

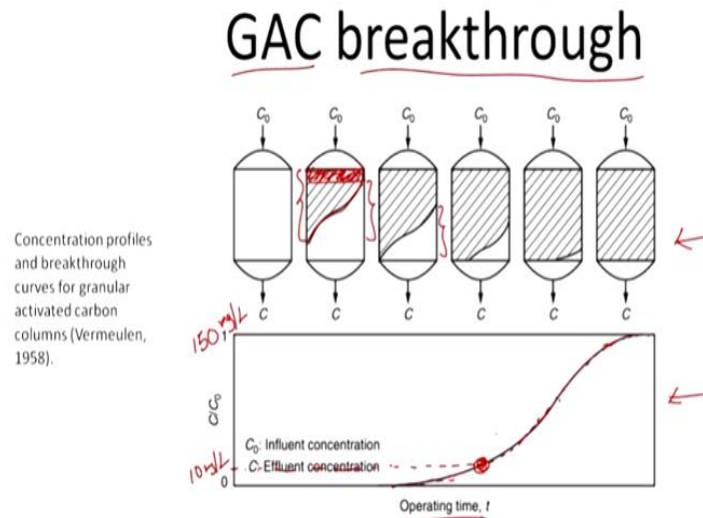
Water and Waste Water Treatment
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Module No # 11
Lecture No # 53
Ion Exchange

Hello everyone, welcome back to the latest lecture session in the last couple of sessions more or less we have been looking at aspects that have come into play relatively recently at least in India. For example we started discussing adsorption and in general we have not applied adsorption in waste water treatment a lot at least in the Indian context. But with various requirements we they are coming into play at least those aspects that look into or use the principles given in adsorption.

One obvious example was granular activated carbon in that context activated carbon as some active sites which can adsorb my organic compounds of interest . And after all these sites have been exhausted I need to replace the relevant activated carbon.

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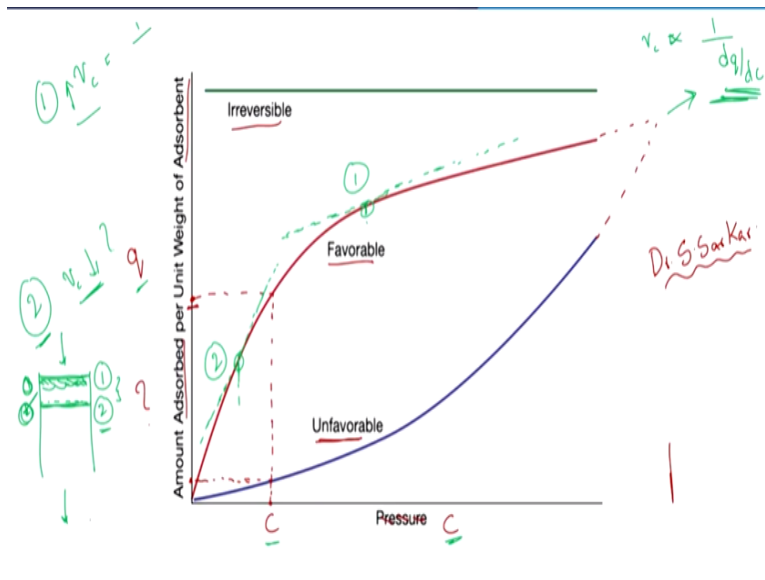


In that context we looked at break through granular activated carbon and breakthrough . this is the mass transfer zone here yes and here it is mass transfer zone here and so forth. what is happening we did discuss this so here this part of the adsorbent there are no more sites available for adsorption. And now the active mass transfer zone is out here.

this profile has some relevant we will look at that for example this is the breakthrough and this corresponds to or this particular graph corresponds to the profile that we see out here. if my inlet concentration is here they say 101 just for sake of it 150 milligram per liter of the compound of interest and I do not want the concentration to be greater than 10 milligram per liter 10 milligram per liter.

And so in during all this time this is time operation time it is fine but here the concentration is reaching my acceptable level the concentration of the effluent and then it is beyond the concentration that I am comfortable with. I would say that the system has achieved break through here itself . that is something to keep in mind but what will decide the shape of this particular tail or such if I may call that or shape of this particular breakthrough . Let us look at that aspect.

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before we go further we did look at it in the context of some of the other aspects there with respect to the isotherms. Typically we have favorable and unfavorable isotherms so here it is q and you have amount absorbed per unit weight of adsorbent. And here pressure but we will look at in terms of concentration in the liquid . , here as you can see at maximum capacity or maximum concentration fine the capacity is the same at maximum concentration though .

But if I look at the cases when the concentration is somewhere out here let us see the concentration at or in the aqueous phase . What do you see we see that there are for the same

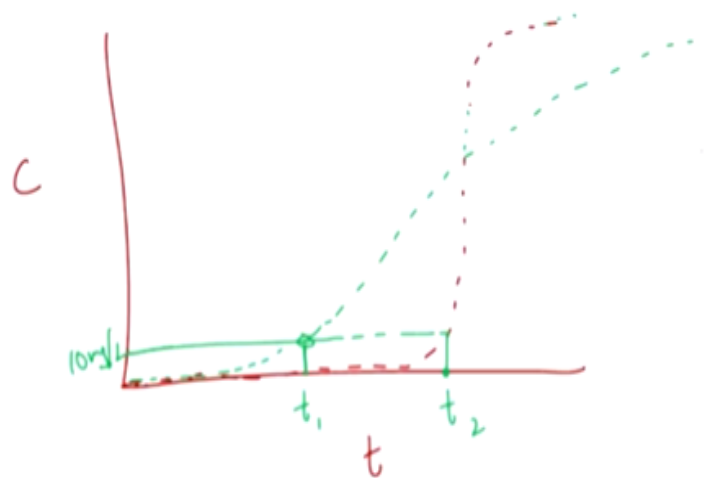
equilibrium q or c pardon me what do we see for the favorable one we see that more amount is adsorbed per unit weight of the adsorbent for this we see that relatively less amount is absorbed per unit weight of adsorbent why is that relevant?

Well if my adsorbent can adsorb more of the compound of interest even at the given concentration in the aqueous phase . We are talking about that particular equilibrium conditions at that particular concentration it means that with less amount of adsorbent I can absorb more of the compound . the volume or the mass of the adsorbent required will be relatively less but with the adsorbent that follows the unfavorable isotherm or such the shape that we have here what will you see there?

Or what would you observe there you need a lot of adsorbent to be able to achieve that given amount of containment removal let us see that is something to keep in mind. some of the concepts here that we are going to discuss I was able to clear by talking to Doctor Suditha Sarkar. thanks to him so that is in general so extreme case of favorable irreversible but rarely will be see that particular case. Favorable and unfavorable this is one aspect to keep in mind.

And in what context were we discussing in this are trying to discuss this regarding this breakthrough curve let us see.

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here the same graph if I am trying to plot it here this is time and this is the concentration in the effluent let us see. the profile can be like this relatively sharper breakthrough or it can be or it can take a different shape too . For example it can be something like this so if I look at the acceptable concentration or the level that I am comfortable with. Here you see that the break through as occurred earlier and for the other case we see that breakthrough has occurred later t_1 and t_2 .

This is the concentration that I am fine with comfortable with yes and how are what factors decides this particular shape of the curve let us look at that. one aspect is that the concentration velocity this particular we are having 150 here. let us consider 200 milligram per liter that zone at which the concentration is 100 milligram per liter or time it is moving down .

In this case it is moving down so if I look at that as concentration velocity looks like it depends upon $\frac{1}{dq}$ by you have terms with respect to porosity q by a yes. And in the denominator though what is that I am going to have this is concentration velocity I am going to have $\frac{1}{dc}$ by dc . This is in a way you have q and c here we have q and we have c here.

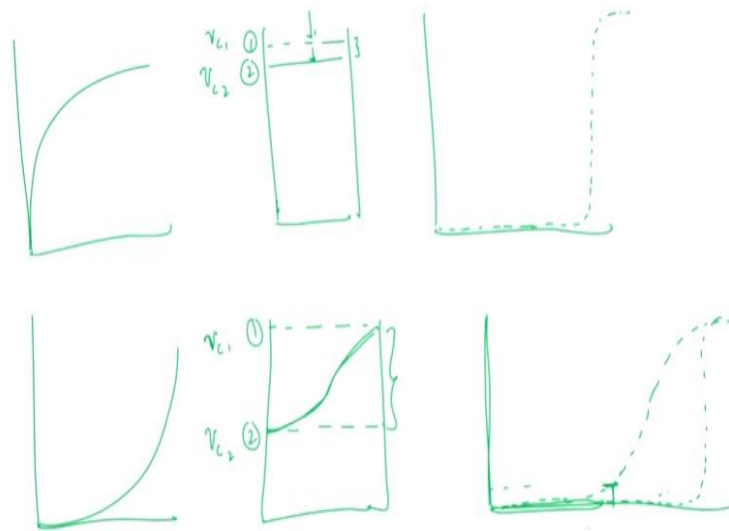
for the favorable let us look at 2 cases 1 case is out here when the system is in equilibrium with higher concentration that is one case yes. And another case is here when it is in equilibrium with lower concentration . this is one aspect yes so as you can see slope relatively flatter relatively steep here. And as we mentioned or looked at earlier we have this concentration velocity to be proportional to $\frac{1}{dq}$ by dc .

there are other terms q by a which is the superficial velocity or the flow velocity and also porosity here $\frac{dq}{dc}$. as you can see there relatively lesser value here so case 1 let me write that here and case 2. in that context what do will have I have $\frac{1}{dq}$ by smaller value I am saying this is case 1 this is case 2. case 1 by smaller value meaning V_c will be relatively high .

And in case 2 slope is steeper so coming back to this particular $\frac{1}{dq}$ by dc , $\frac{dq}{dc}$ is higher so V_c will be relatively lower . case 1 and case 2 why is this relevant as we were looking at it here when it is coming in this direction what is happening here. this phase will be in equilibrium or in contact with or it will be more or less case 1 here . And what about case 2 when it is somewhere out here yes.

case 2 is relatively slow case 2 is somewhere out here so as you can see 1 is relatively fast let me write it here 1 is relatively fast 2 is relatively slow that is what we see. The leading edge or the head which is in equilibrium with relatively lesser concentration is relatively slow but the one or the tail I am using layman term here that is relatively fast. what happens this mass transfer is will be relatively less. Then the kind of breakthrough that you will have let us see if I have a blank slide here.

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the kind of breakthrough that you would have this is the profile so the mass transfer zone is relatively less . here and here so this is the mass transfer zone so that is relatively less so then I will have a sharper breakthrough whenever the breakthrough occurs . that is the case but if it is the case with the unfavorable isotherm so this was the case when we looked at the favorable isotherm.

If it is the case for unfavorable isotherm what is going to happen the reverse is going to happen here we looked at case 1 and case 2 are yes and we see 1 was relatively faster we see 2 was relatively slower. But in this case you can look at the slope what is going to happen so at 2 and here 1 $V c1$ is relatively slower $V c2$ is relatively faster. you can look at the relevant slope here at different cases let us see .

And so what does that mean I am going to have this kind of shape where mass transfer zone is like this or the shape which is similar to what we had here . that is the relevant aspect here,

something like this. what is that going to lead whenever breakthrough is about to occur will I have such a sharp breakthrough no I will have something like this .

I will have something like this and this elongated or this kind of tail shape breakthrough so as you can see if I had sharper breakthrough that would have occurred later yes even though the capacity is the same. you see my breakthrough time is relatively less so that is one aspect to keep in mind or consider so enough of this aspect for now.

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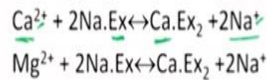
Ion Exchange

Let us move on the next so as I mentioned we are going to look at ion exchange . here the principle is ion exchange I am going to exchange one ion for the other.

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Definition

- Process where ions from solution adsorb onto solid in conjunction with an equivalent amount of ion being released from solid
 - Material to which certain ions are sorbed in exchange for ions already bound to exchanger
- e.g. : Water can be softened by an ion exchanger that absorb Ca and Mg, releases Na in exchange as:



Let us go about and see what it is that we have so as I just mentioned ions from the solution adsorbent to solid. At the same time an equivalent amount of ion is released keep in mind that we are talking about equivalence in with respect to the charge typically here we are talking about ion exchange and charge . Earlier it was adsorption I had just had activated carbon typically hydrophobicity the compound does not stay in want to stay in water it comes and adsorbed on to my activated carbon.

There was no exchange there it was just adsorption so here though we are going to have ions being exchanged something is going to be present on my media or my backbone or the resin and that is going to be exchange for another ion why? There is going to be an issue here or aspect here we will look at that. let us move on material to which ions are solved with in exchange for ions already bound to exchange.

Material to which certain ions or solved in exchanged with ions already bound to the exchanger . example what is it that I have in water I have calcium and magnesium and these I want to remove they will have Ca 2+ and Mg 2+ charge and the one in the resin has Na+ charge. due to the relevant affinity for calcium and magnesium due to the relevant hydrated radius we will come back to that later.

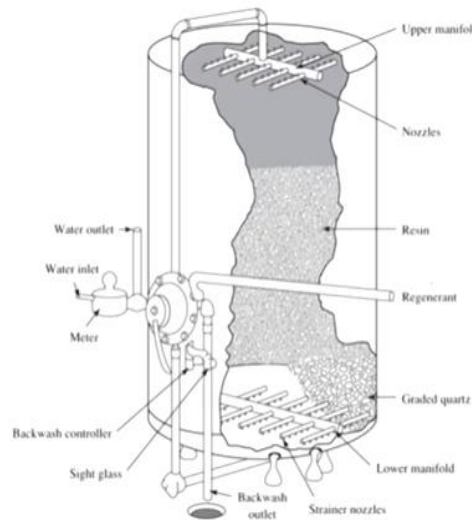
the resin strongly prefer to have calcium and magnesium rather than Na+ so Na+ will released into the solution while calcium and magnesium which are in the solution will be adsorbed onto

the resin so that is one aspect to keep in mind . that is the relevant aspect I have here . I have calcium in the solution and here is the ion exchanger ex is the layman's term that we are using to denote anion exchanger pardon me cation exchanger.

And then 2, sodium are replaced for one calcium why 2 + charge on this and 1+ charge on this . let us see same case with magnesium fine.

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Components of ion exchange vessel



Let us we have components we did look at this so we have the resins and man folds . But I just wanted to present a relevant picture keep in mind that you will have to regenerate it either onsite or off site so that is one aspect to keep in mind. But let me not dwell a lot of time or spend lot of time on this picture.

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Multicolumn ion exchange system

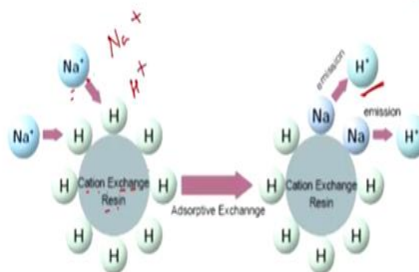


multi-column ion exchange so you see different columns out here yes and this is what you can typically look like let us see.

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Characteristics of material

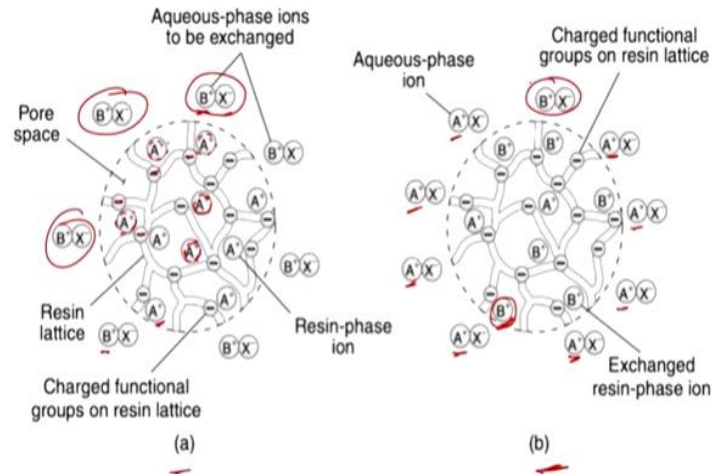
- Has surface charge that attracts oppositely charged ions
 - Negative charge attracts positive ions, i.e. is cation exchanger



characteristic of material well look at what it is. what are we looking for? We want to have a surface charge that attracts the oppositely charged ions let us see. cation exchange resin let us see . it will have negative charge that is why H^+ is relatively down to it or absorbed on to it. And then Na^+ comes into picture and depending upon the relevant affinity it will replace or exchange with H^+ so that is something to keep in mind.

Negative charge attracts positive ions that are why it is called a cation exchange. as you can see cation exchange Na^+ cation positively charged H^+ cation so, we have a cation exchange taking place.

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what does it typically look like let us see we have here so this is the initial case and this the case at equilibrium. what do I have B⁺ and X⁻ compounds in water you have to have charge neutrality that is why you will always have the cation and relevant anions . you have aqueous phase ions which we want to remove I want to remove B⁺ fine I want to remove B⁺. And in the resin has a negative charge yes and even it has to be balanced with respect to charged and that is why you have the ions here .

The relevant positively charged ions yes what is going to happen because the resin has a greater affinity for B⁺ rather than A⁺ what are you going to see? You see that B⁺ is going to be absorbed onto the, rein while A⁺ is going to be released. here I am going to have ion exchange so at equilibrium you see that most of the B⁺ has been removed it is in equilibrium that is why you cannot have 0 you will have relatively less. But you will not have 0 so that is what you see here .

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Types of ion exchangers

- Natural materials
 - Soils (cation exchange capacity, due to negatively charged particles, mostly clays)
 - Zeolites and similar minerals (originally used in water treatment)

types of ion exchangers we have natural materials like soils typically they will have cation exchange capacity why is this? Due to the negatively charged typical negative charge on the glaze let us see that is one aspect to keep in mind. And zeolites they were originally used in water treatment and even now lot of research goes into zeolites. These are the natural materials .

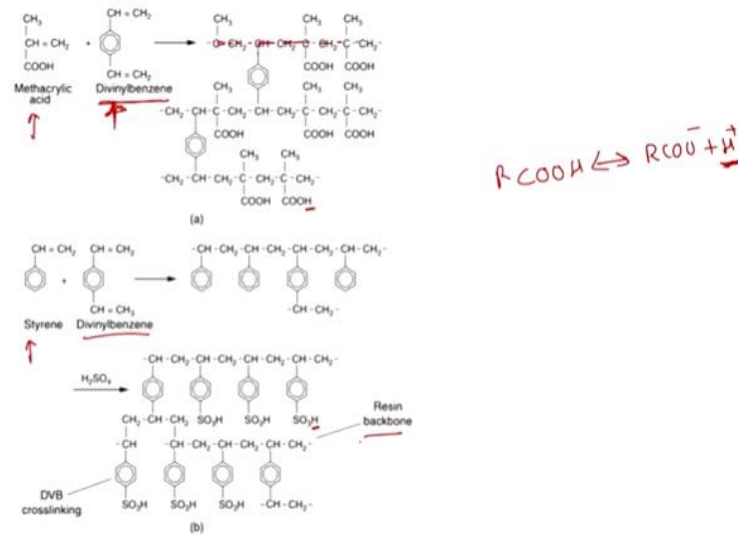
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Types of ion exchangers

- Synthetic ion exchange resins
 - Polymer backbone groups
 - Cross linking groups
 - Exchange groups

And we have moved on or quite a few people now look at applications of synthetic resins . we have synthetic ion exchange resins what do these resins contain. we need a polymer backbone that is one aspect and to interlink or link these backbones you are going to cross linking groups. And for exchange you need the exchange group . One is the backbone 1 to cross link or interlink and one is the exchange group .

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let us look at a picture so here we have relevant picture so here you see the backbone that is coming from here. And here this is the cross linking group so this is the cross linking group here Diviny benzene here also Diviny benzene. 2 cases here styrene is the backbone or leads to the backbone resin backbone as you can see yes. And here it is methylacrylic acid you can see the backbone and then the interlinking between different chains based on this particular crosslinking

And as mentioned exchange groups so exchange groups so COOH R COOH it can be as +H+. it can release this H+ so thus you will have that particular this particular site is the exchange site. And here SO 3 H so H+ can be released and the relevant cation can be absorbed here. you are going to have ion exchange this is one aspect to keep in mind.

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Synthetic Exchange groups

▪ Negative (cation exchanger, strong or weak acid resin)

- Carboxyl ($R-COOH$, $R-COO^-$)
- Sulfonic ($R-SO_3-H$, $R-SO_3^-$)
- Phosphonic ($R-PO_3-H$, $R-PO_3^-$)

▪ Positive (anion exchanger, strong or weak base resin)

- Amines
 - R_4NOH
 - R_4N^+



synthetic exchange groups what else do we have negatively charged so there will be cation exchangers. in the context of these exchange groups we have concept about strong or weak acid resin we will look at what it is about in just a moment. here we have as we just looked at carboxyl groups or COH with and without the proton sulfonic yes.

thus if you can remember and look at your acid base relevant aspects we have this type of a curve for acids and bases. Yes and this is the protonated form HA this form and this is the A- deprotonated form, And we have x axis here we have the concentration here on the y axis as you can see the kind of compound that is going to present is going to depend upon the pH and this particular point at which the concentrations are equal is pKa acid dissociation constant.

if pH is greater than pKa is a constant based on that particular compound from the equilibrium constant if pH is greater than pKa for example here. What does it or which form is going to predominate? This particular form A- is going to predominate but if it is going to present when the pH is less than pKa is less than pH which form is going to be predominant. HA so the issue here is when the compound wants to stay as or in its protonated form HA then it is not going to function as a ion exchanger.

, as you can see pH plays a considerably important role when will this be important? This will be important for weak acid resistance when do we say or call a particular compound or an acid as

weak acid when the pKa is relatively high not relatively low let us see . that is an example of that is this carboxyl and this was discussed in the context of acetic acid .

We looked at some examples in the context of acid based chemistry we looked at earlier. here also one aspect to keep in mind is that the capacity the total capacity also increases depending on pH if the pH is here. capacity is less because while significant fraction present as A- a significant fraction is still present as most of it is present as HA. But if pH of the solution is here relatively further from the pKa what do you see most of the compound is present as A- or would want to be and only some of it only present as protonated form.

greater sites are available for ion exchange for sulfonic this pKa which is out here the pKa will be somewhere out let us see . pKa will be somewhere out here so it almost all pH range it act as an cation exchanger that is why we call this as a strong acid resin. there are advantages and disadvantages depending upon which cases want to look at but we will not go into that now.

different other kinds of cation exchanges if I have cation exchanger I will also have anion exchanger anion negatively charged so the resin needs to have a positive charge . Similarly as we just had strong and weak acid resins we are also going to have strong or weak based resins similarly concept as above. amines typically quaternary amines so that is one thing to keep it or look at. And H4+ so you are going to replace the H here . that is something to keep in mind.

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Resin Type	Functional Group	Ions Removed	Regenerant	Operating pH Range
Strong-acid cationic (SAC) resin	Sulfonate, SO_3^-	Ca^{2+} , Mg^{2+} , Ra^{2+} , Ba^{2+} , Pb^{2+}	HCl or NaCl	1-14
Weak-acid cationic (WAC) resin	Carboxylate, RCOO^-	Ca^{2+} , Mg^{2+} , Ra^{2+} , Ba^{2+} , Pb^{2+}	HCl	>7
Strong-base anionic (SBA) resin	Quaternary amine, $\text{RN}(\text{CH}_3)_3^+$	NO_3^- , SO_4^{2-} , ClO_4^- , HAsO_3^{2-} , SeO_3^{2-}	NaOH or NaCl	1-13
Weak-base anionic (WBA) resin	Tertiary amine, $\text{RN}(\text{CH}_3)_2\text{H}^+$	NO_3^- , SO_4^{2-} , ClO_4^- , HAsO_3^{2-} , SeO_3^{2-}	NaOH or $\text{Ca}(\text{OH})_2$	<6

let us just summarize this or understand this so strong acid cationic resin typically sulfonates relatively low pKa that is why the operating range is pretty much starting from pH greater than 1 . And regenerate we will come back to this we want to regenerate it that is relevant aspect too. the type of ions it can remove and weak acid resin carboxylate as you can see it is operational only beyond it is pKa .

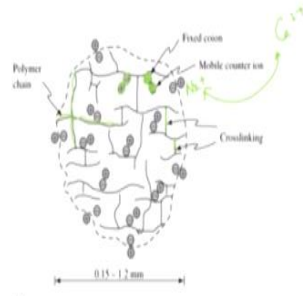
we are looking at relevant pKa and then we will understand the kind of range where it is going to be functional it. Same case as you can see strong base more wider range weak base depending on the pKa it is going to be able to exchange . The relevant anions only when the pH is less than 6 so you can see depending upon your solution pH which one is more acceptable and not.

And one aspect to note is that because the weak acid resin let us look at this weak acid cationic resin at a particular pH we know that it wants to have the proton H+. when you are regenerating it consider the case when all the ion exchange sites of them have been taken up by your compound of interest that you want to remove. But you do not want to through the resin out then it is considerable cost and also you are going to look at what do I need to do with that particular resin.

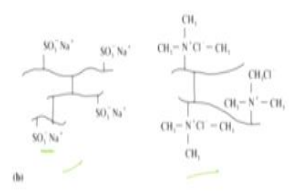
you will regenerate the resin how will you do that? Well it is like reversible reaction you can think of that partially let us not look into the details here. I will add a lot of H+ but with respect to the string acid as you can see it does not have affinity for H+ it tries to release H+ because it is pKa is pretty low. But for weak acid pKa is relatively high at a considerable range that it is strongly wants to take up H+.

it is easier to regenerate the weak acid cation resin compared to the strong acid cationic resin that is one aspect to keep in mind. Let us move on.

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a) The bead is shown as a polystyrene polymer cross-linked with divinyl benzene with fixed co-ions (minus charge) balanced by mobile positively charged counter ions (positive charge)



b) Strong cation exchange resin on left (Na⁺ form) and strong-base on right (Cl⁻ form)

we looked at this but let us just summarize the bead here is polystyrene polymer cross linked with divinyl benzene. This is what we looked at earlier so we have cross linking here the cross linking is due to divinyl benzene. The structure of which we looked at earlier and here we have polystyrene polymers polymer chains. this is the macroscopic view which you are now looking at earlier we looked at the relevant compounds .

With the fixed co-ions minus charge balance by mobile possibly charged counter ions so the counter ions so this is the mobile counter ions. For example Na⁺ is the counter ion and Ca²⁺ will be exchange with this counter ion let us see the fixed ion is giving the relevant charge which is the negative charge to this particular weak acid resin . Because it has a negative charge fixed negative charge it will have opposite counter ion .

The counter ion there so that is what we are looking at here so strong cation exchange resin on the left and strong based on the . this is depend on the pKa value of the relevant group that is something to keep in mind so let us move on.

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Ion exchange resin beads (75 -150 μm diameter)

And what does it actually look like here you see the relevant beads and the diameter is 75 to 150 micron as you can see it is relatively small depending upon your functionality and also the what can I say increase in volume during ion exchange.

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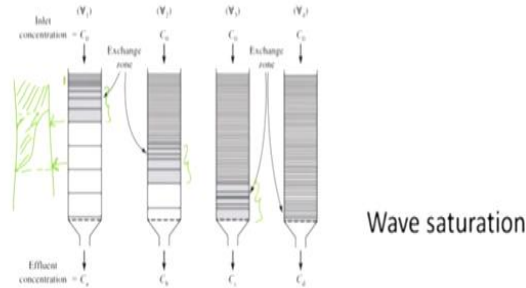
Ion exchange resin beads (500-590 μm diameter)

can have or look at different kinds of sizes here we have relatively bigger diameter 500 to 590 micro meter I just want to present a picture so that you can understand the kind of or how it looks like .

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Ion exchange wave saturation

- For a column of resin, the exchange reactions begin to saturate the upper levels before the lower levels
- The progress of this saturation through the column results in a “wave” of saturation

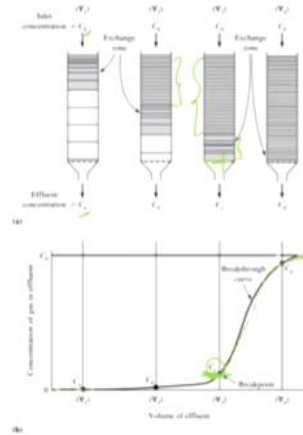


ion exchange wave saturation we looked at this in the context of adsorption. I will not look at that or go through that in detail . But let us just summarize that for a column of resin the exchange reaction begin to saturate the upper level initially we are going to have saturation here before the lower levels yes. And then we use the term mass transfer zone earlier the progress of this saturation through the column results in a wave of saturation.

For example in the earlier context we looked at something like this wave so this has been saturated this has not been saturated yet so that is what we can look at. For example this whole part has been saturated here relatively bigger part at this part here almost none of it has been saturated . that is what we are talking about so the exchange zone has been highlighted here. This is moving through so once it reaches down and depending on your concentration you are going to have relevant breakthrough .

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Ion Exchange Operation



Breakpoint =
Breakthrough
Arbitrarily set based on
design criteria

$$C_{\text{exhaustion}} = 0.95 C_0$$

let us look at it here so we have inlet concentration C_0 and effluent concentration C_a . C_a is below the relevant concentration that I am looking at so that is fine so what do we have here? initially we have lot of active sites or ion exchange sites available and thus most of the cation are being taken up. But as we move further down you see that almost all the sites are being used up and at this particular point we have the break through why are we calling it the break through?

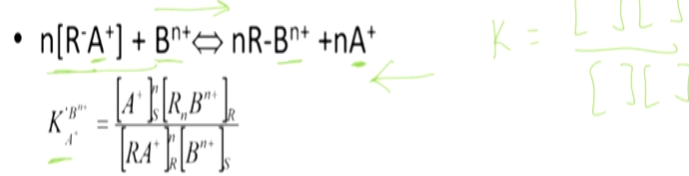
Because my particular concentration of interest has been crossed by the effluent concentration so you can see here mass transfer zone has reached this or exchanged zone has reached my outlet. , the; concentration of the relevant compound in the outlet is going to be higher and if it is higher than the compound or the standard of interest to me. Then I am going to call that the break through and this breakthrough is here.

When it reaches this particular effluent so this shape we looked at it earlier so let us not go into that.

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Selectivity coefficient

General equilibrium reaction:



- Problem is that while activities of solution concentrations can be approximated with molar concentrations, the resin concentrations are very high
- Valid for narrow concentration ranges

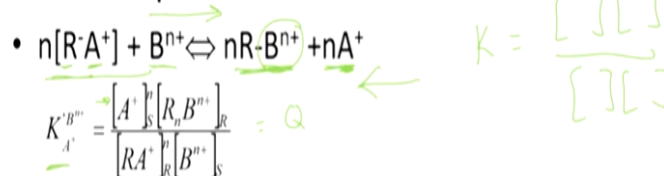
, as we mentioned it is you can represent it as a kind of reaction so here we have the resin and this is the ion in the water . And now A+ is being exchanged with this Bn+ let us see yes. you can write it in terms of the equilibrium constant you have the products in the numerator and in the denominator you are going to have the reactants. that is what you have out here let us see.

if you want to have this reaction going forward what do you want to have you want to have more of this. If you want to have this reaction go forth the backward reaction what do you want to have? You want to increase the concentration of A+ this is the principle for regeneration too . let us not look at that now let me skip this because we discussed this.

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Selectivity coefficient

General equilibrium reaction:



- Problem is that while activities of solution concentrations can be approximated with molar concentrations, the resin concentrations are very high
- Valid for narrow concentration ranges

selectivity of ions so we looked at Na^+ or H^+ as the initial counter ions or the counter ions and why is it that they will be replaced by the calcium or magnesium in my particular solution why? here we are going to talk about selectivity of ions. we have preference of the ion exchange material for 1 ion over another. here we have a particular variable called the selectivity coefficient S and R denote the solution and resin concentration .

If we have Q as equal to 1 no preference for A over B if Q_s is greater than 1 B^{n+1} is going to be preferred over A^+ that is what we want. Q_s is less than 1 you can look at this A^+ is preferred over B^{n+1} if Q_s is greater than 1 what does that mean? That means that the denominator is higher . We had this particular equation here if these, numerator when if it is not at equilibrium so this is Q .

what does it means when the numerator is here it means that the system prefers that A^+ is in the solution and B^+ is adsorbed or is with the relevant co-ion there . this means that it has an affinity for B^+ . If not Q is less than 1 denominator is relatively higher what does it mean? This particular resin has a greater affinity for A^+ so that is what we are talking about let us move on.

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Selectivity

- Stronger attraction to multiply charged ions (Ca^{2+}) than singly charged ion (Na^+) ?
- Stronger attraction for smaller hydrated radius (larger unhydrated radius)
 - Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Be^{2+}
 - ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > OH^-

, stronger selectivity stronger attraction to multiply or multiple charged ions Ca^{2+} than singly charged fine. Why is this whole principle is that? You are going to have ions calcium and you are going to have its un-hydrated radius . Another aspect is the hydrated radius you are going to

have water is polar you are going to have some of these water molecules surrounding this particular calcium ion.

whenever calcium ion moves these water molecules move with it so when this calcium ion is being exchange with Na^+ the system prefers one that has relatively smaller hydrated radius if I am not wrong. We will look at that but the smaller hydrated radius why is that? Osmotic pressure will be applied on the resin and the system will see to it that the one that has less resistance Layman's terms or less osmotic pressure will be taken in.

that is why those compounds or ions pardon me with lesser hydrated radius will be preferred and typically when will that be the case. When it is relatively smaller ion with greater charge . bigger the ion and lesser the charge your affinity typically decreases why it is relevant to the hydrated radius . , strong attraction for smaller hydrated radius and typically it is inversely proportional to the unheated radius as I just mentioned.

here Ba^{2+} SR^{2+} I mean greater than to the affinity this is for cation and this is for anions. But this is the general rule there will be some aspects of here and there but key aspect is to understand that it is the hydrated radius.

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Selectivity

- Advantages of choosing a resin with high affinity for the targeted ion:
 - Sharp breakthrough curve
 - Shorter ion exchange column
 - Greater flow rate applied to column
- Disadvantages
 - Higher regenerant concentration required

if we choose a resin with high affinity for the compound of interest why is that going to be relevant. sharper breakthrough then leading to shorter ion exchange column and then I can have

greater than flow rate and disadvantages if my relevant resin has great affinity for the compound that I am trying to remove later when I am trying to regenerate this particular resin.

it is going to be relatively difficult why is that because it likes the compound so much so that is one aspect to look in.

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Ion exchange capacity Ca²⁺

- Total capacity = all possible exchange sites (meq/g, meq/ml; around 1-4 meq/mL)

- Capacity for target ion = total capacity - capacity used for preferred ions (at breakthrough)

ion exchange capacity we have 2 terms here one is the total capacity and another is the capacity for the target ion. The key is that one aspect deals with the target ion one is about the total capacity. for example we were trying to remove different compounds let us see yes. And we have calcium fine so if my target is calcium but I have other cations that are present.

My particular resin will not only pick up Ca²⁺ it will also exchange or have an ion exchange with the other cations present in the solution depending on the relevant affinity . here I am going to be concerned about total capacity and also capacity for the target ion. all possible exchange sites units typically equivalence per gram or equivalents per liter typically I am having or looking at milli 1 to 4 milli equivalent per milli liter.

For the target ion it is the total capacity minus capacity used for preferred ions let us see at breakthrough. that is how we are going to look at it.

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Operating capacity

- Depends on
 - Flowrate through column
 - Bed depth
 - Selectivity coefficient
 - Exchange ion size
 - Amount of regenerant used (extent of regeneration) ?
 - Composition and concentration of feed solutions
 - Temperature
 - Desired quality of product water



Operation capacity depends upon flow through the column but depth selectivity coefficient exchange ion size yes this is slightly relevant to this selectivity coefficient. Amount of regeneration used our extent of regeneration required why is this? Because the more regeneration that is used the costs are going to add up why because later you have to dispose this regeneration somewhere.

relatively less volume relatively less disposal cost too and also even to get the regenerate you are going to spend less so that is something to keep in mind. Composition and concentration of the feed solution and in what is coming in why is that? If it is just Ca^{2+} and I just want to remove Ca^{2+} fine. But if I have other compounds of interest with greater charge there is a Fe^{3+} well I do not think there will be.

And assuming that the affinity is relatively higher that Ca^{2+} so what is going to happen? The ion exchange resin will take up both Ca^{2+} and Fe^{3+} . the composition and concentration of the field solutions come into play and temperature because everything is about equilibrium constant which is depend upon the relevant temperature. And if my when I say desired quality of water, we know that we are talking about breakthrough .

If my desired quality of water is somewhere out here low concentration I will have one particular operating time if my breakthrough is relatively later. Or if I am if I can accept relatively higher concentration of the compound in my outlet I am going to have a different breakthrough time .

These are the aspects that come into play and one aspect to note when people come up with this different kinds of ion exchanges is that is the affinity fine my resin can remove the calcium or the compound of interest of chromium .

But what about all the; other ions that are also going to be present in the solution so we have to look at that data too the selectivity for that particular compound especially. When we consider the background concentration of the other competition which is from the other cations or such. We are talking about Ca^{2+} for example people typically conduct experiments only on that particular ion of interest and say hey it is 100% removal.

But if it is actual water we are going to have other ions too and these ions are also going to compete for this ion exchange sites especially because these other ions will be at higher concentration. The compound of interest which you want to remove which is toxic will be typically a relatively low concentration. then you have to look at these aspects let us move on.

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Application of ion exchange

- Softening ($\text{Ca}^{2+}, \text{Mg}^{2+}$ Na exchange, regenerate w/ NaCl)
- Nitrate removal (Cl^- exchange, regenerate with NaCl)
- Perchlorate (ClO_4^-) removal (Cl^- exchange, regenerate with NaCl)
- Toxic metal removal/recovery (e.g. $\text{Pb}^{2+}, \text{Hg}^{2+}$), regenerate with HCl (keep pH low to keep metals in solution)
- Demineralization (OH^- , H^+ forms, regenerate with NaOH, HCl)

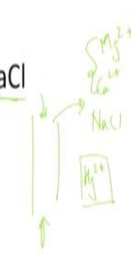
ion exchange where do we use that softening removal of calcium and magnesium ? Na exchange and regenerate with NaCl let us see nitrate removal Cl^- is exchanged nitrate is NO_3^- . And you are regenerating with NaCl so perchlorate very stable Cl^- exchange depends upon the kind of charge Ca^{2+} and Mg^{2+} Na^+ or H^+ exchange and with respect to the anions nitrate and perchlorate we are going to have Cl^- exchange and regenerate with NaCl.

toxic metal removal like for example lead and mercury we are going to look at regeneration with HCl why is it? To keep the pH load to keep in metals in solution if the pH is high you are going to have precipitation of these metals that is what you want . You do not want precipitation to occur that is something you want to avoid that is why we are looking at HCl . Demineralization OH and H forms regenerate with NaOH and HCl .

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Process cycle

- I. Begin to contact water with resin, Ca^{2+} , Mg^{2+} removed, Na^+ added
- II. Capacity of resin reached (all available exchange sites filled with Ca, Mg, no more can be removed), breakthrough of Mg^{2+} then Ca^{2+}
- III. Resin taken offline and regenerated with concentrated NaCl solution
 - More regenerant = More effective regeneration, higher cost
 - Counter current
 - Reuse some of regenerant
 - Disposal of regenerant is important cost



I want to remove the minerals it is all minerals I am not just talking about a particular compound demineralization. process cycle it is just summing up what we looked at earlier first we are going to look at the example of calcium and magnesium I want them to be removed . What is going to happen when it contacts the resin due to the greater affinity calcium and magnesium are now ion exchange or are absorbed onto the relevant resin.

While Na^+ is exchanged we have ion exchange after the capacity of the resin has been reached meaning that there are no more available active sites. Then what do we do? We cannot remove anything and breakthrough has occurred breakthrough of Mg^{2+} and then Ca^{2+} . resin is taken out and; then regenerate with concentrated NaCl as we know it is like a reversible reaction.

the greater the concentration from one side you are going to follow Le Chatelier's principle and it is going to move into the other direction. more regenerate is not ideal why? We will come back to this why it is higher cost? But if it is more regenerate or more concentration more effective

regeneration but we have to balance it out with the needs of higher cost . Or it typically we look at counter current this and this direction so that is counter current and reuse of the regenerate.

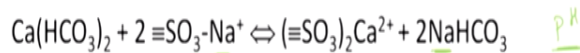
as mentioned these case of ion exchange or such all these are fine but those are a few people who look at degradation I mean ion exchange and then degradation on C2 why is that great? Because what are we doing I am having NaCl and then generating the relevant solution fine. I have now what do I have I have lot of NaCl fine and I have my, high concentration of calcium and magnesium fine.

These are not toxic maybe that is fine but if I have lead or mercury then after regeneration what do I do with it? the key issue that ion exchange absorption we are only changing the phase of the compound from aqueous phase to the solid phase or adsorbed onto the resin. But we still need to look at the disposal cost so that is something to keep in mind let us move on.

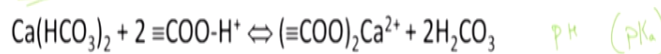
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Process cycle

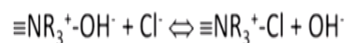
- Strong acid:



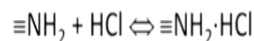
- Weak acid:



- Strong base:



- Weak base:



strong acid resin that is what we have and it now exchanges calcium with sodium that is what we see out here. Weak acid too but here I will have greater operational range of pH relatively limited why because it is weak acid and we have to look at the operational range based on the pKa . strong base OH- Cl- exchange weak base . you can have different kinds of weak base it is kind of an exchange here let me move on.

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Exchange/Regeneration



- Direction of reaction is reversible (L'Chatlier principle) by high concentration of ion (Na^+), regeneration process
 - e.g. sodium exchange/NaCl regeneration
 - $2\text{R}\cdot\text{Na} + \text{Ca}^{2+} \rightleftharpoons \text{R}_2\text{Ca} + 2\text{Na}^+$
 - e.g. hydrogen ion exchange/ HCl regeneration
 - $2\text{R}\cdot\text{H} + \text{Ca}^{2+} \rightleftharpoons \text{R}_2\text{Ca} + 2\text{H}^+$

Exchange and regeneration so it is an reversible reaction it is like $A + B$ goes to $C + D$ A is the resin with Na^+ C is the resin with Ca^{2+} . if I want to move it in this direction what will I do? I will add a lot of D and then rather than going in forward direction it will go in this so it is not a reaction but that is the principle here direction of the reaction is reversible the Le-Chatlier principle by applying high concentration of the ion regeneration process occurs .

We looked at this so we have this this is my resin and it is exhausted I want to regenerate it what do I need to do? I am going to regenerate it in this way fine I should have added this if I want to move it in this way I am going to have NaCl addition. sometimes we are also going to look at NaCl regeneration this is something we have also looked at earlier .

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Typical ranges for design data and criteria for strong acid cation and strong base anion resins

Parameter	Strong acid cation resin	Strong base anion resin	Unit
Exchange capacity	3.6-5.5	1.8-2.0	meq/g as CaCO ₃ } meq/mL as CaCO ₃ }
	1.6-2.2	0.8-1.4	
Operating capacity ^a	50-70	40-60	% of exchange capacity
Moisture content	40-80	35-80	%
Shipping weight (moist)	640-930	670-720	kg/m ³
Screen size	16 × 50	16 × 50	
Service flow rate	200-2000	200-2000	m ³ /d · m ⁻¹ of resin BV/h
	8-40	8-40	
Surface loading rate	400-800	400-800	m ³ /d · m ² or m/d
Backwash rate	12-20	5-7.5	m ³ /h · m ² or m/h
Backwash duration	5-15	5-20	min
Bed expansion	50	50-75	%
Regenerant	NaCl	NaCl	
Regenerant concentration	5-10	2-15	%
Regenerant dose	80-320	80-320	kg NaCl/m ³ of resin
Regeneration flow rate	60-120	60-120	m ³ /d · m ² or m/d
Rinse volume	2-5	2-5	BV/h
	2-5	2-10	
pH range	0-14	0-14	units
Max. operating temp.	140	OH ⁻ form = 60; C ⁻ form = 100	°C
Turbidity limit	5	5	NTU
Iron limit	5	0.1	mg/L as Fe
Total Fe + Mn	0.3	0.3	mg/L
Chlorine limit	1.0	0.1	mg/L of Cl ₂

different aspects to keep in mind one aspects is also moisture content because swelling occurs depending on this size of the ion that is adsorbed or dissolved so that is something also keep in mind. backwash rate just relevant aspects here for cation exchange resin they are relevant capacity keep in mind that we are always looking at equivalence . that is why here we have units in terms of as CaCO₃.

backwash rate is one aspect and how long yes as you can see bed expands by percentage this is something I have mentioned and regenerate typically used let us see.

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Design consideration

- Size of exchanger (amount of exchange material) determines time to breakthrough – convert all concentrations to equivalent units (meq/L or mg/L as CaCO₃, using definition of charge equivalent)
 - **Time to breakthrough** = total exchange capacity of bed/flow of hardness to bed, e.g. day = kg of CaCO₃/(kg CaCO₃/d); total exchange capacity = amount of resin * specific exchange capacity of resin (e.g. kg of CaCO₃ = m³ resin* kg CaCO₃/m³ resin)
 - **Tradeoffs**
 - Large - longer run time, higher capital cost, lower operating costs
 - Small - smaller run time, lower capital cost, higher operating costs

with that we will more or less wipe it up pardon me wind it up design concentration whenever we look at small exchange size of the exchanger . How much either size of my exchanger? What is it going to be depend upon? I need to know what is the total mass of the compound if interest that is coming in? What is the mass of the compound that my particular ion exchanger can take up .

it is the amount of the exchanger material how do I calculate that? Or why is that necessary it determines the time for breakthrough . we convert all concentration to equivalence as equivalence or with respect to CaCO_3 . And time to breakthrough total exchange capacity of the bed by flow of hardness here we are talking about the hardness to the bed total capacity by hardness capacity coming in per time that will give me an idea about the time to breakthrough let us see.

And what about the total exchange capacity that is going to be equal to amount of resin into specific exchange capacity of the resin that is pretty much obvious. tradeoffs if it is relatively large longer run time higher capital cost but lower operating cost. Small it is the other way around so with that we are done with ion exchange and we will move on to looking at or discussing reverse osmosis in the next session with that I will end today's session.