Water Supply Engineering
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Lecture-39
Advanced and Alternate Treatment Systems

Hello friends and welcome back. So, this week we have been talking about disinfection which we covered then the sludge management which we discussed in just the previous lecture. And now we'll be focusing on the next part which is the advanced water treatment. So, this particular class we are going to discuss some of the advanced water treatment operations which are used in drinking water treatment or municipal water treatment facilities.

This advanced treatment systems may not necessarily be advanced okay it is just different than the conventional systems. Some of the systems are like very old age concept based on very old age concept and have a lot of uses as well. But still they are not used in the conventional treatment systems. So, we are saying that as also a part of advanced treatment or alternate treatment systems.

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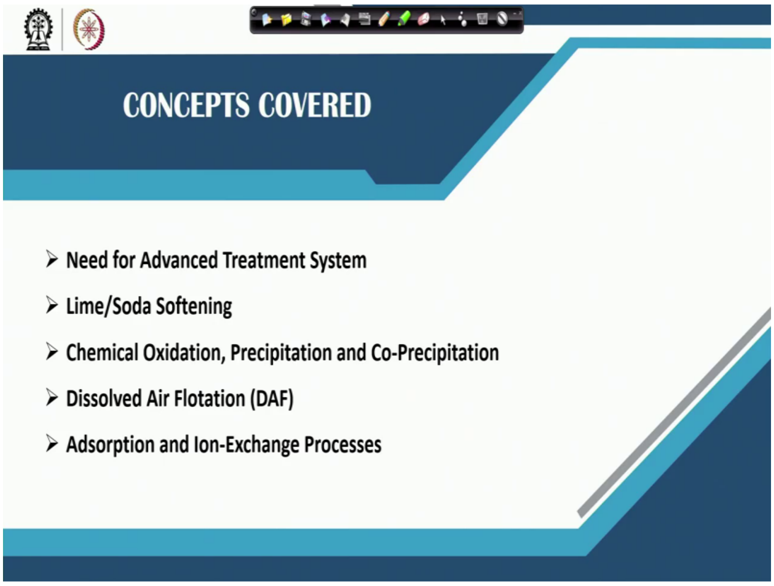

CONCEPTS COVERED

- Need for Advanced Treatment System
- Lime/Soda Softening
- Chemical Oxidation, Precipitation and Co-Precipitation
- Dissolved Air Flotation (DAF)
- Adsorption and Ion-Exchange Processes

So, what we are going to discuss is why we need these advanced or alternate treatment systems. Then, we are going to discuss some of the these systems in this particular class like lime soda softening, the chemical oxidation precipitation and Co precipitation then we will be talking about the dissolve air flotation and particularly about the adsorption and ion exchange processes how they work.

So, this is what we are going to cover in this particular lecture and in then in next class we will be talking about the other advanced treatment process like the advanced oxidation process and the membrane processes.

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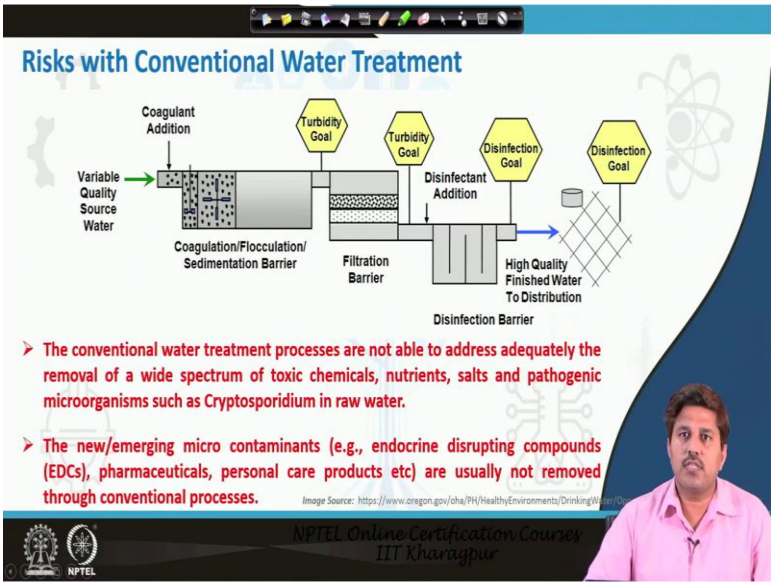

Risks with Conventional Water Treatment

- The conventional water treatment processes are not able to address adequately the removal of a wide spectrum of toxic chemicals, nutrients, salts and pathogenic microorganisms such as Cryptosporidium in raw water.
- The new/emerging micro contaminants (e.g., endocrine disrupting compounds (EDCs), pharmaceuticals, personal care products etc) are usually not removed through conventional processes.

Image Source: https://www.oregon.gov/oha/PH/HealthyEnvironments/DrinkingWater/Op

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So, why we need these advanced treatments is because our conventional water treatment processes are not sufficient enough, are not capable enough to address the removal of all the pollutants that might be present in the water . Te conventional treatment processes are not able to kind of remove the wide spectrum of toxic chemicals, nutrients, salts then pathogenic microorganisms.

Some of the pathogenic microorganisms of course majority are removed. But chlorination as we discussed earlier also might not be able to remove the Cryptosporidium and Giardia easily okay. So, chlorination is in fact the conventional treatment what is usually provided at the drinking water facilities okay. So, of course these can be removed with easily with the UV or ozone but again that they are also a form of advanced treatment only.

Although, we discussed that earlier, while discussing the disinfection process, but they are not the conventional ways of disinfection, conventional means of disinfection is the chlorination. And that might not remove the like all the microorganisms present in the water right.

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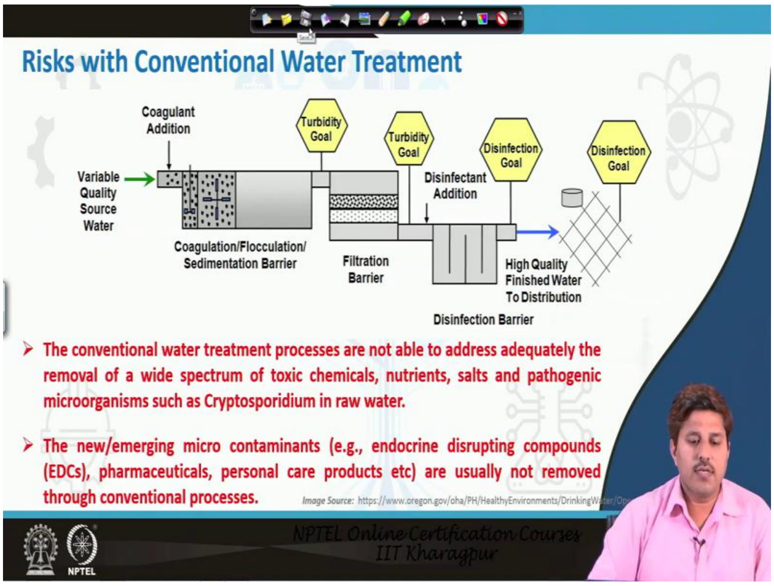
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So, what typically happens like if you see the water that is coming in and then once it is treated so by the time water comes out the correlation flocculation and sedimentation barrier, it achieves the turbidity goal. Then once it crosses the filtration barrier means it comes out of the filtration process, again it works very further to the turbidity goal. And then we add a disinfectant and put disinfection barriers which take care of the disinfection goals.

So we have not actually attempted the removal of any sort of dissolve toxic chemicals, any sort of nutrients that are salts dissolve organics these we have not attempted. So, turbidity is removed very well with the conventional systems particularly, after filtration, we will see the water coming out is very clean. But again it it is only for the coal idle and suspended solids it is not for the dissolved solids right.

And the disinfection process again will take care of majority of the pathogens particularly the chlorination process. If you are adding chlorine it will take care majority of the pathogenic microorganisms but some might still be present in the water. Further there are various new and emerging micro contaminants like EDC's which are known as endocrine disrupting compounds, there are pharmaceuticals, personal care products okay various pesticides.

So, they are also now coming into the water okay. You might just explore any news channel and then you might see that there are particularly like any literature if you focus on that part so you will see that our water sources are contaminated with these compounds with the various pharmaceuticals, personal care products, pesticides, various other persistent organic pollutants. So, they are there in the water and our conventional system does not treat them.

So, if we are consuming that water we are actually like at risk of consuming those contaminants. We are at risk of bringing in those contaminants into our food chain system.

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Advanced/Alternate Water Treatment Processes

Processes

Non-Membrane Systems

- Lime Soda Softening or Precipitation
- Alum or Iron compound co-precipitation
- Dissolved Air Flotation
- Ion Exchange
- Granular Activated Carbon
- Advanced oxidation processes
- UV / Ozone disinfection

Membrane Processes

- Microfiltration
- Ultrafiltration
- Nanofiltration
- Reverse Osmosis
- Electrodialysis

Objectives

- Water softening
- Heavy metals removal
- Nutrients removal
- Emerging contaminants removal
- Advanced microbiol controls

And that is why in order to like avoid that risk, we should look for the advanced treatment systems which have an objective of removal of some of these contaminants. So, typically like these systems have an objective of removal of this say hardness so water softening heavy metals removal, nutrient removals, emerging contaminant removal, or microbial Advanced microbial controls, okay so that is what are the basic objectives.

The processes are in fact, we can separate that processes as a membrane processes, and non membrane processes or we do not like it is just a way to look at them like membrane process might include the microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electro dialysis, non membrane processes are then because for softening purpose. We might go for the line sort of softening or precipitation or we might go for ion exchange okay. For sediment removal again dissolved air flotation might be used.

So if sedimentation is not that effective we can instead switch to the dissolve air flotation we can use alum or iron compound Co precipitation for the removal of iron and some of the other heavy metals like arsenic and those things can be removed. We can use activated carbon for the adsorption of variety of constituents or compounds we can use advanced oxidation processes for the removal of say these particularly these emerging contaminants okay.

So, advanced oxidation process works well on that. And then we can use UV or ozone disinfection, as we discussed earlier, for the advanced microbial controls because their efficiency is higher.

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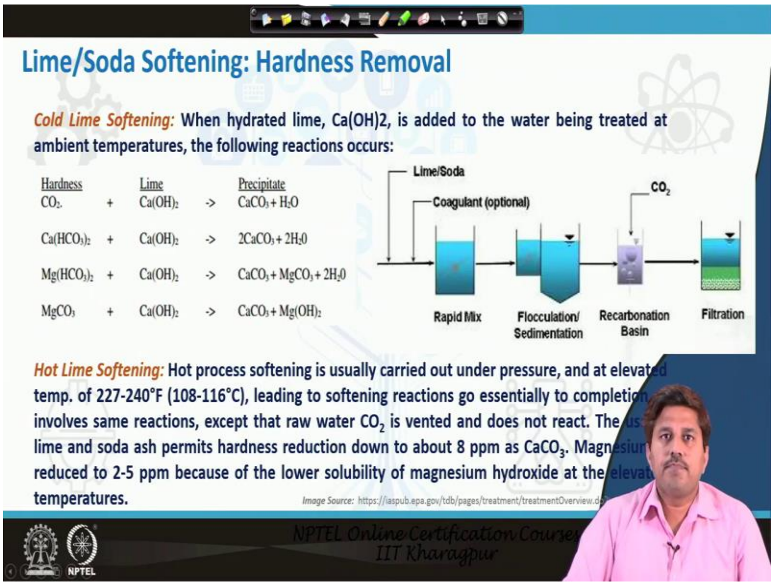

Lime/Soda Softening: Hardness Removal

Cold Lime Softening: When hydrated lime, Ca(OH)2, is added to the water being treated at ambient temperatures, the following reactions occurs:

Hardness		Lime		Precipitate
CO_2.	+	$Ca(OH)_2$	->	$CaCO_3 + H_2O$
$Ca(HCO_3)_2$	+	$Ca(OH)_2$	->	$2CaCO_3 + 2H_20$
$Mg(HCO_3)_2$	+	$Ca(OH)_2$	->	$CaCO_3 + MgCO_3 + 2H_20$
$MgCO_3$	+	$Ca(OH)_2$	->	$CaCO_3 + Mg(OH)_2$

Hot Lime Softening: Hot process softening is usually carried out under pressure, and at elevat temp. of 227-240°F (108-116°C), leading to softening reactions go essentially to completio involves same reactions, except that raw water CO_2 is vented and does not react. The us lime and soda ash permits hardness reduction down to about 8 ppm as $CaCO_3$. Magnesiu reduced to 2-5 ppm because of the lower solubility of magnesium hydroxide at the elevat temperatures.

Image Source: https://iaspub.epa.gov/tdb/pages/treatment/treatmentOverview.d

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So, like for hardness removal purpose, we may go for a simple process, lime soda process again there is nothing advanced too advanced about this process, this is a simple process okay very similar to the coagulation flocculation process. But we may add coagulant here also what we add is lime and soda. And then it basically undergoes like whatever we are adding so hardness compound which is might be because of say this for CO2, calcium bicarbonate, magnesium bicarbonate, magnesium carbonate.

So, they react with the lime and they form a precipitate of calcium carbonate and that way that precipitate then can be removed through filtration or the sedimentation process okay. So, we add the lime, if needed, we may add soda also. So, lime soda will be added similar to the like coagulation flocculation process, will go for a rapid mix for mixing that if needed, we can add certain component also along with or a coagulant add. And then it will go to a flocculation making will be given some time for flocculation and then said clarification or sedimentation process.

So it is exactly the same. Lime soda softening is can be done at normal temperatures normal ambient temperature then, it is known as the cold lime softening or it can be done at elevated temperature in the range of 108- 116 degree Celsius generally and then we refer this as a hot lime softening. The difference between hot limes softening and cold lime softening in the basic process is not significant okay. All the reaction means majority of these reaction that happens in the cold lime softening, same reaction or happens in the hot line softening as well.

The major difference here is though that these reactions in the like at ambient temperature does not go to the completion whereas, when at elevated temperature these reactions will essentially go to the completion. So, these reactions get completed so like more of these hardness causing compounds are converted to their precipitate and remove. So, we get better efficiency over here.

The only reaction that does not take place at elevated temperature is the first one listed here okay. So, this will not happen in a hot lime softening because the raw water CO2 will be wented out when we are basically doing at a elevated temperature. So, use of lime and soda has basically permits the reduction down to about 8 ppm as a calcium carbonate magnesium reduced to about 2 to 5 ppm because of the lower solubility of magnesium hydroxide okay ,at particularly elevated temperature .

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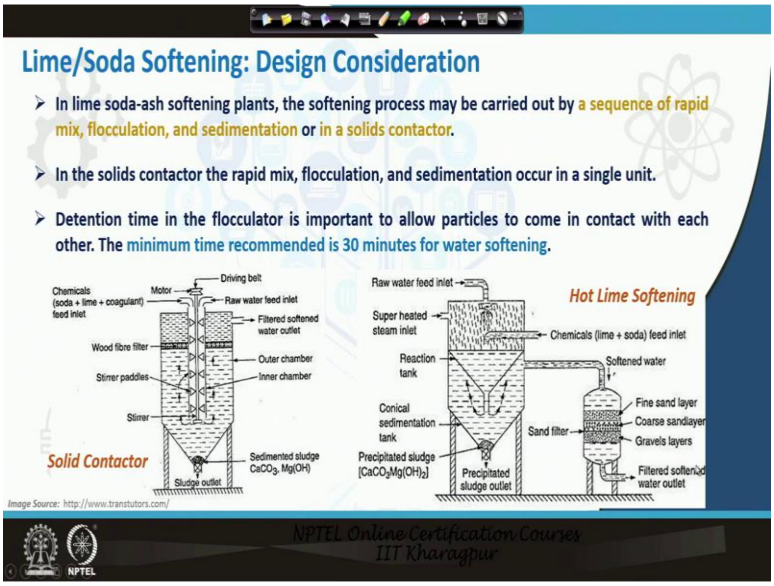

Lime/Soda Softening: Design Consideration

- In lime soda-ash softening plants, the softening process may be carried out by a sequence of rapid mix, flocculation, and sedimentation or in a solids contactor.
- In the solids contactor the rapid mix, flocculation, and sedimentation occur in a single unit.
- Detention time in the flocculator is important to allow particles to come in contact with each other. The minimum time recommended is 30 minutes for water softening.

Image Source: http://www.transtutors.com/

So hot lime softening can produce very good results and can reduce the hardness in a like very efficient manner. The design way if you see it is just basically a contact chamber is needed practically. So, either we can combine this with the coagulation flocculation process as well, if you want to do that okay. Or we can use the solid contractor or that system as well. So, like in lime soda as softening plants it we make this may be carried out by a sequence of rapid mix flocculation and sedimentation as it is done for the coagulation flocculation process.

So, it can be combined also or it can be done in a different stages. So, like the lime soda addition mixing and sedimentation at one stage and then coagulant mixing addition at the next stage or it can be done in a simple solid contractor. So, solid contractor all these processes are like process still remains the same but they are done in a single unit okay. So, like this example of a solid contractor in a normal case, okay so, we can add say chemicals here and then we go we mix it completely.

So, this is our we add the raw water and chemicals and then we mix it so this basically works as a rapid mix and then it is allowed to basically go here. So, here settlement takes place okay and this acts as a basically flocculation and clarification system. Sludge settles comes out and then through a wood filter the water from the through this filter wood fiber filter comes at the top and then filtered softened water might be collected here.

And the sedimented sludge which is practically calcium carbonate or magnesium hydroxide will be collected at the bottom. In the hot lime softening also the same process is done. Only thing is it is done at an elevated temperature so we put the raw water inlet feed we put superheated stream in order to temperature control, we add the chemicals and then, everything is mixed here, reaction takes place. However, settlement processes we want to do at a like again lower temperature.

So, we do not settle it here at a raw temperature we channelize it then then softened water is bought here and then it is filtered. Some settlement like will be taking place here but then it is gets filter and the filtered water outlet will be getting the soft water that way. So, this is how the process is done.

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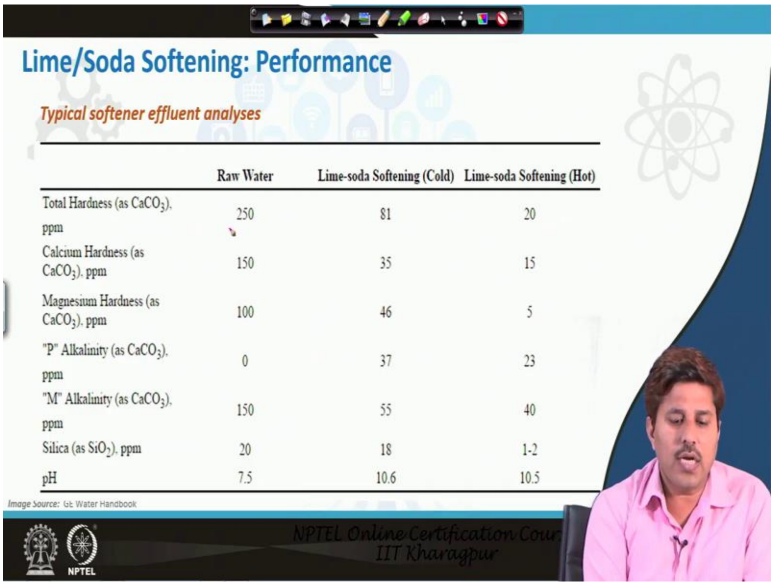

Lime/Soda Softening: Performance

Typical softener effluent analyses

	Raw Water	Lime-soda Softening (Cold)	Lime-soda Softening (Hot)
Total Hardness (as $CaCO_3$), ppm	250	81	20
Calcium Hardness (as $CaCO_3$), ppm	150	35	15
Magnesium Hardness (as $CaCO_3$), ppm	100	46	5
"P" Alkalinity (as $CaCO_3$), ppm	0	37	23
"M" Alkalinity (as $CaCO_3$), ppm	150	55	40
Silica (as SiO_2), ppm	20	18	1-2
pH	7.5	10.6	10.5

Image Source: GE Water Handbook

If you see the typical performance of hot line softening and cold lime softening so in the cold like if raw water inlet has a total hardness of say around 250, so through code lime soda it comes to 81 through hot lime soda it can come down to 20. The calcium hardness say off this to 50 the calcium hardness is 150 and magnesium is 100 so calcium hardness will be reduced down to 36 magnesium hardness will be reduced down to 46 here it is just 5 and 15.

So, it is very effective in the removal of magnesium hardness particularly you see here from 100 to 46 means, 54 percent removal efficiency and here it is basically 54 percent removal efficiency and here it is 95 percent removal efficiency. Then, like the Alkalinity and these things can also be reduced. Silica also can be reduced through this pH here initially 7.5 so in cold lime softening and hot lime softening pH will increase because we are adding lime.

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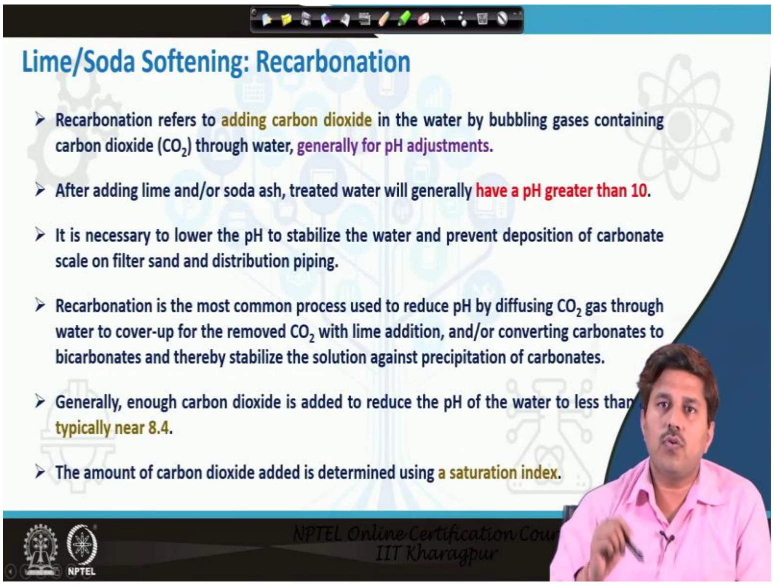

Lime/Soda Softening: Recarbonation

- Recarbonation refers to adding carbon dioxide in the water by bubbling gases containing carbon dioxide (CO_2) through water, generally for pH adjustments.
- After adding lime and/or soda ash, treated water will generally have a pH greater than 10.
- It is necessary to lower the pH to stabilize the water and prevent deposition of carbonate scale on filter sand and distribution piping.
- Recarbonation is the most common process used to reduce pH by diffusing CO_2 gas through water to cover-up for the removed CO_2 with lime addition, and/or converting carbonates to bicarbonates and thereby stabilize the solution against precipitation of carbonates.
- Generally, enough carbon dioxide is added to reduce the pH of the water to less than typically near 8.4.
- The amount of carbon dioxide added is determined using a saturation index.

Now since pH increases, we need to basically control the pH in the final affluent because we cannot supply a water which is having pH greater than 10. So, generally because pH increase is greater than 10 so, we do a recarbanation step where basically we add carbon dioxide in water by bubbling this carbon dioxide gas. And that is basically used generally for the pH adjustment so through this recombination process it we get the pH back to the normal level.

Typically like it should be brought to less than 8.7 typically near 8.4 it is brought okay and recarbanation is generally the most common process for reducing this pH, the way it achieves is diffuses co2 gas through the water to cover up whatever the co2 has removed because whatever co2 was there either through heated it will went out or when we add the lime so co2 will react with the lime and it will go away so this leads to increase in the pH.

So we like replace that co2 back into the system by the recarbanation process so that brings like pH little down and also like it converting carbonates to again bi-carbonates and thereby stabilizing the solution. So, that way pH can be controlled. The amount of carbon dioxide that is required to be added will be basically depending on the saturation index of the system at what temperature we are trying to achieve that.

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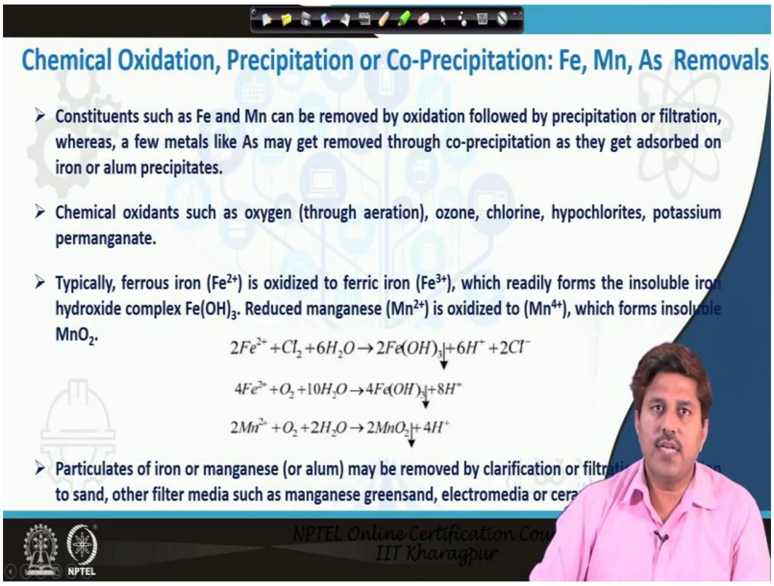

Chemical Oxidation, Precipitation or Co-Precipitation: Fe, Mn, As Removals

- Constituents such as Fe and Mn can be removed by oxidation followed by precipitation or filtration, whereas, a few metals like As may get removed through co-precipitation as they get adsorbed on iron or alum precipitates.
- Chemical oxidants such as oxygen (through aeration), ozone, chlorine, hypochlorites, potassium permanganate.
- Typically, ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which readily forms the insoluble iron hydroxide complex $Fe(OH)_3$. Reduced manganese (Mn^{2+}) is oxidized to (Mn^{4+}), which forms insoluble MnO_2.

$$2Fe^{2+} + Cl_2 + 6H_2O \rightarrow 2Fe(OH)_3\downarrow + 6H^+ + 2Cl^-$$

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3\downarrow + 8H^+$$

$$2Mn^{2+} + O_2 + 2H_2O \rightarrow 2MnO_2\downarrow + 4H^+$$

- Particulates of iron or manganese (or alum) may be removed by clarification or filtr
to sand, other filter media such as manganese greensand, electromedia or cera

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So, that is about the softening process, simple lime soda process. There are other chemical treatments which might be added as an additional components or additional units in the water treatment schemes. These could be like the simple chemical oxidation precipitation or Co precipitate and can results in the removal of compounds like iron and manganese are sending these kind of compounds can be removed. So, compounds like iron and magnesium can simply be removed by the oxidation followed by the precipitation or filtration okay.

So, what we can do, we can use a chemical oxidant. Generally, like like we can just simple use, we can simply use oxygen which can be provided through variation. So, practically if you are having aeration before radiation you need before say coagulation flocculation then we do not need separate unit for removal of the these kind of heavy metals. But many times if you do not if you are not providing aeration and if say we are not kind of getting a groundwater which is we are getting a groundwater which is reaching iron and magnesium materials, so then we may need to add a chemical oxidant.

And since we are not aeration so we can use like ozone chlorine, hypochlorite, potassium permanganate, any of these sort of oxidant can be used okay. And what these oxidant do they basically convert the ferrous iron to ferric iron which basically settles now as a ferric hydroxide. And they like reduced manganese plus 2 is oxidized to manganese plus 4 and then settles as they manganese oxide.

So like either we use chlorine oxygen or whatever oxidant we can use it is not necessarily that chlorine or oxygen has to be used any like ozone or hypochlorite or potassium permanganate or there are a few other oxidants as well. So, all of them basically what they do they react with and convert ferrous to ferric and as a result because it is in the water so it will convert to ferric hydroxide and that will precipitate.

Similarly manganese converts into insoluble manganese oxide and then that also precipitate, precipitate of these iron and manganese may be removed either by clarification or filtration so either we like put it to a sedimentation Basin and then remove it or we can just simply use a filter sand filter or other. There are other media is also very popular and particularly for the removal of iron and manganese. This manganese green sand is a very popular media. So, we can use this manganese green sand or electro media or some ceramic media may also be used for the purpose of filtration.

So this is how we remove some of the dissolved substances through chemical oxidation and precipitation. Some compounds might be actually removed through Co precipitation as well like few metals like arsenic. So, they get removed through Co precipitation as they get adsorbed on the iron or alum precipitates. So, if there are arsenic present in the system okay which is useful in the groundwater. So, surface water sources which go through the typical conventional treatment systems would not require arsenic removal unit because arsenic is unlikely to present in the surface water.

But the groundwater sources let us say if they are having substances like arsenic so, arsenic can like this the iron hydroxide or ferric hydroxide precipitates which are being formed they act as an adsorbent for the arsenic and arsenic can come and stick to the surface of these hydroxide and because these are precipitating, these are settling so along with arsenic will also settle. So, arsenic leaves the liquid phase come adsorbed to the the surface of these compounds and in the process it gets precipitated.

So that is how arsenic can also be removed through a process like Co precipitation. So, actually it is a precipitation of arsenide on but arsenic iron or alum but arsenic also gets precipitated alongside.

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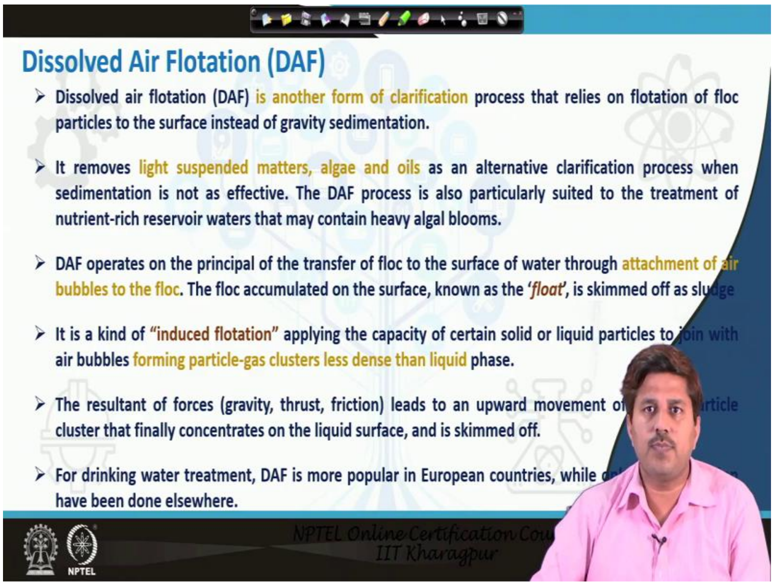

Dissolved Air Flotation (DAF)

- Dissolved air flotation (DAF) is another form of clarification process that relies on flotation of floc particles to the surface instead of gravity sedimentation.
- It removes light suspended matters, algae and oils as an alternative clarification process when sedimentation is not as effective. The DAF process is also particularly suited to the treatment of nutrient-rich reservoir waters that may contain heavy algal blooms.
- DAF operates on the principal of the transfer of floc to the surface of water through attachment of air bubbles to the floc. The floc accumulated on the surface, known as the '*float*', is skimmed off as sludge
- It is a kind of "induced flotation" applying the capacity of certain solid or liquid particles to join with air bubbles forming particle-gas clusters less dense than liquid phase.
- The resultant of forces (gravity, thrust, friction) leads to an upward movement o[illegible]rticle cluster that finally concentrates on the liquid surface, and is skimmed off.
- For drinking water treatment, DAF is more popular in European countries, while [illegible] have been done elsewhere.

The other alternate process which can be used is the dissolved where floatation which is a substitution for the sedimentation or clarification process. So, the dissolve air flotation or DAF is basically another form of clarification which relies on the floatation of the floc particles, instead of the gravity sedimentation. So, in sedimentation what happens that the specific gravity of the particles is higher and they tend to settle at the bottom.

Here we create a system where the specific gravity of the net cluster it is not just particle particle may still have a little higher specific gravity. But we make that particle to attach stick with an air bubble because air bubble is a very lightweight and immense particle sticks to that so they form a kind of cluster and then cluster is relatively lighter than the water and then that flows okay. So, that comes out and then it floats on the top which is known as the float and then it is skimmed off.

So, basically through the attachment of air bubbles to the floc okay and then we get these flocs accumulated on the surface and then they float off. So, this induced floatation which is provided through the dissolved air flotation okay is basically applies to the capacity of certain solid and liquid particles to join with them and then this forming a particle gas cluster which is less dense than the liquid phase.

The resultant force because it is less dense so, the gravity, thrust and friction and buoyancy see and everything combined, it will lead to an upward movement of these gas particle cluster and finally they go on the surface. This is basically dissolve your floatation is a very effective for the removal of these sediments which are relatively lighter weight okay. So, it's particularly suited to the treatment of nutrient rich reservoir waters that may contain heavy algal bloom okay.

Then if water is containing say light suspended matters, algae oil, these kind of compounds are more effectively removed through dissolved air floatation than the simple or plain sedimentation process. Even after the flocculation process so micro flocs and those things many times people like not many times but quite a few places it is dissolved where floatation is used particularly in the European countries okay.

So, it is more popular relatively in the European countries at less at other places worldwide there is very limited installation not many places it is installed.

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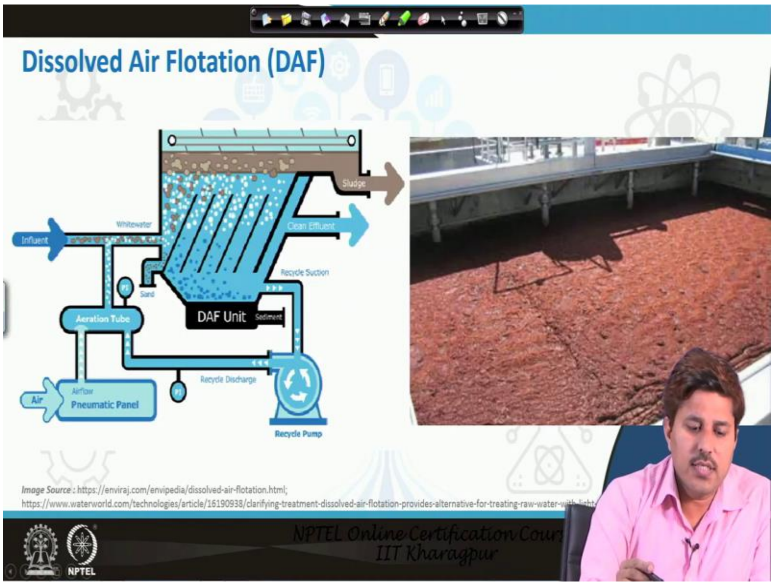

Dissolved Air Flotation (DAF)

Image Source : https://enviraj.com/envipedia/dissolved-air-flotation.html; https://www.waterworld.com/technologies/article/16190938/clarifying-treatment-dissolved-air-flotation-provides-alternative-for-treating-raw-water-with-light-

So, how it works the principle is simple we let the influent come in okay and basically through pneumatic panel, we take air and we supply air at a much larger weight okay much larger pressure and flow like the flow of air is quite large here so what happens it reduces lot of bubbles and then these particles which are present in the influent gets stick to the air bubbles and then they will float at the top and then through a skimmer process they will be collected as a sludge.

So like this you can see an example this is basically top of a dissolve air floatation system. So, this kind of like all the sludge particles will be coming on the top okay you can see here that all the sludge particles will be coming on the top and then they are float they are basically skimmed off from there. So, the water beneath this surface which is looking very dirty is relatively much cleaner okay. All this dirty layer all this, the flocs or sludge particle.

So dissolver floatation is used for just as we were discussing in the previous lecture as well. That it is one of the mechanisms for the sludge thickening as well okay. So, instead of like for what is if we send in an influence which is containing or the sludge stream then we can use the DAF unit for collecting this sludge also which is more thickened. So, that way we can use the dissolve air flotation systems.

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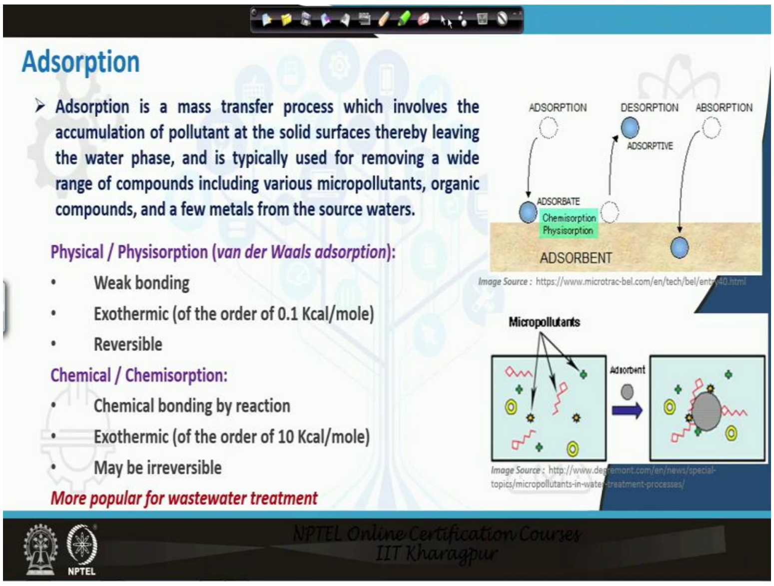

Adsorption

- Adsorption is a mass transfer process which involves the accumulation of pollutant at the solid surfaces thereby leaving the water phase, and is typically used for removing a wide range of compounds including various micropollutants, organic compounds, and a few metals from the source waters.

Physical / Physisorption (*van der Waals adsorption*):

- Weak bonding
- Exothermic (of the order of 0.1 Kcal/mole)
- Reversible

Chemical / Chemisorption:

- Chemical bonding by reaction
- Exothermic (of the order of 10 Kcal/mole)
- May be irreversible

More popular for wastewater treatment

Image Source : https://www.microtrac-bel.com/en/tech/bel/entry40.html

Image Source : http://www.degremont.com/en/news/special-topics/micropollutants-in-water-treatment-processes/

The another process which is recognized as advanced treatment systems are adsorption which is practically a mass transfer process. And what adsorption does we have been discussing this from time to time but now, like if we talk about the exact process itself, so, adsorption is the process which involves the accumulation of the pollutant at a solid surface. So, we are having a solid surface let us say this surface is absorbent okay.

And we are having contaminant present contaminant mass present in the liquid so that actually leaves the liquid phase come stick to the solid phase okay. So that process is called adsorption. If it is attaching to the surface it is called adsorption if it is entering into the body of the adsorbent this is known as the absorption so that is difference between adsorption and absorption. In adsorption it will retain stick to the surface in absorption.

It might actually come into the body of the adsorbent material and if it leaves back we call that process desorption. Now, this attachment at the surface particularly which is important is either physical attachment which is known as physics option or chemical attachment which is known as chemists option. So, physical attachments are basically the weak bonding. These are generally the exothermic processes, reversible reactions, whereas chemical reactions are through chemical bonding reactions.

They are also generally exothermic, but the order of the energy is much higher and they may be irreversible okay. These types of systems are more popular for wastewater treatment. However, in water treatment also for the removal of some like specific micropollutants or organic compound or some metals these adsorbents are used. So, these adsorbents can be like used for removal of arsenic also.

So, iron based or activated alumina based adsorbents are popular for the mole of arsenic fluoride also can be removed through adsorption process. In fact many of the micropollutants tend these can be removed. So, like we have these micropollutants say in the medium and we add an adsorbent and majority of them come and stick to the surface of the adsorbent so, water gets relatively cleaner so, that is what is the basic adsorption process.

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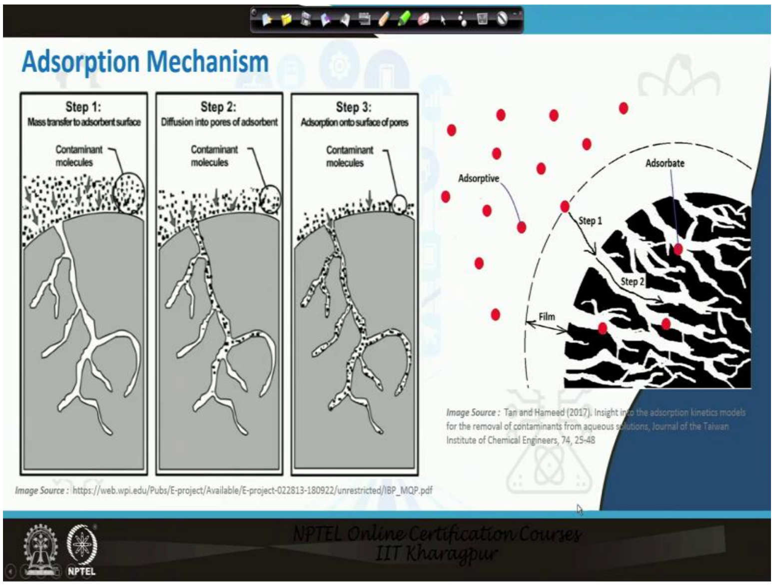

Adsorption Mechanism

Image Source : Tan and Hameed (2017). Insight into the adsorption kinetics models for the removal of contaminants from aqueous solutions, Journal of the Taiwan Institute of Chemical Engineers, 74, 25-48

Image Source : https://web.wpi.edu/Pubs/E-project/Available/E-project-022813-180922/unrestricted/IBP_MQP.pdf

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If you see the mechanism okay so mass transfer of the adsorbent surface it first comes from the surface. Then if it is a porous medium so it can diffuse within the pores and it can stick get attached to the surface within the pores as well. So, that is how the like if you see the microscopic mechanism for the adsorption process.

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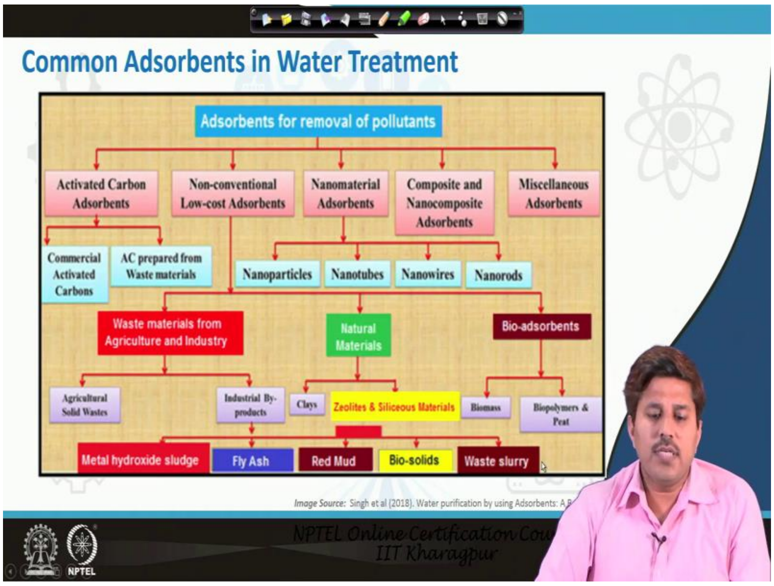

Common Adsorbents in Water Treatment

Adsorbents for removal of pollutants

- Activated Carbon Adsorbents
  - Commercial Activated Carbons
  - AC prepared from Waste materials
- Non-conventional Low-cost Adsorbents
  - Waste materials from Agriculture and Industry
    - Agricultural Solid Wastes
    - Industrial By-products
      - Metal hydroxide sludge
      - Fly Ash
      - Red Mud
      - Bio-solids
      - Waste slurry
  - Natural Materials
    - Clays
    - Zeolites & Siliceous Materials
  - Bio-adsorbents
    - Biomass
    - Biopolymers & Peat
- Nanomaterial Adsorbents
  - Nanoparticles
  - Nanotubes
  - Nanowires
  - Nanorods
- Composite and Nanocomposite Adsorbents
- Miscellaneous Adsorbents

Image Source: Singh et al (2018). Water purification by using Adsorbents: A R

The common adsorbents that are used for removal of water pollutants they are the activated carbon base adsorbents, so granular activated carbon powder activated carbon that those kind of compounds, a nano material based adsorbent so nanoparticles nano tubes, nano wires, nano rods then the composite and nano composite adsorbents okay. There are non-conventional low-cost adsorbent as well. So, like waste material based or agricultural industry based adsorbent and then there are some bio adsorbents.

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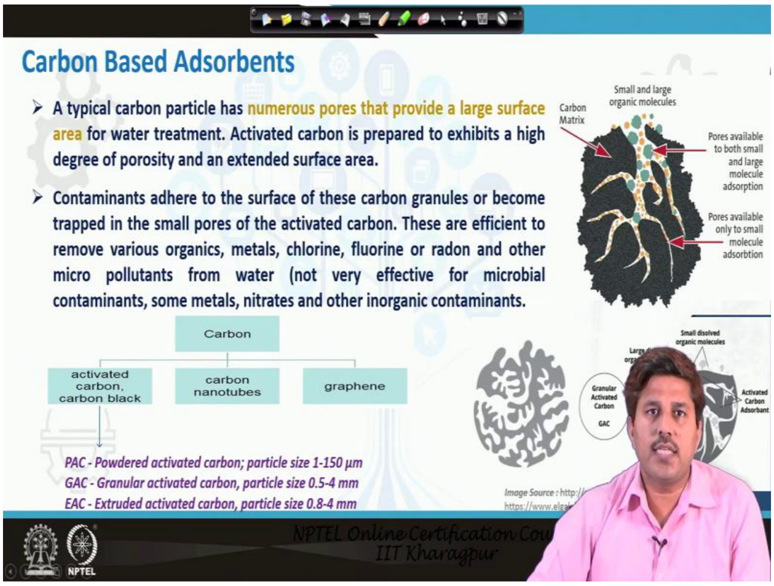

Carbon Based Adsorbents

- A typical carbon particle has numerous pores that provide a large surface area for water treatment. Activated carbon is prepared to exhibits a high degree of porosity and an extended surface area.
- Contaminants adhere to the surface of these carbon granules or become trapped in the small pores of the activated carbon. These are efficient to remove various organics, metals, chlorine, fluorine or radon and other micro pollutants from water (not very effective for microbial contaminants, some metals, nitrates and other inorganic contaminants.

Carbon

- activated carbon, carbon black
  - PAC - Powdered activated carbon; particle size 1-150 µm
  - GAC - Granular activated carbon, particle size 0.5-4 mm
  - EAC - Extruded activated carbon, particle size 0.8-4 mm
- carbon nanotubes
- graphene

Image Source : http://
https://www.elgal

So these there are like variety of adsorbents are there but the one which are most used are carbon-based adsorbents particularly for the removal of water contaminants or water treatment.

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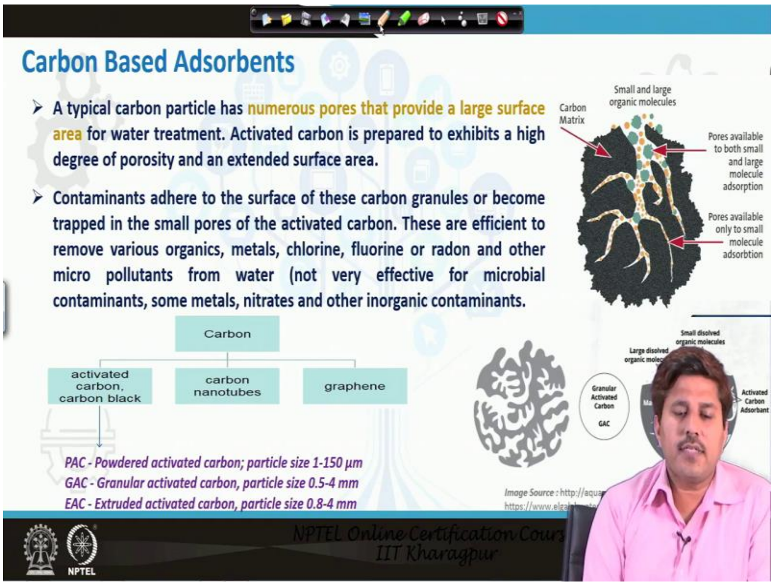

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Carbon
activated carbon, carbon black
carbon nanotubes
graphene

PAC - Powdered activated carbon; particle size 1-150 μm
GAC - Granular activated carbon, particle size 0.5-4 mm
EAC - Extruded activated carbon, particle size 0.8-4 mm

Image Source : http://aqua
https://www.elgal

These carbon adsorbents are like carbon typically has numerous pores and provide a large surface area and if it is if like we activate that, so then, it exhibits a very high degree of porosity and extended surface area. So, because of this porosity and extended surface area this contaminant gets kind of attached to the pores within the medium itself, within the activated carbon itself.

This is very efficient in removal of organics, metals, chlorine, fluorine radon various other micropolitan present in the water, okay. It is not very effective for removal of microbial contaminants metals and kind of various inorganic constituents. So, typical like activated carbon will have a matrix like this and within the pore structures it can go so microscopic weight is basically there are lot lot of pores and then adsorbents can get stick to that.

So in carbon we can have carbon nanotube we can use graphene's we can use activated carbon or carbon black and then it can come in the different forms like the powder activated carbon where particle size is of the order of 1 to 150 micro meter. Then granular activated carbon particle size is 0.5 to 4 millimeter okay and the extruded activated carbon where particle size is around 0.8 to 4 millimeter.

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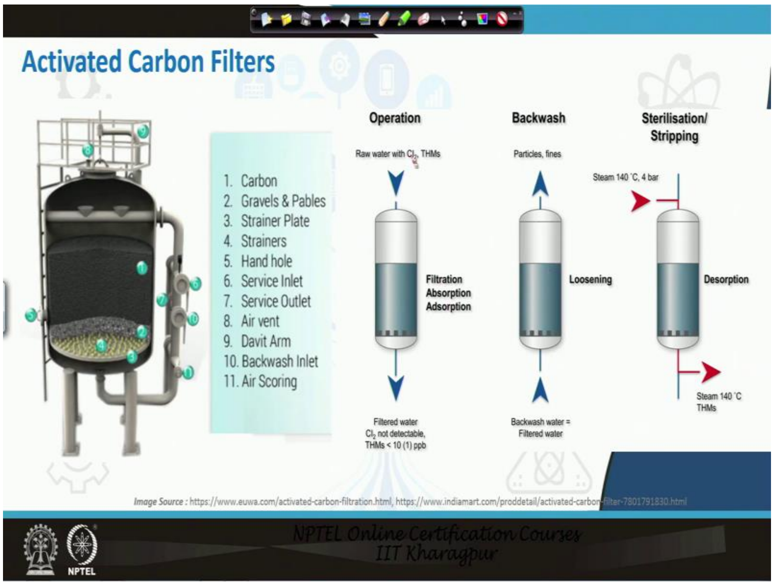

Activated Carbon Filters

1. Carbon
2. Gravels & Pables
3. Strainer Plate
4. Strainers
5. Hand hole
6. Service Inlet
7. Service Outlet
8. Air vent
9. Davit Arm
10. Backwash Inlet
11. Air Scoring

Image Source : https://www.euwa.com/activated-carbon-filtration.html, https://www.indiamart.com/proddetail/activated-carbon-filter-7801791830.html

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So that way like these are there and it is GAC and PAC particularly the granular activated carbon has very like popular role in the water treatment so many places it is used for the adsorption of the contaminants from the water even in the wastewater as well. So, if you see the like activated carbon filter you may have a chamber like this where basically this a layer of activated carbon would be there okay.

So, this is the activated carbon layer then we can have the granules and pebbles at the bottom, we will add the most bottom will have a strainer plate and then strainers and then we can actually have an influential for pouring the water. And if it is done in a pressure mostly it is done in a pressure system, so then we will mean the pressure control devices okay. Usually the operation is from the top to bottom.

So, the water will be put at the top and then under pressure or sometimes even by gravity also if you are not applying pressure it will flow to the bottom. But generally because the pore sizes are small so it is mostly like pressure operated. The filtered water water will pass through this layer of the adsorbent similar to like filtration process. And in the process the contaminant will get adsorbed and the filtered water will be getting which is basically the treated water.

Now what happens that when this cycle goes on the impurities are getting entrapped in the layer of the carbon or of the adsorbent. So, adsorbent has a capacity to adsorb and once like substantial amount of water has passed through a lot of impurities are already trapped in the medium. So, it slowly or progressively loses its ability to adsorb because it has already saturated with the contaminants. So, like if you have X amount of surface area and all the adsorbent, all the surface area is occupied with the contaminant.

So, in that case either flow will stop or the removal will not be effective through these media. So, in that case is the adsorbent media is regenerated or a backwash process is used. So, backwash water is like again similar to the filtration step we push the treated water from the bottom it flows through up and then basically takes it makes it to some like loosened or fluidized state and takes the particles in the spent. So that is generally the backwash water.

In most cases it is done this way only whereas basically the direction of the flow is from top to bottom whereas for the back washing purpose it goes from the bottom to top, so up flow basically it is a counter-current process. The flow operation flow is from top to bottom whereas backwash flow is from bottom to top okay. So, that is about like its operation.

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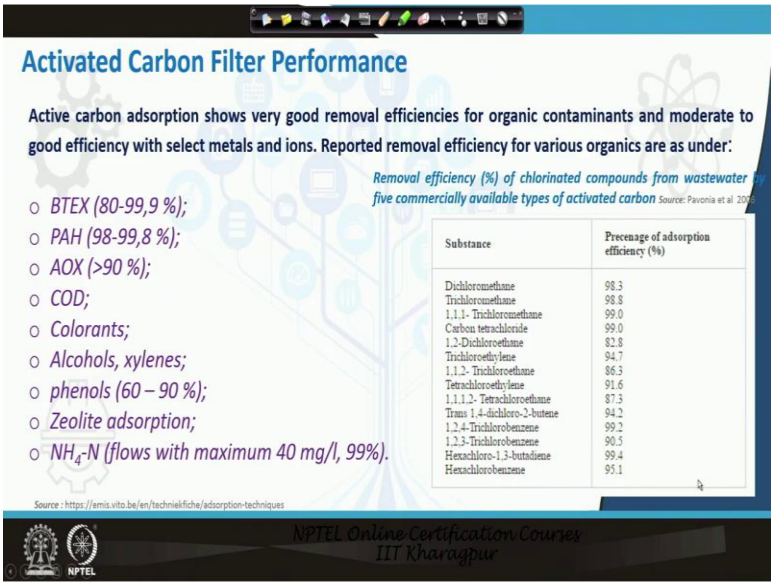

Activated Carbon Filter Performance

Active carbon adsorption shows very good removal efficiencies for organic contaminants and moderate to good efficiency with select metals and ions. Reported removal efficiency for various organics are as under:

- *BTEX (80-99,9 %);*
- *PAH (98-99,8 %);*
- *AOX (>90 %);*
- *COD;*
- *Colorants;*
- *Alcohols, xylenes;*
- *phenols (60 – 90 %);*
- *Zeolite adsorption;*
- *NH_4-N (flows with maximum 40 mg/l, 99%).*

Removal efficiency (%) of chlorinated compounds from wastewater by five commercially available types of activated carbon Source: Pavonia et al 2006

Substance	Precenage of adsorption efficiency (%)
Dichloromethane	98.3
Trichloromethane	98.8
1,1,1- Trichloromethane	99.0
Carbon tetrachloride	99.0
1,2-Dichloroethane	82.8
Trichloroethylene	94.7
1,1,2- Trichloroethane	86.3
Tetrachloroethylene	91.6
1,1,1,2- Tetrachloroethane	87.3
Trans 1,4-dichloro-2-butene	94.2
1,2,4-Trichlorobenzene	99.2
1,2,3-Trichlorobenzene	90.5
Hexachloro-1,3-butadiene	99.4
Hexachlorobenzene	95.1

Source : https://emis.vito.be/en/techniekfiche/adsorption-techniques

If you see the performance it is very effective for the removal of organic contaminants and moderately moderate to goody-good efficiency so, for the removal of the selected metals and ions. More sever for organic recalcitrant compounds this is more preferred and if you see various organics like benzene, toluene, xylene etc, then, poly aromatic hydrocarbons, COD, colorants, alcohol phenols. So, it can actually remove very nicely.

For certain like these are the chlorinated compounds or chlorinated or make compounds various pesticides and these things you see the removal efficiencies are like around in the rate of 98% 99% mostly in that range okay. So, it is very effective in removal of these impurities.

Then there is another process which is ion exchange which is somewhat similar to adsorption process okay.

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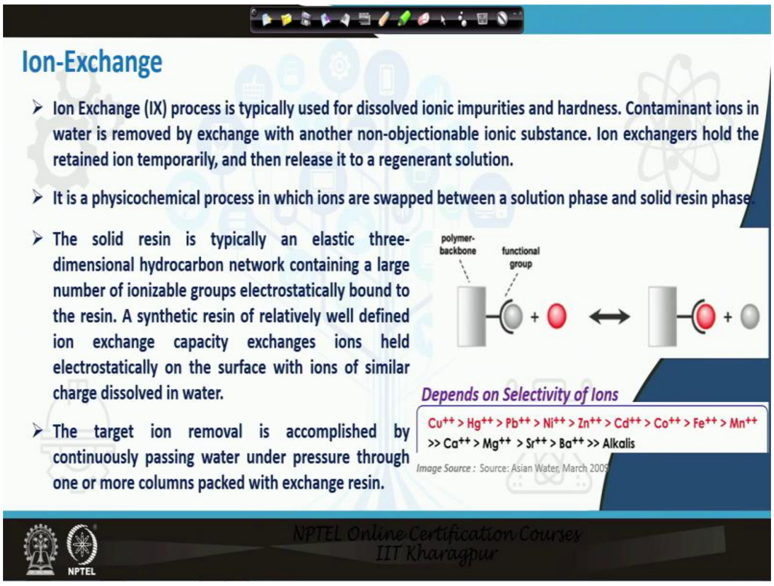

Ion-Exchange

- Ion Exchange (IX) process is typically used for dissolved ionic impurities and hardness. Contaminant ions in water is removed by exchange with another non-objectionable ionic substance. Ion exchangers hold the retained ion temporarily, and then release it to a regenerant solution.
- It is a physicochemical process in which ions are swapped between a solution phase and solid resin phase.
- The solid resin is typically an elastic three-dimensional hydrocarbon network containing a large number of ionizable groups electrostatically bound to the resin. A synthetic resin of relatively well defined ion exchange capacity exchanges ions held electrostatically on the surface with ions of similar charge dissolved in water.
- The target ion removal is accomplished by continuously passing water under pressure through one or more columns packed with exchange resin.

Depends on Selectivity of Ions

$Cu^{++} > Hg^{++} > Pb^{++} > Ni^{++} > Zn^{++} > Cd^{++} > Co^{++} > Fe^{++} > Mn^{++} >> Ca^{++} > Mg^{++} > Sr^{++} > Ba^{++} >>$ Alkalis

Image Source : Source: Asian Water, March 2009

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The difference is that in adsorption there is a surface and material comes and sticks to the surface in ion exchange we have a polymer backbone attached to a functional group. That functional group is already having a ion which is of which is which is say less pollutant ion on which does not have any polluting effect. So, less harmful ion which is not a harmful ion. so it is already holding an ion.

And what happens that the contaminant ion, if you want to remove say this contaminant ion so there is a swapping between these two ions, this non-toxic ion or the ion which is not harmful will be released. This is actually not harmful okay so this will be released. And the ion which you want to remove from the water will stick to the polymer backbone. So, there is a strapping takes place or the exchange takes place exchange of ions takes place and that's why this process is known as the ion exchange process.

So, this is typically like it can remove the dissolved ionic impurities obviously for non ionic impurities it will not work because it is ion exchange process so it has to work on only ionic impurities. The contaminant ion in the water will be removed by exchange with another non objectionable and ionic substance okay. And this is retained then this is retained in this for some time and when basically again the entire resin or entire set up gets saturated then this is washed out okay.

So, then we put a regenerate solution again which swaps this ion which takes away this ion and again put a like ion of which is a non objectionable and back to the resin okay and the resin is again ready for use. So, it is a practically physical chemical process where ions are trapped between a solution phase and the solid phase. The solid phase reason is typically in kind of elastic three-dimensional hydrocarbon network and this basically contains a large number of ionizable groups which has electrostatically bound through this resin.

The target ion removal is accomplished by continuously passing the water. So, we are actually passing the water continuously under pressure through one or more columns packed with the exchange. Now, which ions will be removed because see we you have a place where you can you have a place where there is one iron is already attached and you want another and to come and strap it okay.

But it is not just in the water there is just one ion there might be more than one different type of ions is present so which one is going to come and swap this depends on the selectivity of ion. So, the resin may be very selective at times that resin is particularly selective to one say one type of ion so it will actually pick those and first. But many resins are not that selective so they have a like range of selectivity or preferences for different times like a copper will be preferred over mercury will be preferred over LED will be preferred over nickel will be preferred over Jing cadmium.

So, that way least preferred is alkali an and these things so if we are having a system with the alkali and which is not toxic anyway not too toxic anyway, so we are actually having a resin with alkali ion and say we are in water we are having a zinc ion or say cadmium ion now this cadmium ion or zinc ion has very high affinity as opposed to the alkali and so when they are present in the solution, this alkaline will be released and the zinc or cadmium and will come and stick to the exchanger raisins.

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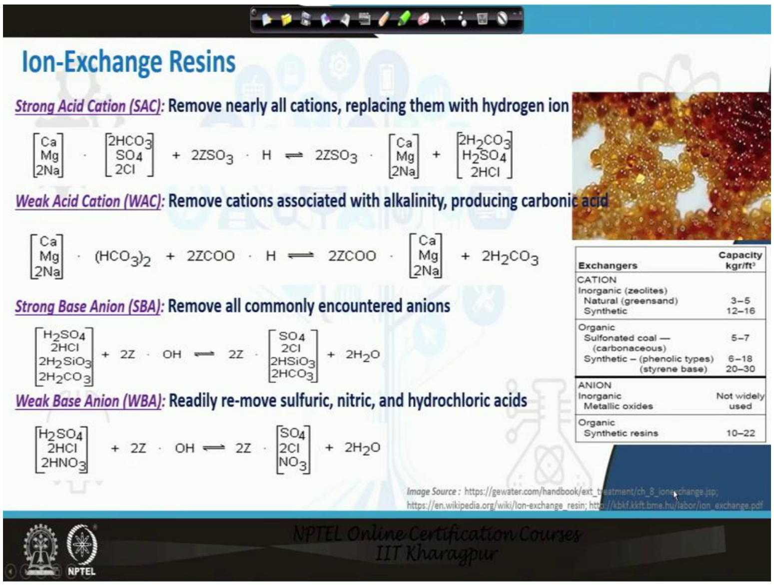

Ion-Exchange Resins

Strong Acid Cation (SAC): **Remove nearly all cations, replacing them with hydrogen ion**

$$\begin{bmatrix} Ca \\ Mg \\ 2Na \end{bmatrix} \cdot \begin{bmatrix} 2HCO_3 \\ SO_4 \\ 2Cl \end{bmatrix} + 2ZSO_3 \cdot H \rightleftharpoons 2ZSO_3 \cdot \begin{bmatrix} Ca \\ Mg \\ 2Na \end{bmatrix} + \begin{bmatrix} 2H_2CO_3 \\ H_2SO_4 \\ 2HCl \end{bmatrix}$$

Weak Acid Cation (WAC): **Remove cations associated with alkalinity, producing carbonic acid**

$$\begin{bmatrix} Ca \\ Mg \\ 2Na \end{bmatrix} \cdot (HCO_3)_2 + 2ZCOO \cdot H \rightleftharpoons 2ZCOO \cdot \begin{bmatrix} Ca \\ Mg \\ 2Na \end{bmatrix} + 2H_2CO_3$$

Strong Base Anion (SBA): **Remove all commonly encountered anions**

$$\begin{bmatrix} H_2SO_4 \\ 2HCl \\ 2H_2SiO_3 \\ 2H_2CO_3 \end{bmatrix} + 2Z \cdot OH \rightleftharpoons 2Z \cdot \begin{bmatrix} SO_4 \\ 2Cl \\ 2HSiO_3 \\ 2HCO_3 \end{bmatrix} + 2H_2O$$

Weak Base Anion (WBA): **Readily re-move sulfuric, nitric, and hydrochloric acids**

$$\begin{bmatrix} H_2SO_4 \\ 2HCl \\ 2HNO_3 \end{bmatrix} + 2Z \cdot OH \rightleftharpoons 2Z \cdot \begin{bmatrix} SO_4 \\ 2Cl \\ NO_3 \end{bmatrix} + 2H_2O$$

Exchangers	Capacity kgr/ft³
CATION	
Inorganic (zeolites)	
Natural (greensand)	3–5
Synthetic	12–16
Organic	
Sulfonated coal — (carbonaceous)	5–7
Synthetic – (phenolic types)	6–18
(styrene base)	20–30
ANION	
Inorganic	
Metallic oxides	Not widely used
Organic	
Synthetic resins	10–22

Image Source : https://gewater.com/handbook/ext_treatment/ch_8_ionexchange.jsp; https://en.wikipedia.org/wiki/Ion-exchange_resin; http://kbkf.kkft.bme.hu/labor/ion_exchange.pdf

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So, there are different types of ion exchange resins okay. The strong acid cations which removes nearly all cations replacing them with the hydrogen ions and then weak acid cations which removes the cations associated with the alternative producing kind of carbonic acid. Then we have strong base and ions which removes commonly all encountered anions and then weak base and ions which removes the sulphuric, nitric and hydrochloric acid kind of compounds okay.

And typically a resin will look like this and we may get the details like for if you see the capacity, so for cationic raisins geo light, the natural it is in the range of this synthetic and foreign ion, so like each region comes with its own capacity mentioned that how much it can adsorb.

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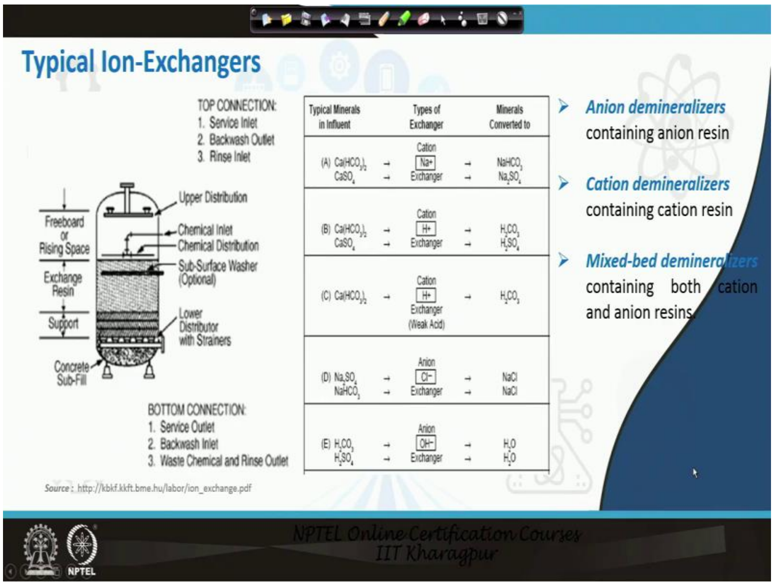

Typical Ion-Exchangers

TOP CONNECTION:
1. Service Inlet
2. Backwash Outlet
3. Rinse Inlet

BOTTOM CONNECTION:
1. Service Outlet
2. Backwash Inlet
3. Waste Chemical and Rinse Outlet

Typical Minerals in Influent		Types of Exchanger		Minerals Converted to
(A) $Ca(HCO_3)_2$ $CaSO_4$	→ →	Cation $\boxed{Na+}$ Exchanger	→ →	$NaHCO_3$ Na_2SO_4
(B) $Ca(HCO_3)_2$ $CaSO_4$	→ →	Cation $\boxed{H+}$ Exchanger	→ →	H_2CO_3 H_2SO_4
(C) $Ca(HCO_3)_2$	→	Cation $\boxed{H+}$ Exchanger (Weak Acid)	→	H_2CO_3
(D) Na_2SO_4 $NaHCO_3$	→ →	Anion $\boxed{Cl-}$ Exchanger	→ →	NaCl NaCl
(E) H_2CO_3 H_2SO_4	→ →	Anion $\boxed{OH-}$ Exchanger	→ →	H_2O H_2O

- ***Anion demineralizers*** containing anion resin
- ***Cation demineralizers*** containing cation resin
- ***Mixed-bed demineralizers*** containing both cation and anion resins.

Source : http://kbkf.kkft.bme.hu/labor/ion_exchange.pdf

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Typical ion exchangers are similar to the adsorption units. Ion exchanger also is a very quick process because it's the ionic exchange so we do not need much of much time to like for process to complete. So, it take it proceeds very quickly so as soon as water is exposed it will like swap the ions and it will pass through and then procedure is similar okay. The typical reactions can be this and we can have an ion demineralizer which is containing an ionic reason for the removal of anions.

We can have cation demineralizer which is containing the cationic reason for removal of cations or we may have mixed bed demineralized which basically contains both the resin and can eventually remove both type of the ions.

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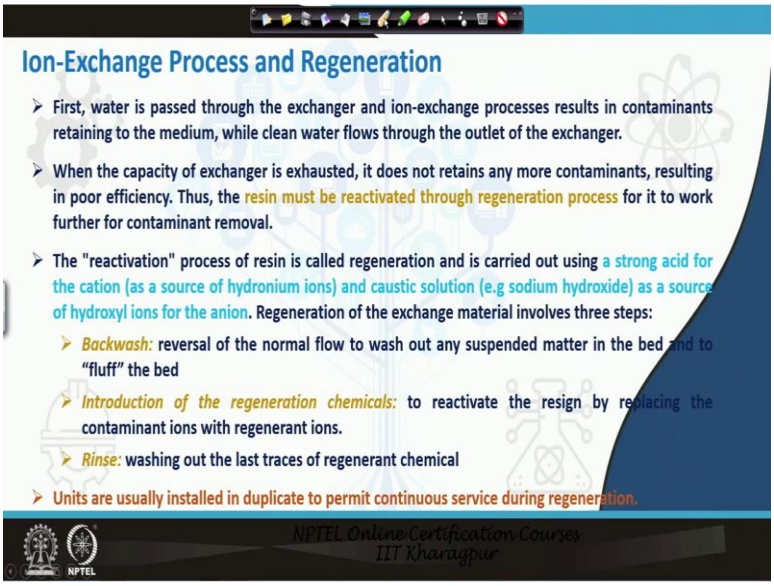

Ion-Exchange Process and Regeneration

- First, water is passed through the exchanger and ion-exchange processes results in contaminants retaining to the medium, while clean water flows through the outlet of the exchanger.
- When the capacity of exchanger is exhausted, it does not retains any more contaminants, resulting in poor efficiency. Thus, the resin must be reactivated through regeneration process for it to work further for contaminant removal.
- The "reactivation" process of resin is called regeneration and is carried out using a strong acid for the cation (as a source of hydronium ions) and caustic solution (e.g sodium hydroxide) as a source of hydroxyl ions for the anion. Regeneration of the exchange material involves three steps:
  - *Backwash:* reversal of the normal flow to wash out any suspended matter in the bed and to "fluff" the bed
  - *Introduction of the regeneration chemicals:* to reactivate the resign by replacing the contaminant ions with regenerant ions.
  - *Rinse:* washing out the last traces of regenerant chemical
- Units are usually installed in duplicate to permit continuous service during regeneration.

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The regeneration process of ion exchanger is also very important unlike adsorbent. Adsorbent regeneration is again like through simple back washing and then we can achieve. But here we have to use a particular solution which makes your generally the acid or alkali regenerant are used. So, we use these solutions so that whatever impurities are entrapped in the resin they get back into this paint and the resin is ready for the use again.

So what happens like in the normal process, water will be passed through the exchanger and an exchange process will result in the contaminant removal. Now, once the capacity of exchanger is exhausted, it will not retain any more contaminants and then, we must reactivate the resin through regeneration process and this process is basically we use a strong acid for the cation resins and a caustic strong castex solution as a source of hydroxyl and for the anions.

And then we do backwards means reversal of normal flow to wash out so that generally flops the bed we introduce the regenerated chemical there so that it can actually like take away it can replace the contaminated ion with the regenerant ion which we want to use. And then after that we rinse it so that our system is again ready for use okay. Units are generally starting like we install in duplicate so that the continuous service is in short the one when one unit is in regeneration.

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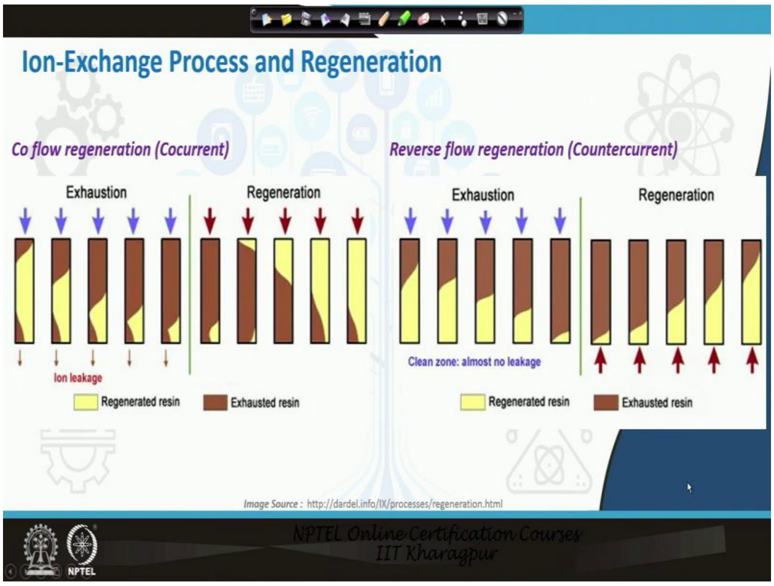

Ion-Exchange Process and Regeneration

Co flow regeneration (Cocurrent)

Reverse flow regeneration (Countercurrent)

Image Source : http://dardel.info/IX/processes/regeneration.html

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It is not that the system has completely stopped we can use the another unit for the purpose. Now the regeneration can be Co flow or reverse flow regeneration. So, co flow is let us say we are passing the like during the normal operation we are passing water from the top. So, let us say these are the exhausted ions so initially from the top will start the ions getting exhausted and slowly progressively we will see that majority of this is exhausted.

Once this is exhausted then, we start passing the regenerated solution. So, it will start flushing these exhausted items and then progressively we will see that majority of this is again available for reuse okay. Ah The other mechanism is the counter current or reverse flow regeneration where again the normal operation is similar. But regeneration time we actually start back flow so, we start like a flow we pass the solution from the bottom and collect it from the top.

The difference here is that when you after regeneration because it is being washed out from the bottom so, you may have some amount left in the corner. And when you start flow again this call the things in the corner might come out okay with the flow. So, the treatment efficiency might not be that good once you start this system whereas in counter current because you are flushing from the bottom, so even if some contaminant is left over, it will be left over at the top, and then, when you start the exhaustion process when you start basically the normal operation process so the bottom portion from where water is coming is clean and as a result will be basically getting cleaner stuff.

So there was almost no leakage where there is possibility of ion leakage because there are ions retained in the bottom. So, the possibility of a leakage will be there during normal service operation if you are doing a co flow regeneration whereas in counter current regeneration that problem is taken care of.

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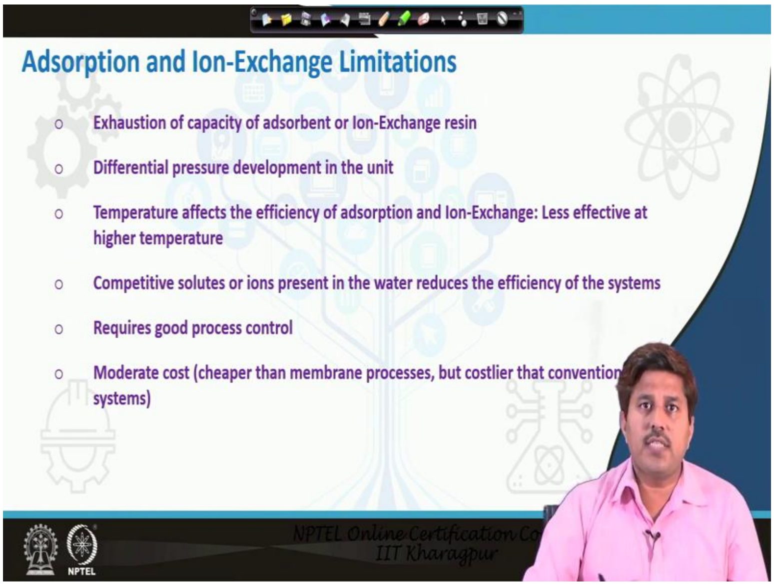

Adsorption and Ion-Exchange Limitations

- Exhaustion of capacity of adsorbent or Ion-Exchange resin
- Differential pressure development in the unit
- Temperature affects the efficiency of adsorption and Ion-Exchange: Less effective at higher temperature
- Competitive solutes or ions present in the water reduces the efficiency of the systems
- Requires good process control
- Moderate cost (cheaper than membrane processes, but costlier that convention systems)

Now these adsorption and ion exchange process has certain limitations as well. So, the exhaustion of capacity like if the capacity is exhausted then we need to kind of either regenerate it or use it regeneration also might be done for several cycles, but not for infinite time. So, it if it gets completely exhausted then we have to kind of change the media or resin. There is a possibility of differential pressure development in the unit working under pressure the temperature also affects the efficiency of these processes.

So, these are less effective at higher temperature because at higher temperatures the kinetic energy of the particles are more. So, they not like they not prefer to get stick to it one place because of higher kinetic energy they will move being more like rotation or motion period and that is allowed in the fluid. So, once they come and stick to the solid surface their transitional motion or rotational motion is stopped. So, in order to ensure that they want to remain in the fluid so this adsorption is lesser at higher temperature and so is the ion exchange.

Then, competitive solutes are and present in the water will also reduce the efficiency of the system as we were discussing if you are having more than one solute in case of adsorption or more than one ion in case of the ion exchanger systems, so the efficiency might get reduced, because there will be competition you have limited space, limited resins space for these ions to get attached or limited surface area for the different solutes to come and stick in the adsorption process.

So if there are more number or more different type of solutes or ions are present so they will compete with each other and as a result the efficiency total efficiency might get decreased. This requires a good process control and cost wise they are of work at a moderate cost. So, they are cheaper than membrane process but costlier than the conventional system. So, with this we conclude this lecture here.

In the next class we will be talking about few more Advanced treatment units primarily the Advanced oxidation process and the membrane process. So, see you in the next class, thank you for joining.