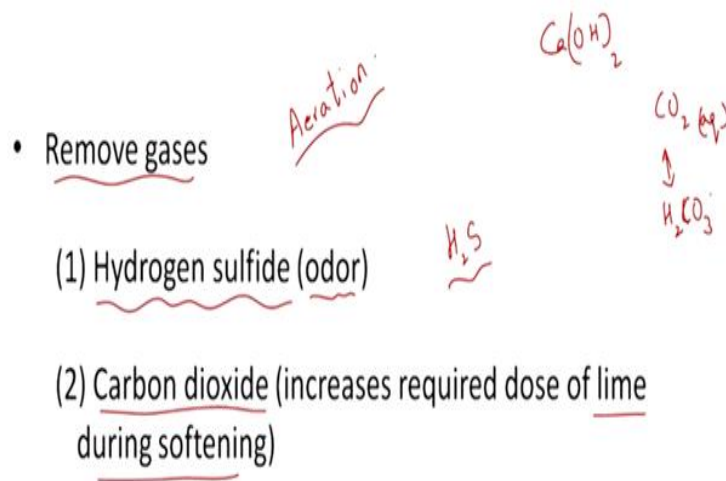


We are going to discuss aeration today. But we did come across this aeration earlier, where did we come across this? That was not in the context of water treatment though or drinking water treatment. It was in the context of wastewater treatment or sewage. It was in the context of sewage treatment or wastewater treatment there we were looking at supplying oxygen, electron acceptor to the relevant microbes.

That they can catalyse the reaction where our waste is oxidized by oxygen that is where we looked at, in the context of water treatment too we are going to come across or use aeration, but where are we going to use this? Typically, this if it is used will be used before primary treatment during or at the far end of preliminary treatment but the reason, we are discussing it here now is

I wanted to look at the discussion or consider discussion with respect to specific compounds in one go. Here we are talking about aeration, let us look at what a compound is it that we typically trying to remove by aeration?

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If there are any gases that I want to remove, that is something that I can look at by applying or employing aeration. Here, I am talking about changing phase, hydrogen sulphide H<sub>2</sub>S remarkably reducing compound or strong reducing agent, it is corrosive too. And also, more importantly even at very low concentrations, it gives out considerable odour, like a rotten egg smell.

Depending on your source, you might have to remove your hydrogen sulphide. But rarely do we come across this in the context of water treatment. But that is something I wanted to point out. And if you have access carbon dioxide or H<sub>2</sub>CO<sub>3</sub> in your water to save upon your dose of lime during softening, you can purge this carbon dioxide rather than adding lime.

If you remember the lime soda water softening process, all the lime that we added initially, was to neutralize the carbon dioxide that in the dissolved phase, which is in equilibrium with

$\text{H}_2\text{CO}_3$ . Or one other way is to strip the water of carbon dioxide, that is one particular way, we are going to pass air through it and the equilibrium is going to change and this carbon dioxide is going to leave the relevant system, that is one aspect.

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## Iron and Manganese removal

But typically, at least in the context of water treatment, we are going to look aeration in the context of our iron and manganese removal.

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### Iron and Manganese removal

- Iron II ( $\text{Fe}^{2+}$ ) and Manganese II ( $\text{Mn}^{2+}$ ) exist in acidic and reducing environments (e.g. wetlands and in aquifer below wetlands)
- $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  are soluble and remain in water following conventional treatment but precipitate at the point of use, causing stains in plumbing fixtures and in laundry
- Support growth of Iron bacteria (Iron slimes) in well screens and distribution systems

Let us first understand why we need to look at removal of iron and manganese. And what are the typical states or forms these are present in and in what forms are they troublesome to us. Anything in excess is an issue and we also already looked at the Bureau of Indian standards, which presents the information about the different standards for different compounds. You can look at the standards there.

Here we are looking at Iron in the +2 oxidation state, ferrous and manganese too in the +2 oxidation state. But in which conditions do they exist? They exist in reducing conditions, typically which goes hand in hand with acidic conditions. Reducing conditions meaning reducing environment where is that going to be prevalent? That is going to be prevalent when your system has no access to the oxygen

Which is one of the most widely available electron acceptor or the oxidizing agent out there. Where on earth will you have little oxygen, so it is below the surface. The aquifer below subsurface, you will have relatively low oxygen content. That is one aspect to keep in mind. Typically, iron deposits or Fe 2+ is present. And if you have an industry nearby, why I am saying this is?

We now have an industrial zone nearby Roorkee near Haridwar rather. And the villages surrounding this particular industrial zone are experiencing the adverse effects of very high ferrous iron and they did not face this issue earlier. One aspect was, rather than waste water being discharged that is high in iron content.

Another aspect that was occurring was acidic water coming in contact and then deposits which were immobile now being mobile Fe<sup>2+</sup>. And then they creating havoc with the digestive system of the relevant villages. And also, once they take this Fe<sup>2+</sup> out, that is going to also oxidize to Fe<sup>3+</sup>. Fe<sup>3+</sup> is more insoluble than Fe 2+ and that is going to create issues too. We will look at that later. That is one aspect to keep in mind.

Where are we here? Reducing environments, typically we see them in the subsurface. And one aspect to notice, Fe<sup>2+</sup> and Mn<sup>2+</sup> are remarkably soluble, why is that an issue or not an issue? If it is insoluble, they would have precipitated out in the subsurface. Because they are soluble, at least because these forms of Fe<sup>2+</sup> and Mn<sup>2+</sup> are soluble, they will flow with the groundwater.

They will flow with the groundwater and what else remain in water following conventional treatment but precipitate at the point of use. One aspect is they will flow with the groundwater and can create issues or stains whenever you use them in your bathroom or sink or such. You would have seen these yellowish orangish stains that is typically due to iron and or manganese. Another aspect is because they are soluble.

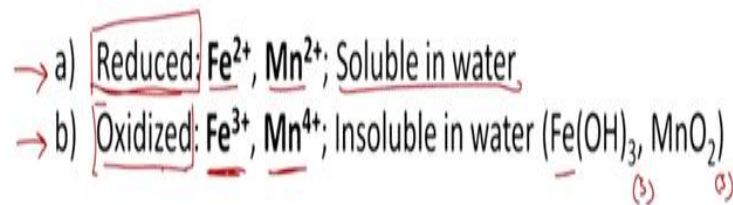
Until now we have looked at primarily suspended solid removal in water treatment followed by disinfection. Depending upon the dose, you will not remove  $\text{Fe}^{2+}$  or  $\text{Mn}^{2+}$  but we will come back to that. In water we are typically trying to remove suspended solids because  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  are soluble typically, they will not be removed by conventional treatment. But once you use them or during your usage and when they are exposed to oxygen for a certain duration,

They are going to precipitate out after transforming into  $\text{Fe}^{3+}$  or  $\text{Mn}^{4+}$  if I am not wrong and that will lead to stains on the plumbing fixtures and in laundry, that is something to keep in mind. And it also looks like it also supports the precipitation, supports the growth of iron bacteria or iron slimes in well screens and distribution systems. That is something to keep in mind.

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- Oxidize iron and manganese

### 1. Oxidized/reduced forms



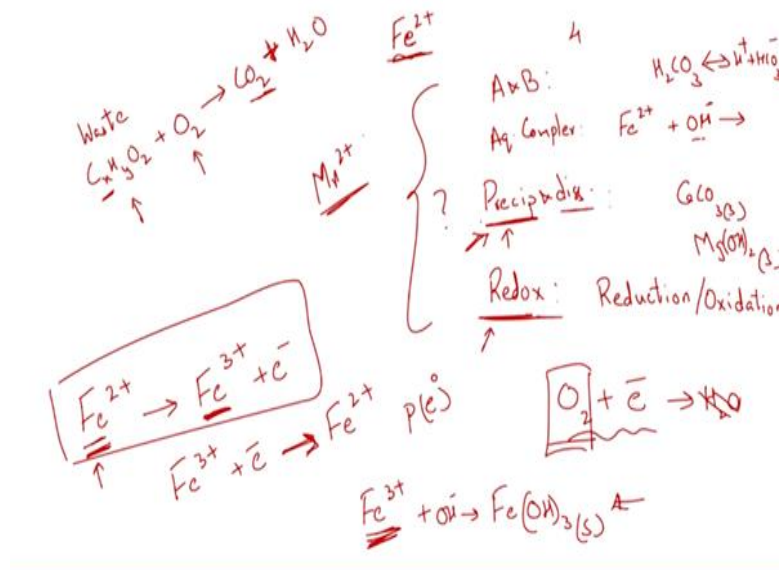
First, we need to understand some background or have some background before I go to that, let us look at what we have. Typically, we are concerned with the reduced forms which can be oxidized due to the change in the environmental conditions. Reduced forms, which are more mobile, more mobile because they are soluble in water, or  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  reduced form, oxidation state is relatively less.

It is the one that has the electron with the electron that is why it is reduced or less oxidation state here. If it is oxidized it has given away the electron to an electron acceptor. Then the oxygen state will increase  $\text{Fe}^{3+}$ , it is losing an electron with the negative charges being lost.

You have oxidized form here and also oxidized here. But the issue here is that now these  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$ , they are not soluble.

But they will precipitate out in the form of a  $\text{Fe}(\text{OH})_3$  or  $\text{MnO}_2$ , this is one background. Here we are coming across some terms which I freely used in the context of wastewater and sometime in the water treatment but here let me look at some of the aspects here.

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Here we are talking about inorganics,  $\text{Fe}^{2+}$  not an organic compound but an inorganic compound. In organics relevant chemistry, there are 4 major aspects to look at, acids and bases. In this context, the example was  $\text{H}_2\text{CO}_3$  acid being in equilibrium with  $\text{H}^+$  and  $\text{HCO}_3^-$ . This is acid and base and then we have aqueous complexes.  $\text{Fe}^{3+}$  or even  $\text{Fe}^{2+}$  if it is at higher pH, we know it can form a complex with a ligand  $\text{OH}^-$ , electron rich, it can form complexes and what else?

We have precipitation and dissolution. The compound can be dissolved or if it is in far excess of the stoichiometric ratios or such, the precipitation can occur, in that context or where did we come across this? We looked at lime softening and we were trying to remove calcium by precipitating it out as  $\text{CaCO}_3$  solid or magnesium hydroxide the solid. We came across this earlier, the application of precipitation.

Another aspect I think we briefly touched upon in the waste water aspect or waste water relevant topic was redox, transfer of electrons. You are going to have reduction and oxidation going hand in hand. In the context of wastewater, the reduced compound was our waste  $\text{C}_x\text{H}_y\text{O}_z$  and the electron acceptor was oxygen. And then the final products if everything goes

according to plan would have been carbon oxide and water, you see relatively more oxidized form of carbon.

Carbon is being oxidized and this was the reduced compound and this is the oxidizing agent, which is oxidizing, your reduced compounds, that is what you see out here, similarly here, we are going to use these principles to understand how to remove  $\text{Fe}^{2+}$ , key aspect is that  $\text{Fe}^{2+}$  can be oxidized to  $\text{Fe}^{3+}$ . In general, I should have written it the other way  $\text{Fe}^{3+} + \text{electron}$ .

This is the standard way of writing as in the reduction the standard way. For this you will have the Pe naught values, you can think of it as your  $\log k$  or such or one by  $n \log k$ , where  $n$  is the number of electrons. Anyway, you have this as you can see were depending upon the transfer of electron one form can go to the other.

Here  $\text{Fe}^{2+}$  is in this phase initially, but once it comes in contact with an electron acceptor, what is the electron acceptor? Electron acceptor is the oxygen, I am not balancing it out here. Let me not go into that aspect, so oxygen can take the electron which is being given by  $\text{Fe}^{2+}$  and thus this  $\text{Fe}^{2+}$  can transform into  $\text{Fe}^{3+}$ . Please note that for redox reaction to go through, you have to have both the reduction and oxidation occurring, there can never be only oxidation without reduction, why is that?

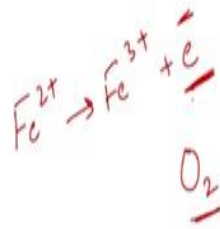
Because electrons they would not float around in water, there can never be a pool of electrons unlike the case of a pool of  $\text{H}^+$  and then pH being affected. If you want to have a redox reaction occurring, you need to have a reducing agent or reductant and oxidant, that is something to keep in mind. Here  $\text{Fe}^{2+}$  is the reductant but it needs an electron acceptor for this reaction to go through, that happens when you have oxygen in contact.

What happens to  $\text{Fe}^{3+}$  that is formed? We know that  $\text{Fe}^{3+}$  is remarkably insoluble typically very insoluble, it is not soluble it does not stay in water or does not want to stay in water even at relatively medium or such concentrations. It will precipitate out as this solid, you can use this particular principle to try to remove  $\text{Fe}^{3+}$ , similarly we are going to look at or can look at  $\text{Mn}^{2+}$ .

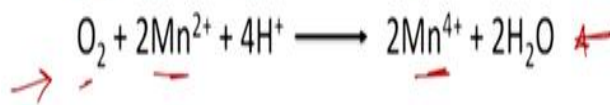
Keep in mind that we are looking at oxidation of  $\text{Fe}^{2+}$ , redox oxidation of  $\text{Fe}^{2+}$ . And then we are looking at precipitation of the  $\text{Fe}^{3+}$  that has been formed when we oxidized  $\text{Fe}^{2+}$ , that is something to keep in mind. Principles that we use are redox and precipitation and dissolution. Let us move on and look at the relevant aspects.

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- Oxidize iron and manganese



## 2. Oxidation by oxygen in air (can be slow if pH is low)



To oxidize iron and manganese, let us look at the overall reaction here. Earlier we looked at one half reaction,  $\text{Fe}^{2+}$  going to  $\text{Fe}^{3+} + \text{electron}$ . And who is going to accept this electron? Oxygen is going to accept the electron, oxidizing agent electron acceptor, that is what you have in the presence of oxygen,  $\text{Fe}^{2+}$  can in relatively acidic conditions be oxidized to  $\text{Fe}^{3+}$ .

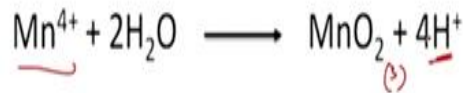
And similarly,  $\text{O}_2 + \text{Mn}^{2+}$ , it can go to  $\text{Mn}^{4+}$  or be oxidized to  $\text{Mn}^{4+}$ , one aspect here is especially for this reaction, if the pH is low, this is particularly low or even neutral at least for this particular reaction. It is pretty slow this particular reaction and that is something to keep in mind but we will come back to that. Now that we have  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$  form, these are from here  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$  which are oxidized after oxygen oxidizes which are formed after oxygen oxidizes  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ .

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- Oxidize iron and manganese

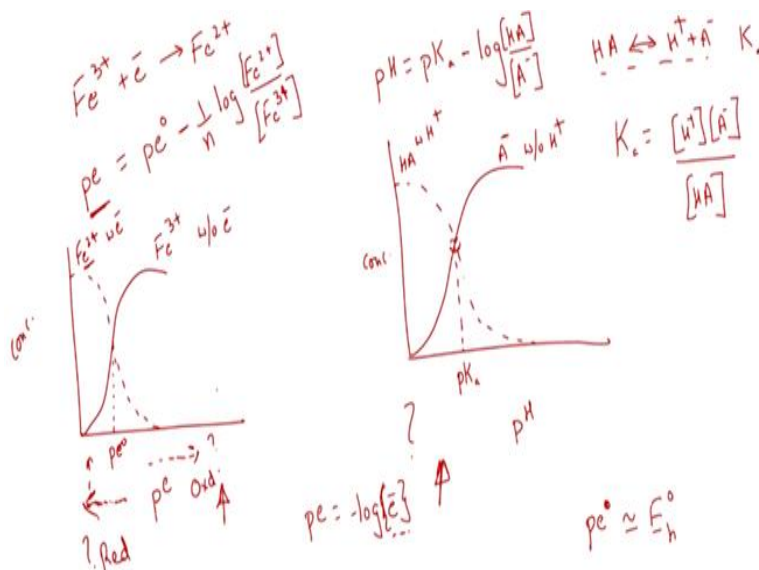
### 3. Formation of precipitates (relatively rapid)



As you can see  $\text{Fe}^{3+}$ , it is acting as Lewis acid here.  $\text{Fe}^{3+}$ , it will precipitate out as  $\text{Fe}(\text{OH})_3$  solid or  $\text{MnO}_2$  the solid and thereby releasing  $\text{H}^+$ , that is something to keep in mind. The previous step, which we looked at where we are looking at oxidation, that is relatively slow and it is specifically dependent on pH. And the precipitation do surprisingly is typically fast enough.

In general, redox reactions are typically either pretty fast or they never reach equilibrium depends on the relevant environment, redox reactions that is always the case kinetics playing great or considerable role. Let us move on here without digressing further. This is the aspect but we need to look at some background. For example, let me write one more aspect here.

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For acids and bases, you can come up with an equation, for example if it is HA acid dissociating to  $H^+ + A^-$  and that the equilibrium constant is  $K_a$ ,

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

This will be the concentration which we are trying using to approximate activity  $pH = pK_a - \log \frac{[HA]}{[A^-]}$ . It is just taking the log of them and playing around with the values and you will get it. We know that  $K_a$  equilibrium constant is  $H^+$  into  $A^-$  by HA.

I am just giving the basics here that people who are interested in learning can look at it in detail so that they can apply it later, this is the aspect and from here, we came up with one graph. And this point where both the protonated form, HA is the protonated form with proton and  $A^-$  is the deprotonated form without proton. Where the pH at which their concentrations are equal is going to be the  $pK_a$ . And on this we have pH and on this we have the concentration.

Similarly, for  $Fe^{3+} + \text{electron} \rightarrow Fe^{2+}$ , you can come up with a relevant equation that will look something like the  $pe$  is going to be equal to  $pe^0 - 1$  by  $n$ ,  $1$  by  $n$  is equal to number of electrons being transferred, here it is  $1$   $\log Q'$ .  $Q'$  is the one without the electron,  $\log$  of  $Fe^{2+}$  concentration by  $Fe^{3+}$ , you can come up with this particular equation for this half reaction.

Similarly, I can draw this particular graph here. Here I have  $pe$ , which will give me an idea about whether it is reducing conditions or oxidizing conditions. How  $pe$  out here and relevant concentrations out here let us see, I will have a profile something like this. And the point at which both are equal should be equal to  $pe$  naught.

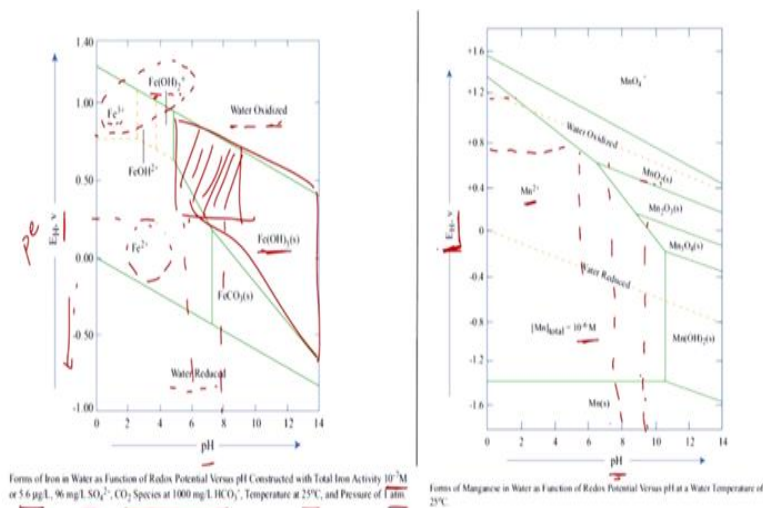
$pe$  naught can be looked at or you can transform that to  $E$  h naught. We will look at that later but keep that in mind. That is one aspect to keep in mind,  $pe$  naught. Here you will have the reduced form, the one with the electron. For example, here it is the one with  $H^+$ , here it is the one with electron here. And the one without electron will be out here and here it is without  $H^+$  or the proton.

Now why did I draw this particular graph first? Because as you can see, we looked at this graph earlier multiple times and the graph we are looking at now is similar to the graph on the right but what does it tell you when the  $pe$  is less.  $pe$  is equal to minus log activity of the electron, when will the  $pe$  be less?  $pe$  will be less when the electron concentration is high.

This is the hypothetical value, when we say activity of the electron. Anyway, when  $Pe$  less that means reducing conditions prevailing, when reducing conditions prevail what form is predominating?  $Fe^{2+}$  is predominating and when oxidizing conditions prevail when you have  $Pe$  high, oxidizing conditions prevail, this is reducing conditions. Here oxidizing conditions, what form is prevailing? You can see  $Fe^{3+}$  is prevailing.

This also gives you an idea about which form predominates when water has certain characteristics. With a simple ORP probe, you can put it in water and see whether it typically is in reducing conditions or oxidizing conditions, let us look at that particular piece of information.

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Peter Shanahan. 1.85 Water and Wastewater Treatment Engineering, Spring 2006, Massachusetts Institute of Technology. MIT OpenCourseWare, <https://ocw.mit.edu>. License: Creative Commons BY-NC-SA.

$E_h$  as I mentioned you can look at it in terms of  $Pe$  of the particular sample and you have pH here on the x axis, this is like a predominance area diagram something that we looked at earlier, forms of iron in water as function of redox potentials versus pH constructed with what is the total iron activity, it is  $10^{-7}$ . And this total iron can be in the form of  $Fe^{2+}$  or  $Fe^{3+}$  which can also be precipitated out. That is something to keep in mind.

And it also has some sulphate and other carbonate species, temperature and pressure are given. But let us not go into that. When the  $E_H$  is high, water is oxidized when our oxidizing conditions prevail when  $Pe$  or  $E_H$  which is less reducing conditions prevail, that is something to keep in mind. When reducing conditions prevail and pH is relatively less, you see  $Fe^{2+}$  predominates but in relatively oxidizing conditions, what do you see?

You see that  $\text{Fe}^{3+}$  prevails. Here, you see the aqueous complexes which we discussed earlier. But at slightly higher pH or neutral pH, you see that  $\text{Fe}(\text{OH})_3$  starts predominating. Here it is the zone that I am talking about. In the neutral pH, this is the neutral pH, in this range more or less pH 7 or 6 to 8. And this relatively oxidizing conditions, what do you see?

$\text{Fe}^{2+}$  will not stay as  $\text{Fe}^{2+}$ , it will be oxidized and that oxidized  $\text{Fe}^{3+}$  will precipitate out, that is what you see here. We are going to use this particular background to look at the pH that you want to maintain. Same case with  $\text{Mn}^{2+}$  here, Mn total, manganese total is  $10^{-6}$ , at low pH and relatively reducing conditions, it stays as  $\text{Mn}^{2+}$  but at relatively higher pH here, note that the oxidation does not occur at neutral pH values.

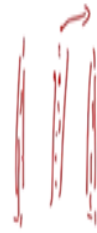
That is something to keep in mind, it is relatively high pH values typically we are looking at each pH of 9. At pH of 9, you will see that the solid is going to be formed. Even though if you want to have it at neutral pH, you can do that but then the Eh or the redox potential has to be pretty high, that's something to keep in mind. You can understand how it transforms or how the system transforms between one form to the other based on the Eh and the pH based on the redox potential and the pH.

In groundwater where there is no oxygen, typically reducing conditions prevail. That is why  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  are abundant. But out here above the surface where oxygen which is an oxidizing agent is plenty, you are going to have oxidizing conditions prevailing. And thus, you see that the oxidized forms are going to prevail. And in general, at neutral pH, if oxygen conditions prevail, you see  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  they precipitate out as a  $\text{Fe}^{3+}$  and  $\text{MnO}_2$ , so that is something to keep in mind.

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# Iron and Manganese removal

Fe and Mn can be addressed in many ways :



1. In-situ treatments:- Injection wells around water supply wells to precipitate Fe and Mn in the ground.  
( $E_H$  vs pH diagram)

Let us go through. Iron and manganese can be removed, In-situ is in place itself, injection wells around the water supply wells. For example, if this is my water supply well, that is drawing water out. I can have injection of oxidizing agents or such that I am going to inject oxidizing agents or such around my particular extraction well. This is my extraction well, so that I can precipitate out  $Fe^{2+}$  and  $Mn^{2+}$ .

It can be as simple as purging it with oxygen or a benign oxidizing agent. That is something to keep in mind.

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# Iron and Manganese removal

- Fe and Mn can be addressed in many ways :
2. Sequestration:- Phosphate chemicals added to water to bind with and "Sequester" Fe and Mn, preventing later precipitation

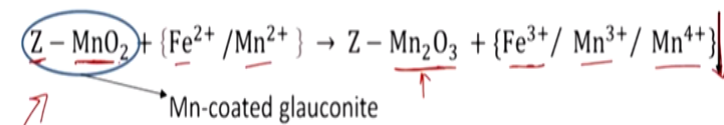
Sequestration, we talked about aqueous complexes being in one other form into which the inorganics especially the metals can transform, for that you need to ligand. Ligand and that we looked at was  $OH^-$  but here if you add phosphate, that will make the relevant  $Fe^{2+}$  and

$Mn^{2+}$  remarkably more soluble and they typically would not precipitate. Here they are using the term sequestration, so that is one particular aspect.

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3. Treatment with Greensand (glaucanite):- Natural ion exchanger with Fe and Mn.

Removal Reaction:



Regeneration with potassium permanganate



Treatment with green sand natural iron it is not exactly to call this an ion exchange but let us see the relevant reaction. You have going to have green sand and they are going to coat it with this  $MnO_2$ , quite different ways to coat it. And when that comes in contact with  $Fe^{2+}$  at relatively higher residence time, you can see the relevant, this is going to be reduced.

But you see that  $Fe^{3+}$ ,  $Mn^{3+}$  and  $Mn^{4+}$  are going to be formed which are the oxidized forms, which are then going to precipitate out, that is one particular way, this is the media which is coated with  $MnO_2$ . But after sometime, all that media will have to be regenerated because it is been exhausted. This  $MnO_2$  is being reduced. I am going to add a strong oxidizing agent to oxidize this reduced compound or reduced form of manganese and  $MnO_3 + KMnO_4$  goes to this particular form.

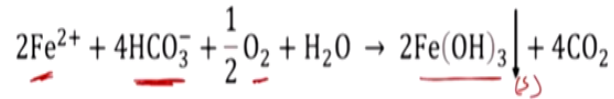
I am oxidizing it so that it can be reused, the media can be reused here. What is the media? The media is green sand.

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#### 4. Oxidation

- Goal: oxidize  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  to get precipitates

a) Aeration: works for Fe, not for Mn



- Precipitated iron is then settled and filtered  
(most removal by filtration)

Oxidation, so we know that we can form precipitates, the title of this session was aeration. In general, as we saw even at relatively moderate redox potentials, relatively higher by I mean not very high but high enough oxidizing potentials or redox potentials. And at neutral pH, you can easily remove Fe in the form of  $\text{Fe}(\text{OH})_3$ . But Mn not really, you have to see to it that the pH is higher if you want relatively faster kinetics.

That is something to keep in mind. What is it that can happen? This is the overall reaction out here, this is added or is relevant if not the pH is going to decrease, that is one aspect to keep in mind,  $\text{Fe}^{2+}$  reduced form, oxygen oxidant, reducing agent oxidizing agent and then you have the relevant precipitate out here. And then once it is precipitated out, you can let it settle and filter it out.

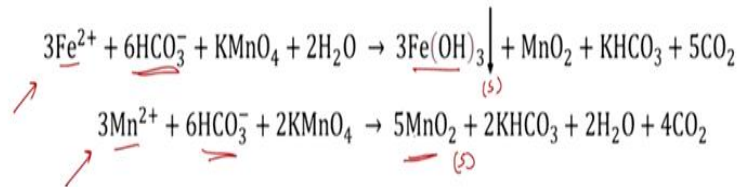
As I mentioned, aeration typically we will use that in the preliminary treatment or before primary treatment.

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b) Chemical oxidation

Fe<sup>2+</sup> - NOM

- Addition of stronger oxidizing agent – Chlorine or KMnO<sub>4</sub>
- Precipitated iron settled and filtered
- Reaction with permanganate



Or you can add chemical oxidizing agents. Chlorine, different forms of chlorine, KMnO<sub>4</sub> but this is typically costly and with respect to Mn<sup>2+</sup> or if you have a Fe<sup>2+</sup> bound to natural organic matter, it is very difficult to remove it. If we looked at aqueous complexes, we need metal and ligand. Ligand examples what did we look at? We looked at OH<sup>-</sup>, we looked at phosphates and another ligand electron rich is anywhere which is a nuisance.

And as you can see it is also act as a ligand and complexes with Fe<sup>2+</sup>. Fe<sup>2+</sup> and NOM, at least with Fe<sup>3+</sup> it does form it. You see that if you are adding an oxidizing agent, you will might not be able to oxidize the Fe<sup>2+</sup> because it has formed a complex with the natural organic matter, that is something to keep in mind when you are adding oxidizing agents or even trying aeration when your NOM is very high if it is bound with the relevant metal, that is something to keep in mind.

KMnO<sub>4</sub>, relatively strong oxidizing agent but relatively costlier too so the relevant reactions, so here we will look at stoichiometry or such, these are the kinds of questions that are typically asked so that is for you to look at, HCO<sub>3</sub><sup>-</sup> typically to see to it that the pH does not decrease. Without it the pH is going to decrease, here you have the relevant solids being formed and then Fe<sup>2+</sup> being oxidized then Mn<sup>2+</sup> being oxidized and precipitated out.

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## 5. Lime-Soda ash softening

- Fe and Mn removed during softening if pH is raised above 9.8

And lime soda ash softening, Fe and Mn can also be removed during softening if pH is raised above 9.8. If you look at that  $E_H$  pH diagram, you will be able to visualize that. Some of it can be removed during lime soda of softening too. With that we are done with aeration. And then we will move on to looking at residuals and their relevant treatment. With that I will end today's session. Thank you.