

Course: Adsorption Science and Technology: Fundamentals and Applications

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Week 08

Lecture 40 | Ion Exchange Cycle: Illustrative Problem

Hello everyone. Welcome to this final lecture on this course of adsorption science. So, today in this lecture we are going to show or illustrate you know small problem related to this ion exchange cycle or based on the concepts of this ion exchange cycle that we have discussed in the previous class. And this is very relevant from a practical perspective for water softening applications for boiler feed water treatments in power plants for production of high purity you know deionized water relevant for other applications in chemical industry pharmaceuticals etcetera. So, the problem that we are going to talk about involves a fixed bed resin or a fixed bed ion column and in that k in that we will have first a loading cycle for the ion exchange and then it will be subsequently followed for the regeneration and displacements. So, let us first look into the problem. So, this problem is about softening.

So, softening is a process of where you try to reduce the hardness of the water contributed mainly by the you know this calcium and magnesium ions. So, this is a softening of hard water in a fixed bed fixed resin bed, ion exchange column. So, feed at 25 centigrade which contains 400 ppm. So, ppm stands for parts per million by weight of course, this calcium chloride and 50 ppm of sodium chloride.

So, the bed is 8.5 feet diameter by 10 feet high of gel resin with cation capacity of 2.3 equivalent per litre of bed volume. So, this is given in volumetric units not in mass units. So, the resin void fraction ϵ_b , is the bed porosity is 0.38. The flow rate the loading rate is 15 gallons in a FPS unit per minute feet square. Displacement rate is 1.5 gallon per minute feet square. So, this is displacement you know washing regeneration all same rate. The displacement and regeneration solutions displacement and regeneration solution or aqua saturated solution.

So, the saturation amount of NaCl is around 20 percent 26 percent in fact. So, below above that by weight fraction you cannot possibly you know add more solution. So, that is like the saturated concentration for NaCl in water. Of course, density of the feed consider considering it to be very dilute like 400 ppm and all it can be considered to be as 1000 kg per meter cubes or 1 kg per liter. So, the thing that we have to find out here.

Softening of hard-water in a fixed (resin) bed ion-exchange column.

Feed @ 25°C containing 400 ppm (by wt.) CaCl_2 & 50 ppm (by wt.) NaCl. Bed is 8.5 ft diameter by 10 ft high of gel resin with a cation capacity of 2.3 eq/L of bed volume.

Resin void fraction (ϵ_b) = 0.38.

Loading rate 15 gal/min. ft²

(Displacement rate 1.5 gal/min. ft²
Washing, Regeneration)

Displacement & regeneration solution are aqueous saturated NaCl. (~26% wt)

Find (a) Feed solution (volumetric) rate
(b) Loading time to breakthrough
(c) Loading wave front velocity
(d) Regeneration solution (volumetric) flow rate

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(e) Displacement time
(f) check for favourability of regeneration:

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So, find or estimate first is the feed solution flow rate volumetric flow rate, which is of course, if you see here the loading rate is given in terms of heat square. So, multiplying with the cross sectional you can help us in finding out the loading the solution flow rate. So, this is like given in terms of you know linear velocities I would say. So, you have to find out the volumetric flow rate first thing. Second is the loading time to break through loading time to break through.

So, how long can you load this system or how long can you make that ion exchange to happen in this system. Third is the loading wave front velocity. So, we have to use our concepts of ion movements that we discussed in the last lecture. Next is regeneration solution volumetric flow rate which is again very similar to the loading flow rate. We are also asked to find out the displacement time and the final point is to check for favorability of regeneration right.

So, this as you can understand is a question on regeneration or cyclic operation of this ion exchange bed. So, after the loading is completed then one has to charge in the you know this concentrated solution for regeneration displacement and regeneration. So, is a cyclic operation of this fixed bed. Now, let us talk about how do you approach this pollution you know problem. So, some quick information is that this molecular weight of calcium chloride is 111, molecular weight for NaCl is 58.5. So, the concentration of calcium chloride in equivalents per liter concentration of calcium chloride is 400 ppm, you divide that with molecular weight and you multiply that with so ppm is like parts per million. So if you could treat it to be in terms of you know like milligrams per liter or something then you have to make it like in terms of liters and all. So this is the conversion, which is equal to 0.0036 moles per liter. And since the valency of calcium is 2, so in that case it becomes 0.0036, 0.0072 equivalents per liter. For NaCl, 50 ppm divided by the molecular weight times 10 to the power 6 that is like parts per million.

So, this turns out to be 0.000855 moles per liter and since the valence is 1 this is the amount of equivalent ions or the equivalent number of molecules per liter. Now coming these are some generic things as we have converted the calcium chloride and NaCl and this is like the equivalent of the ions of calcium and sodium. Now the bed cross sectional area is πd^2 by 4. So this is like the column diameter which is π by 4 this is given as 8.5 feet so this is 56.7 feet square so of course the feed flow rate feed volumetric flow rate is 15 gallon per minute feet square and if it is multiplied with 56.7 the cross sectional

area of feet square then this turns out to be 851 gallons per minute which is equivalent to 3219 liters per minute when you can just convert that gallons to liters in this case. So, now coming to the loading wave front which is very important probably write this in the next slide. So, this loading or behind the loading wave front behind the loading wave front in the which is in equilibrium actually.

(e) Displacement time
(f) check for favourability of regeneration.

Solution analysis.

Mol. wt. of $\text{CaCl}_2 = 111$ MW of $\text{NaCl} = 58.5$

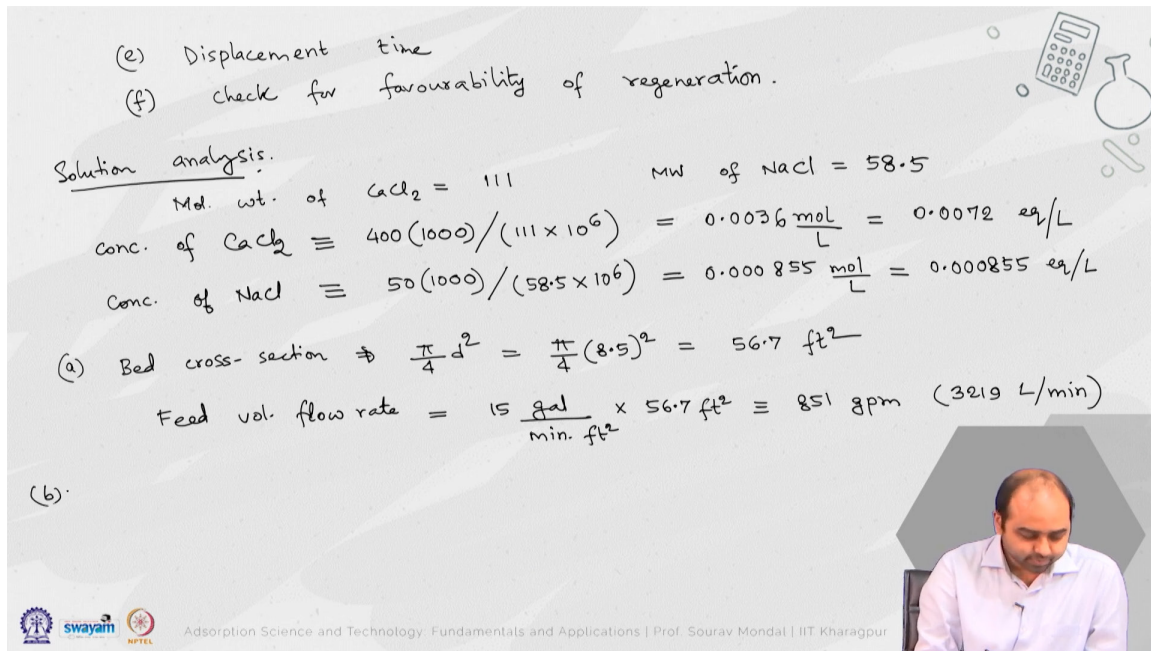
conc. of $\text{CaCl}_2 \equiv \frac{400(1000)}{(111 \times 10^6)} = 0.0036 \frac{\text{mol}}{\text{L}} = 0.0072 \text{ eq/L}$

conc. of $\text{NaCl} \equiv \frac{50(1000)}{(58.5 \times 10^6)} = 0.000855 \frac{\text{mol}}{\text{L}} = 0.000855 \text{ eq/L}$

(a) Bed cross-section $\Rightarrow \frac{\pi}{4} d^2 = \frac{\pi}{4} (8.5)^2 = 56.7 \text{ ft}^2$

Feed vol. flow rate $= 15 \frac{\text{gal}}{\text{min. ft}^2} \times 56.7 \text{ ft}^2 \equiv 851 \text{ gpm} \quad (3219 \text{ L/min})$

(b).



The equivalent fraction of calcium ions this x is 0.0072 by the total amount of ions which is like partly calcium and some amount of sodium is also there. So, 0.0072 plus 0.000855. So, this is we are doing it because the feed also contains some amount of sodium ions. So, this becomes 0.8938. So, this is in. So, since NaCl is exchanged NaCl is exchanged the total concentration of the you know calcium ions is a total amount of the ions that is present in the solution actually this 0.0072 equivalent per and the value of Q the total amount of ion exchange sites present in the resin is already given that is 2.3 equivalent per liter. Now, the value of this selectivity coefficient or this equilibrium constant of calcium with respect to sodium is 5.2 by 2 that is 2.6. Now writing down the equilibrium relation which is K is equal to Q by C in this case for between calcium and sodium because n is equal to 2 this turns out to be y 1 minus x square divided by x 1 minus y square So here this is all calcium.

So I should take some care to write this as calcium because sodium is also present in the solution and of course we are writing down this equilibrium only for calcium because sodium is not getting exchanged in the process here and this constant is for preferential selectivity of calcium over sodium. So this is squared, this is squared. So if you put in the

numbers here, so k is 2.6, q is 2.3. So sorry, this is c by q , pardon my mistake, ct by q . So that is 0.0072 by 2.3 times y is something that we are trying to find out x is 1 minus 0.00 sorry 0.8938 divided by 0.8938 1 minus y calcium you rearrange this equation this looks like left hand side is 830.6 right hand side is $0.0126 y$ calcium by 1 minus y calcium whole square. So, if you solve this quadratic equation solving the quadratic solving the quadratic equation. You will get the solution of $C A^2$ plus as 0.99611 and the other root is also very important to note that is 1.0039 it is a quadratic equation. So, we will be getting two solutions. Now of course, this is not a feasible solution this is not feasible because mole this equivalent fraction cannot be more than 1 . So, this is the solution that we consider here for this concentration of calcium or the concentration fraction of calcium in the resin phase.

Now, this bed volume we know it is 56.7 is the cross sectional area multiplied with the height that is 10 feet. So, this gives us 567 feet cube which is equivalent to 16000 square feet. 60 liters of the bed. Total bed capacity we are interested in finding out the volume because the total bed capacity or the resin capacity or the ion exchange capacity.

So, total ion exchange capacity is given this q is given in terms of per liter of the bed volume. So, that is the reason. So, this q is liters of bed volume not liters of solution. So, this ion exchange capacity is this Q times the bed volume that is $16,060$.

So, the value of Q is 2.3 . So, if you put the numbers you will get $36,940$ equivalent amounts that is the ion exchange capacity or the total ion exchange capacity of the bed. The amount of calcium that is absorbed by the resin is Y times this total ion exchange capacity is 36940 . So, using the number of Y of 0.99611 , this number turns out to be 36796 . equivalents of calcium that is adsorbed or present in the resin phase.

(b) Behind the loading wave front in the feed
eq. fraction of Ca^{2+} , $x_{\text{Ca}^{2+}} = \frac{0.0072}{(0.0072 + 0.000855)} = 0.8938$

Since no NaCl is exchanged, $c_T = 0.0072 \text{ eq/L}$ $Q = 2.3 \text{ eq/L bed}$

$K_{\text{Ca}^{2+}, \text{Na}^+} = 5.2/2 = 2.6$

$K_{\text{Ca}^{2+}, \text{Na}^+} = \frac{c_T}{Q} \frac{y_{\text{Ca}^{2+}}(1-x_{\text{Ca}^{2+}})^2}{x_{\text{Ca}^{2+}}(1-y_{\text{Ca}^{2+}})^2} \Rightarrow 2.6 = \frac{0.0072}{2.3} \frac{y_{\text{Ca}^{2+}}(1-0.8938)^2}{0.8938(1-y_{\text{Ca}^{2+}})^2}$

$\Rightarrow 830.6 = 0.0126 \frac{y_{\text{Ca}^{2+}}}{(1-y_{\text{Ca}^{2+}})^2}$

Solving the quadratic eqn:
 $y_{\text{Ca}^{2+}} \sim 0.99611 \text{ \& } 1.0039$
NOT feasible

Bed vol. $(56.7)(10) = 567 \text{ ft}^3$
 $(16,060 \text{ L})$

Total ion-exchange bed capacity, $\nearrow 2.3$
 $(16060) \cdot =$

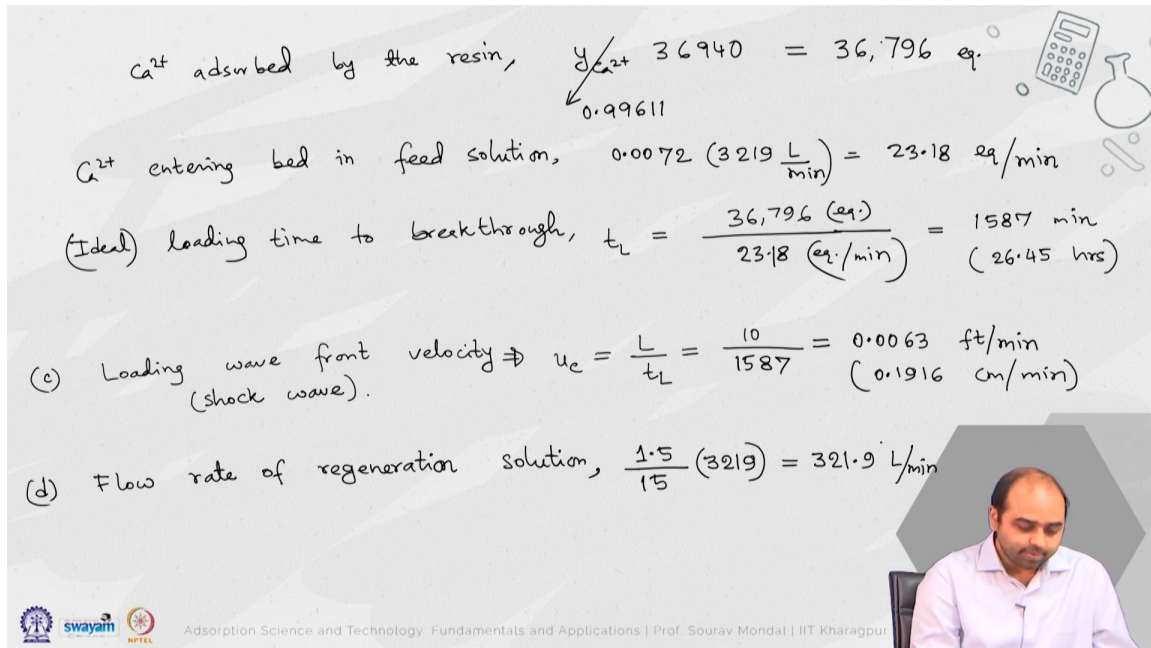
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So, calcium entering bed in feed solution is 0.0072 times the feed flow rate this is like liters per minute So, this gives us 23.18 equivalents per minute of the calcium that is entering in the feed and the calcium that is absorbed is like 36000 almost. So, the ideal loading time to breakthrough is when all the you know sites in the resin is filled by the calcium present in the feed solution. So, in this case this 36796 equivalents amount of the ion exchange sites to be filled up by calcium because that is the maximum equilibrium capacity that it can go at this concentration of 400 ppm is filled up by the amount of you know calcium or the equivalents of calcium that is coming through from the feed is 23.

18. that this is the equivalent amounts of calcium that is coming through the feed and this is the equivalent amounts of calcium that the bed can take up at this or at the equilibrium condition that is the capacity of the bed that it can absorb the you know resin. So, this if you work out the numbers this comes out to 1587 minutes which is equivalent So, this is the breakthrough time for this bed of 10 feet at this particular you know of concentration of the feed . Coming to the third part the loading wave front velocity which is this ion front velocity. So, we assume this to be a you know shock wave like scenario or a sharp wave. this length of the bed divided by the you know breakthrough time.

So, that is 10 by 26.5 or if I want to write this in terms of minutes then it will be 1587 which is equal to 0.0063 feet per minute. or in terms of centimeter this is 0.1916 centimeters per minute. Next coming to the flow rate of regeneration solution which is

1.5 times 3219/15. So, that is equal to 321.9 liters per minute. Now coming to the displacement time. So, as you know that this displacement is done using the regenerated solution. So, the time needed to flow time needed for 321.9 liters per minute to displace liquid from the voids that is the displacement time.



Handwritten calculations on a whiteboard:

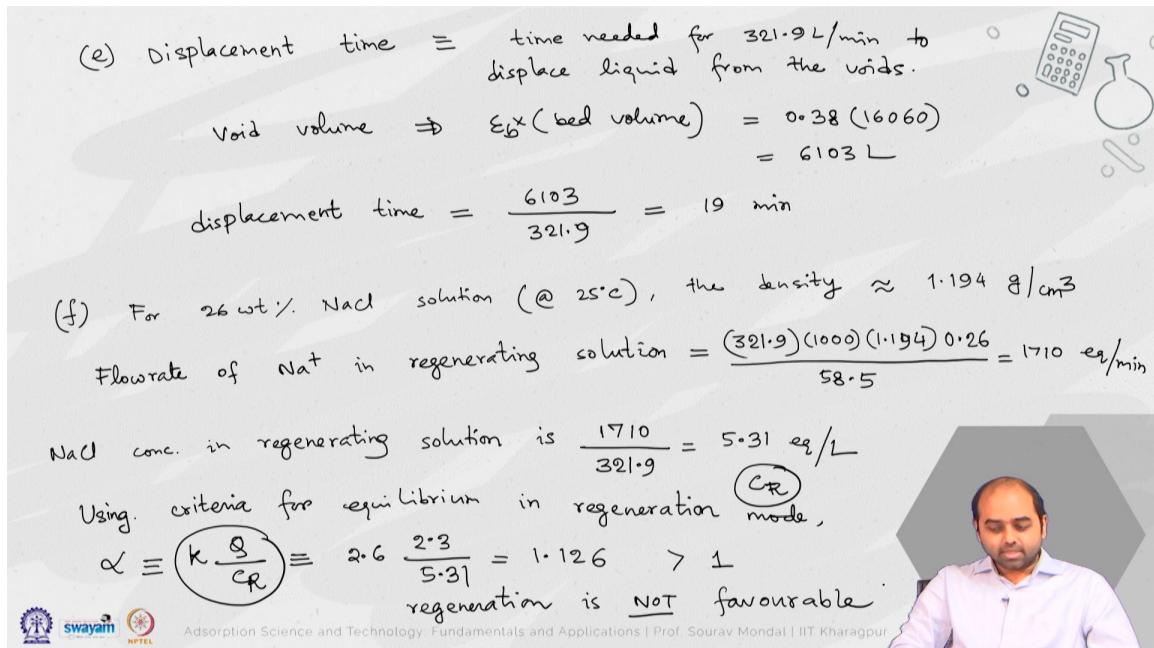
- Ca^{2+} adsorbed by the resin, $\frac{y}{x} Ca^{2+} = \frac{36940}{0.99611} = 36,796 \text{ eq.}$
- Ca^{2+} entering bed in feed solution, $0.0072 (3219 \frac{L}{min}) = 23.18 \text{ eq./min}$
- (Ideal) loading time to breakthrough, $t_L = \frac{36,796 \text{ (eq.)}}{23.18 \text{ (eq./min)}} = 1587 \text{ min}$ (26.45 hrs)
- (c) Loading wave front velocity $\Rightarrow u_c = \frac{L}{t_L} = \frac{10}{1587} = 0.0063 \text{ ft/min}$ (0.1916 cm/min)
- (d) Flow rate of regeneration solution, $\frac{1.5}{15} (3219) = 321.9 \text{ L/min}$

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So, the void volume is the porosity bed porosity times the total bed volume. So, that is equal to 0.38 times 16,060 liters which turns out to 6,103 liters. So, displacement time so, it is only in that porous region or in the void region the fluid can be driven out. So, the displacement time is 6103 the void volume divided by the this flow rate or the regeneration wave front velocity that is 321.9 liters per minute. So, this turns out to be around 19 minutes. So, 19 minutes is the displacement time. Now coming to the last part is to check whether regeneration is favorable or not. So, for 26 weight percent because the regeneration solution is sodium chloride. So, 26 weight percent sodium chloride solution is used as the regeneration solution present at 25 degree centigrade.

The density is If you take it from some Perry's handbook or some other you know resources, you will find out that this is almost 20 percent enhancement. So, this is around 1.194 gram per centimeter cube. So, the normal water density is 1 gram per centimeter cube, but adding sodium chloride increases it by 20 percent almost. So, the flow rate of sodium ions in the regenerating solution is 321.9 times 1000 times the density 1.194 that is the weight percent of sodium divided by the molecular weight 58.45 and this gives 1710 equivalent per minute of sodium ions in the regenerating solution. The NaCl concentration is regenerating solution is by 321.9. So, that turns out to be 5.31 equivalent

per you know litre in this case and this could be the amount of you know the concentration C_t for the regeneration equilibrium or for the regeneration process. So, using you know this criterion for this equilibrium in regeneration mode, we see that k times this C let us call this as like C_R because this is a concentration in the regeneration mode. If this quantity, we try to find out for here this turns out to be 2.6 times Q is 2.3 and here it is 5.31. So, this is 1.126 and this is nothing but your alpha for the regeneration part. of this monovalent and divalent exchange sorry divalent and monovalent exchange. And in this case the concentration of the sodium in the regenerating phase is used for the total concentration for the equilibrium. And, the we see here that this is greater than 1. So, since the alpha is you know greater than 1 for the regenerating scenario the equilibrium is not favorable.



(e) Displacement time $\equiv$ time needed for 321.9 L/min to displace liquid from the voids.

Void volume $\Rightarrow E_b \times (\text{bed volume}) = 0.38 (16060) = 6103 \text{ L}$

displacement time $= \frac{6103}{321.9} = 19 \text{ min}$

(f) For 26 wt% NaCl solution (@ 25°C), the density $\approx 1.194 \text{ g/cm}^3$

Flowrate of Na^+ in regenerating solution $= \frac{(321.9)(1000)(1.194)0.26}{58.5} = 1710 \text{ eq/min}$

NaCl conc. in regenerating solution is $\frac{1710}{321.9} = 5.31 \text{ eq/L}$

Using criteria for equilibrium in regeneration C_R mode,

$\alpha \equiv \left(k \frac{Q}{C_R} \right) \equiv 2.6 \frac{2.3}{5.31} = 1.126 > 1$

regeneration is NOT favourable

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So, here the regeneration is not favorable in terms of this value of this alpha greater than 1. So, I hope this is something that I want to stress upon that what happens during the regeneration and how do you calculate the regeneration time and the regeneration wave front. This is a small problem on this ionic cyclic exchange here we have assumed the shock wave scenario or self sharpening front which may not be the case for regeneration at least because it is So, the regeneration would be like a diffuse wave front and one need to account for the you know this particularly the diffusion effects and work out the you know the diffuse movement of the ions to find out from the equilibrium using the Donnan exclusion coefficient what would be the solute wave front velocity during the regeneration particularly for diffuse movements . This is the final lecture of this course I believe all of you found this topic to be quite interesting and useful for your curriculum in

whichever field you are in and whatever you know objectives of your work this can be to some extent be useful and valuable for your career. Thank you and I wish you all the best for your future endeavours in your career and in your workplace. Thank you.