Lecture 7: Ion Exchange

Water Treatment Technology

Water Resources Engineering
Civil Engineering
ENGC 6305

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Ion Exchange

1. Principles of Ion Exchange

A. Definition of Ion Exchange :

- Ion exchange is a unit process in which ions of a given species are displaced from an insoluble material (called resin) by ions of a different species in solution.
- The exchanged ions have the same charge, that's to say, positive ions are exchanged for positive ions, for example:

Na^{+} is exchanged for Mg^{+2} and Ca^{+2}.
OH^{-} is exchanged for NO_3^{-} .

- The exchange resin is either a naturally occurring material such as zeolite or synthetic organic material . Resins are either cationic or anionic. The resins are usually beads or granular particles having a size of about 0.1 to 1.0 mm. See Figures 7.1 and 7.2

Figure 7.1 Ion Exchange resin

Figure 7.2 Ion Exchange resin

Ion Exchange

- Cationic resins are materials that have reactive groups that can give up positive ions in exchange of other positive ions from the liquid phase
- Anionic resins are materials that have reactive groups that can give up negative ions in exchange of other negative ions from the liquid phase.
- The exchange of ions is governed by the relative preference and the strength of ions to replace others. The preference series for the most common cations and anions is given in the next slide.
- From the cation or the anion preference series, the ion in the upstream of the series can replace or remove all the ions down stream of the series. such as Ba^{+2}. For example Ba^{+2} is able to remove all the ions lower in the series such as Na^{+}. And SO_4^{-2} is able to remove all the ions lower in the series such as OH^{-}.

Ion Exchange

Preference series shows which ions exchange

For cation exchangers:

$Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{+2} > Cd^{+2} > Cu^{2+} > Co^{2+} > Zn^{2+} > Mg^{2+} > Ag^{+} > Cs^{+} > Rb^{+} > K^{+} > NH_4^{+} > Na^{+} > H^{+}$

For anion exchangers:

$SO_4^{-2} > CLO_4^{-} > I^{-} > NO_3^{-} > CrO_4^{-2} > CO_3^{-2} > Br^{-} > CL^{-} > HCO^{-} > F^{-} > OH^{-}$

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B. Types of ion exchange resins:

- Both anion and cation resins are produced from the **same basic organic polymers**. They **differ** in the **ionizable group** attached to the **hydrocarbon network**. It is this **functional group** that determines the chemical behavior of the resin.
- Resins can be broadly classified as strong or weak acid cation exchangers or strong or weak base anion exchangers.

The following are the main materials that are used as ion exchangers:

- Zeolite (natural occurring mineral called greensand).
- Synthetic organic polymers.

Synthetic polymers are the mostly used ion exchange resins in water treatment.

Ion Exchange

C. Use of Ion Exchange in water treatment:

Ion exchange is used in water treatment for the following two applications:

1. Softening :

   The resin used for softening is called the sodium exchanger. In this exchanger Na^+ is changed for polyvalent cations , specially Ca^{+2} and Mg^{+2}. The chemical reactions of ion exchange softening is shown in the following slide. See Figure 7.3

2. Demineralization:

   Two resins are used in demineralization the first is called the hydrogen (H^+) exchanger which is used to remove positively charged ions (such as nickel, copper, and sodium), and the second is called the hydroxyl (OH^-) exchanger which is used to remove negatively charged ions such as sulfates, nitrates, carbonates, chromates and chlorides). The chemical reactions of ion exchange softening is shown in the following slide. See Figure 7.4

Ion Exchange

2. Ion exchange chemistry:

A) Sodium cation exchange:

Softening:

$$Ca^{+2} + 2Na.R \longrightarrow Ca.R + 2Na^{+}$$

$$Mg^{+2} + 2Na.R \longrightarrow Mg.R + 2Na^{+}$$

Regeneration: using strong brine (NaCl)

$$Mg.R + 2NaCl \longrightarrow 2Na.R + MgCl_2$$

$$Ca.R + 2NaCl \longrightarrow 2Na.R + CaCl_2$$

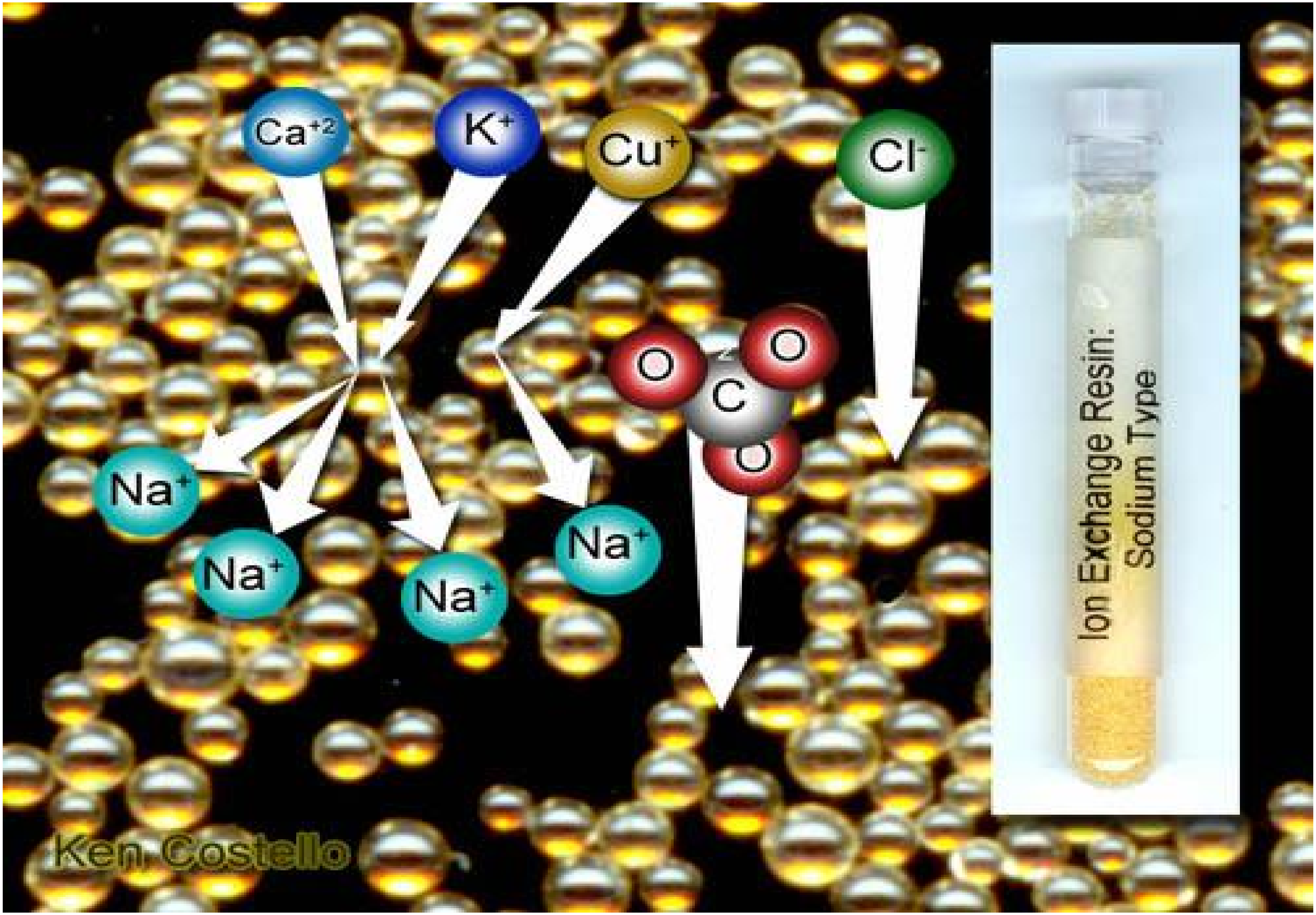

Figure 7.3	Sodium type ion exchange resin

Ion Exchange

B. Demineralization (Deionization):

i) Hydrogen cation exchange:

$$M^{+a} + aH.R \longrightarrow M.R_a + aH^+$$

Examples: $Ca^{+2} + 2H.R \longrightarrow Ca.R_2 + 2H^+$

$$Na^+ + H.R \longrightarrow Na.R + H^+$$

Regeneration: using strong acid

$$Ca.R + H_2SO_4 \longrightarrow 2H.R + CaSO_4$$

$$2Na.R + H_2SO_4 \longrightarrow 2H.R + Na_2SO_4$$

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Demineralization (Deionization) continued:

ii) Hydroxyl anion exchange:

$$A^{-b} + bR.OH \longrightarrow R_b.A + bOH^-$$

Examples:

$$NO_3^- + R.OH \longrightarrow R.NO_3^- + OH^-$$

$$CO_3^{-2} + 2\ R.OH \longrightarrow R_2.CO_3^{-2} + 2OH^-$$

Regeneration: using strong base (caustic soda)

$$R.NO_3^- + NaOH \longrightarrow R.OH + NaNO_3$$

$$R_2.CO_3^{-2} + 2NaOH \longrightarrow 2R.OH + Na_2CO_3$$

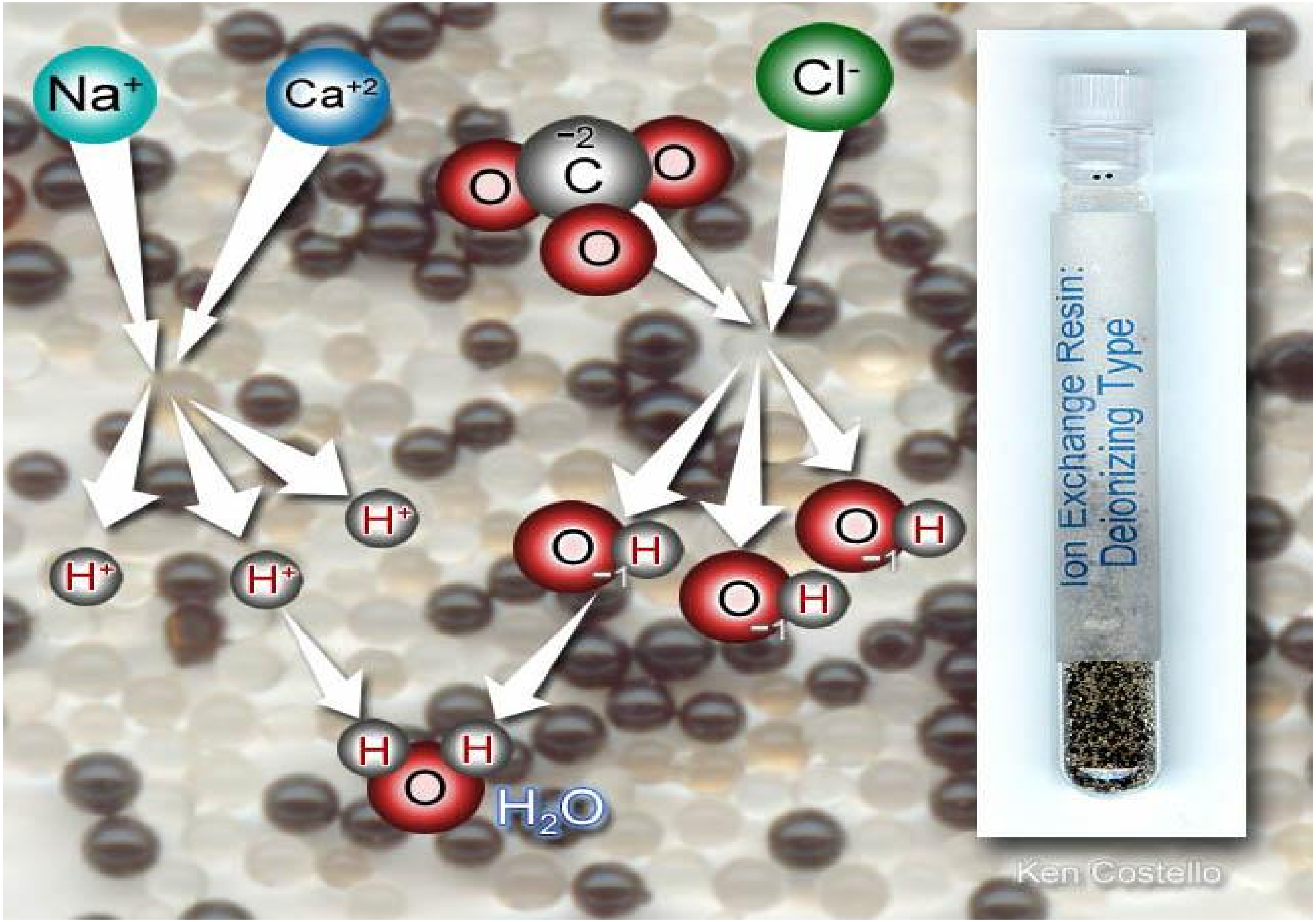

Figure 7.4 | Deionizing type ion exchange resin

Ion Exchange

C. Regeneration ion exchangers:

- Each resin has a limited capacity of exchanging ions.
- After a certain time of operation the resin reach its maximum capacity and no further ions are removed from the liquid phase. At this point is said to have reached the breakthrough concentration (similar to adsorption).
- After reaching the breakthrough concentration of the cation or anion under consideration, the ion exchanger tank is taken off line.
- For sodium exchangers, a strong brine of NaCl is pumped in the resin bed to add the Na+ ions to restore the exchange capacity of the resin by replacing the cations (Ca^{+2} and Mg^{+2}) that were attached to the resin during the operation. The strength of the brine overcomes the strength of the bond between the cations (Ca^{+2} and Mg^{+2}) and the resin.
- For demineralization, a strong acid such as H_2SO_4 or HCl is used to regenerate the Hydrogen resin, a strong base such as caustic soda (NaOH) is used to regenerate the Hydroxyl resin.

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3. The ion exchange system in water treatment:

a) Configuration of the ion exchanger (Figure 7.5):

- The main component of the ion exchanger is a cylindrical steel tank with the following typical dimensions:

  Diameter 1-2 m

  Height 3-4 m (typical to the adsorption tanks)
- The ion exchange bed occupies 1-3 meters of the tank height and supported from the bottom with an under drain system.
- The water inters from the top (downflow) by an influent distributor piping system and applied at the rate of 0.5 to 7 $L/s.m^2$.
- When breakthrough is reached the tank is taken off-line and backwashed by applying water form the bottom upwards to remove any suspended solids.
- After backwashing the regeneration solution is also pumped from the bottom up wards at the rate of 0.7 to 1.5 $L/s.m^2$. The same influent distributor is used to drain the upflow backwash water and the regeneration solution (brine, acid or base). At the end of the regeneration the bed is washed with clean water to remove the residual of the regeneration solution
- An under drain piping system is installed at the bottom to collect the treated water, and used to pump the upflow backwash water and the regeneration solution.

Ion Exchange

Figure 7.5	Typical ion exchange installation

Ion Exchange

b) Pretreatment:

- The influent to the ion exchanger should be filtered to remove turbidity.
- Dissolved Organic matter should be removed by GAC before the IE because the organic may coat th resin and reduce its exchange capacity.
- The IE is efficient for TDS less than 1000 mg/L.

c) Sizing ion exchanger :

- The sizing of the ion exchanger depends on the following factors:

i) Contact time
ii) Hydraulic loading rate
iii) resin depth
iv) number of columns.

d) Multiple tanks Operation:

- Ion exchange tanks can be operated in parallel or in series. Figures 7.6 illustrates the series operation.
- A minimum of two parallel carbon contactors is recommended for design.
- Multiple units permit one or more units to remain in operation while one unit is taken out of service for backwashing and generation or maintenance.

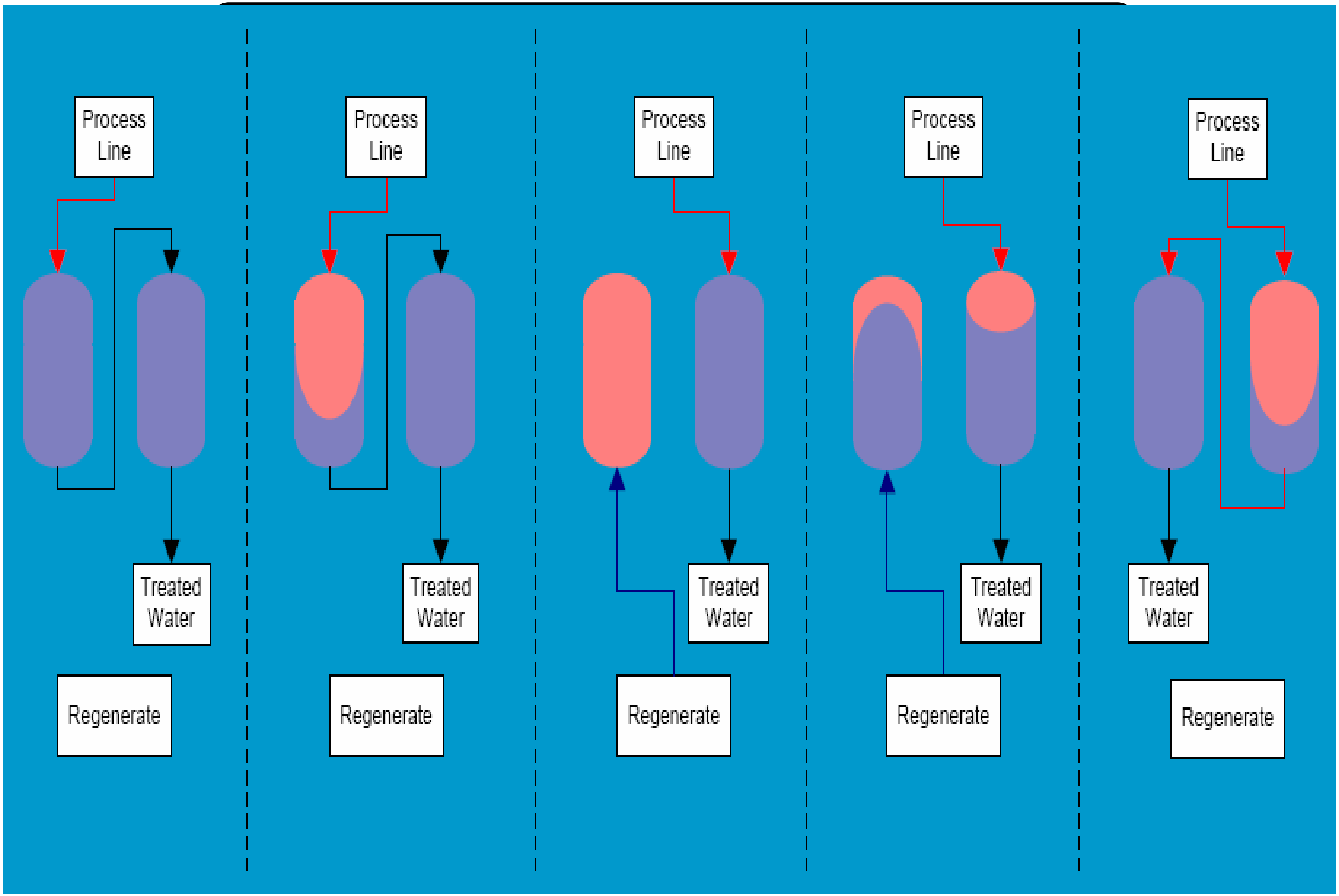

Figure 7.6 Ion Exchanger tanks operated in series

Ion Exchange

4. Exchange capacity of ion exchange resins:

- Ion Exchange resins have a limited number of exchange site available, and the total solid phase concentration "q_0" is termed ion exchange capacity.
- For cation exchange resins, "q_0" is in the range of 200 to 500 meq/100mg of resin.
- During the exchange, the resin should be electrically neutral thus the all the exchange sites should be occupied either by the original ion (such as Na+) or by the replacing ions (such as Ca^{+2} and Mg^{+2}) and the ion exchange occupancy should be equal to "q_0" at any time.
- Many equations were developed to determine exchange capacity. The most famous equation is the Thomas kinetic equation (Eq. 7.1). used for ion exchange columns.

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Thomas kinetic equation for ion exchange capacity:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_1 q_0 M}{Q} - \frac{k_1 C_0 V}{Q} \quad \text{.......... ....(7.1)}$$

C = effluent concentration of the ions, mg/l or meq/l

C_0 = influent concentration of the ions, mg/l or meq/l

k_1 = rate constant, L/d . eq

q_0 = maximum solid phase concentration of exchange solute, eq/kg of resin

M = mass of resin, kg

V = throughput volume, L

Q = flowrate, L/d

This equation is a linear equation in the form : y = mx+ c.

Slope = $\frac{k_1 C_0}{Q}$

Intercept = $\frac{k_1 q_0 M}{Q}$

To apply this equation it is necessary to perform a laboratory column test or pilot scale column to obtain the breakthrough curve. See Fig. 7.7

Ion Exchange

5. Ion Exchange process analysis in the Fixed bed

a) Mass transfer inside the Ion exchange bed:

When the polluted water is pumped on the ion exchange bed the, the pollutant ions replace the exchangeable ions in the resin. The area of the ion exchange bed in which the exchange occurs is called the mass transfer zone (MTZ) See Figure 7.7.

-No further adsorption occurs below the MTZ and the water leaving the MTZ zone contains the minimum concentration value of the pollutant that the bed can produce.

-With time a zone of saturation is created above the MTZ in which the resin has reached its maximum exchange capacity and no further replacement occurs. The equilibrium concentration C_e of the pollutant in water in this zone is the same as C_0.

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-The Zone below the MTZ essentially clean zone and no adsorbed material on it.

-With time the saturation zone depth increases and the MTZ is pushed down until we reach to a point where the clean zone disappears and breakthrough occurs.

- Breakthrough is said to have occurred when the effluent concentration reaches to 5% of the influent concentration (i.e, $C_b = 0.05C_0$).

-After additional time the MTZ start to decrease until it disappears and the bed is called exhausted. Exhaustion of the bed is assumed to have occurred when the effluent Concentration is equal to 95% of the influent concentration (i.e, $C = 0.95C_0$)

-The length of the MTZ is calculated from the following equation (6.3):

$$H_{MTZ} = Z\left[\frac{V_E - V_B}{V_E - 0.5(V_E - V_B)}\right] \quad \text{.............................(7.2)}$$

where H_{MTZ} = length of mass transfer zone, (m)

Z = height of the adsorption column, (m)

V_E = throughput volume to exhaustion, m^3

V_B = throughput volume to breakthrough, m^3

-The area above the breakthrough curve is equal to the mass of the pollutant adsorbed in the column and equal to: $X = \int_0^V (C_0 - C)\, dV$ ....(6.4)

Ion Exchange

MTZ = δ

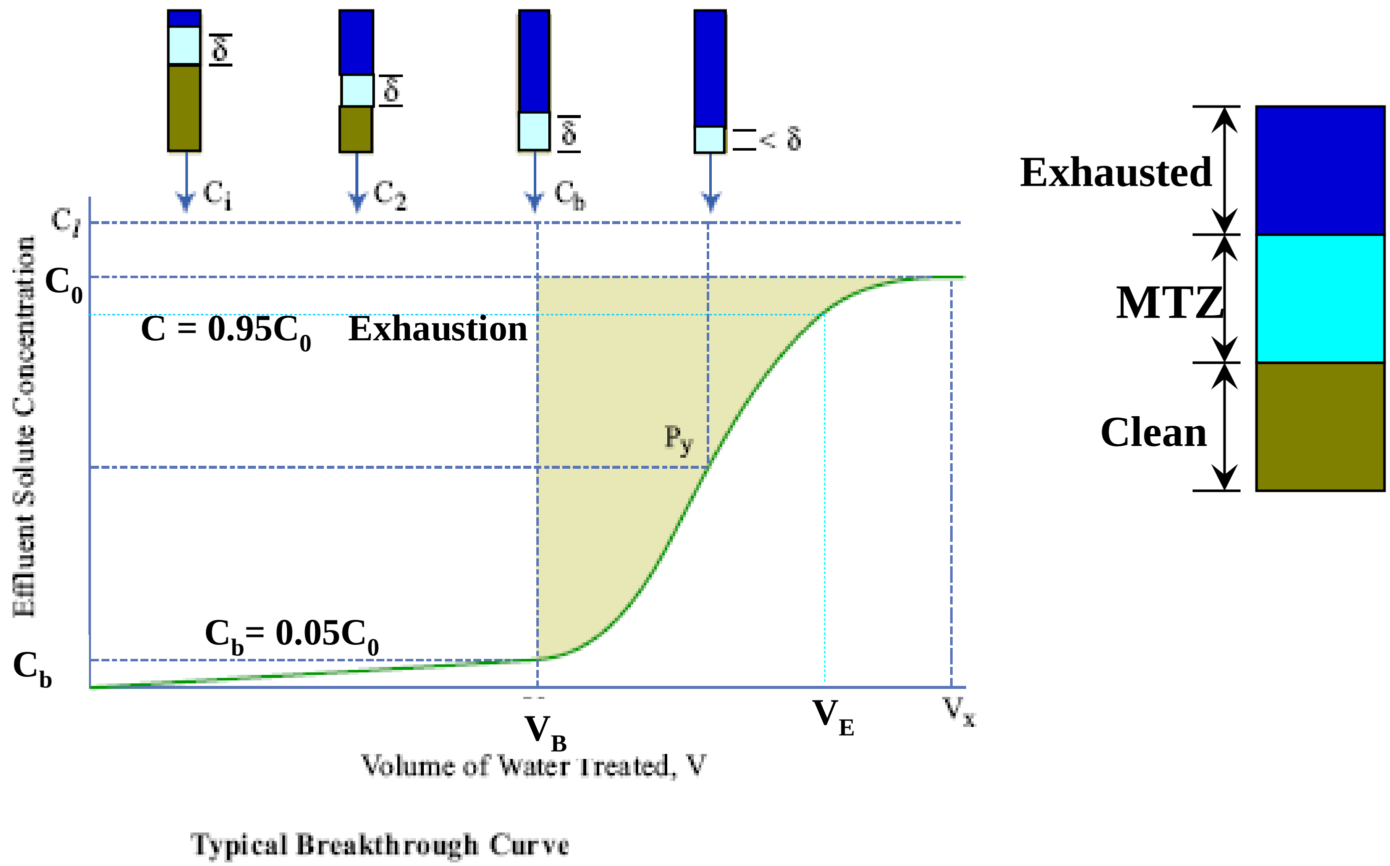

Figure 7.7

Ion Exchange

Example 7.1 :

Ion Exchange in Waste Treatment

An industrial wastewater with 107 mg/ℓ of Cu^{+2} (3.37 meq/ℓ) is to be treated by an exchange column. The allowable effluent concentration, C_a, is 5% C_0. A breakthrough curve, shown below 3.6, has been obtained from an experimental laboratory column on the sodium cycle. Data concerning the column are as follows: inside diameter = 1.3 cm, length = 45.7 cm, mass of resin = 41.50 gm on a moist basis (23.24 gm on a dry basis), moisture = 44%, bulk density of resin = 716.5 kg/m³ on a moist basis, and liquid flowrate = 1.0428 ℓ/d. The design column flowrate will be 378,500 ℓ/d, the allowable breakthrough time is 7 days of flow, and the resin depth is approximately twice the column diameter. Using the kinetic approach to column design, determine:

1. The kilograms of resin required.
2. The diameter and depth.
3. The height of the sorption zone.

Ion Exchange

Example 7.1 … Cont'd:

Solution:

-The data obtained from the lab experiment is summarized in columns (1) and (2) in the Table to the right.
-The data in columns 1 and 2 are used to draw the breakthrough curve as Shown in figure 7.8.
-The data is arranged in columns 4,5 and 6 in the forms necessary to plot the Thomas equation as Shown in figure 7.9.

I *Reduced Data from Breakthrough Test*

(1) V (liters)	(2) C (mg/ℓ)	(3) C (meq/ℓ)	(4) C/C_0	(5) C_0/C	(6) $C_0/C - 1$
15.9	4.45	0.14	0.041	24.29	23.29
16.9	9.85	0.31	0.091	10.97	9.97
18.1	17.16	0.54	0.159	6.30	5.30
19.1	27.56	0.88	0.259	3.86	2.86
19.5	40.03	1.26	0.371	2.70	1.70
20.0	49.56	1.56	0.459	2.18	1.18
20.7	62.90	1.98	0.582	1.72	0.72
21.2	68.89	2.20	0.647	1.55	0.55
22.0	86.41	2.72	0.800	1.25	0.25
22.9	94.03	2.96	0.871	1.15	0.15
23.4	98.17	3.09	0.917	1.09	0.09
24.0	102.93	3.24	0.961	1.05	0.05
26.0	107.00	3.37	1.000	1.01	0.01

Ion Exchange

Example 7.1 … Cont'd:

- From Fig 7.9 the slope $\boxed{\frac{k_1 C_0}{Q}}$ = 0.7583 L^{-1}

$$k1 = Slope * \frac{Q}{C_0} = 0.7583 L^{-1} \bullet \frac{1.0428\ L/d}{3.37\ meq/L} \bullet \frac{1000\ meq}{1\ eq} = 234.6\ L/(d \bullet eq)$$

- From Fig 7.9 the intercept $\boxed{\frac{k_1 q_0 M}{Q}}$ = 15.33 L^{-1}

$$q_0 = \text{intercept} \bullet \frac{Q}{k_1 M} = 15.33 \bullet \frac{(1.0428\ \text{L/d})}{(234.6\ \text{L/d} \bullet \text{eq}) \bullet 23.4\ \text{g}} \bullet \frac{1000\ \text{g}}{1\ \text{kg}} = 2.932\ \text{eq/kg}_{\text{resin}}$$

-Mass of resin needed for the full scale column Can be found from the Thomas equation :

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_1 q_0 M}{Q} - \frac{k_1 C_0 V}{Q}$$

Ion Exchange

Example 7.1 … Cont'd:

$$\ln\left(\frac{C_0}{0.05\,C_0}-1\right)=\ln\left(\frac{1}{0.05}-1\right)=2.9444$$

$$\frac{k_1 q_0 M}{Q}=\frac{234.6\ L/(d\bullet eq)(2.932\ eq/kg)(M\ \ kg)}{378500\ L/d}$$

$$\frac{k_1 C_0 V}{Q}=\frac{234.6\ \ L/(d\bullet eq)(3.37\ \ meq/L)*(1\ eq/1000\ \ meq)}{378500\ \ L/d}\bullet\frac{(7d\bullet 378500L)}{d}$$

-Substitute the three above terms in the Thomas equation and solve for M:

M = 4670 kg dry weight of resin

- Resin volume = (4670 kg)(1/0.56)(716.5 kg/m^3) = 11.6 m^3

Resin volume = $(\pi/4)(D^2)(2D)$ = 11.6 m^3

D = 1.95 m (diameter of the column)

Z = 2D = 3.9 m (depth of the resin bed)

-Since it was assumed that the breakthrough occurs after 7 days (at $C=0.05C_0$) then the breakthrough Volume (V_B) = 7*378500 = 2.65 X 10^6 L

-To find (V_E) at C= 0.95 C_0 apply Thomas equation and solve for V, the result is: (V_E)= 5.47 X 10^6 L

- Since V_B, V_E, and Z are known find H_{MTZ} apply equation 7.2, so $\longrightarrow H_{MTZ}$= 2.69 m

Ion Exchange

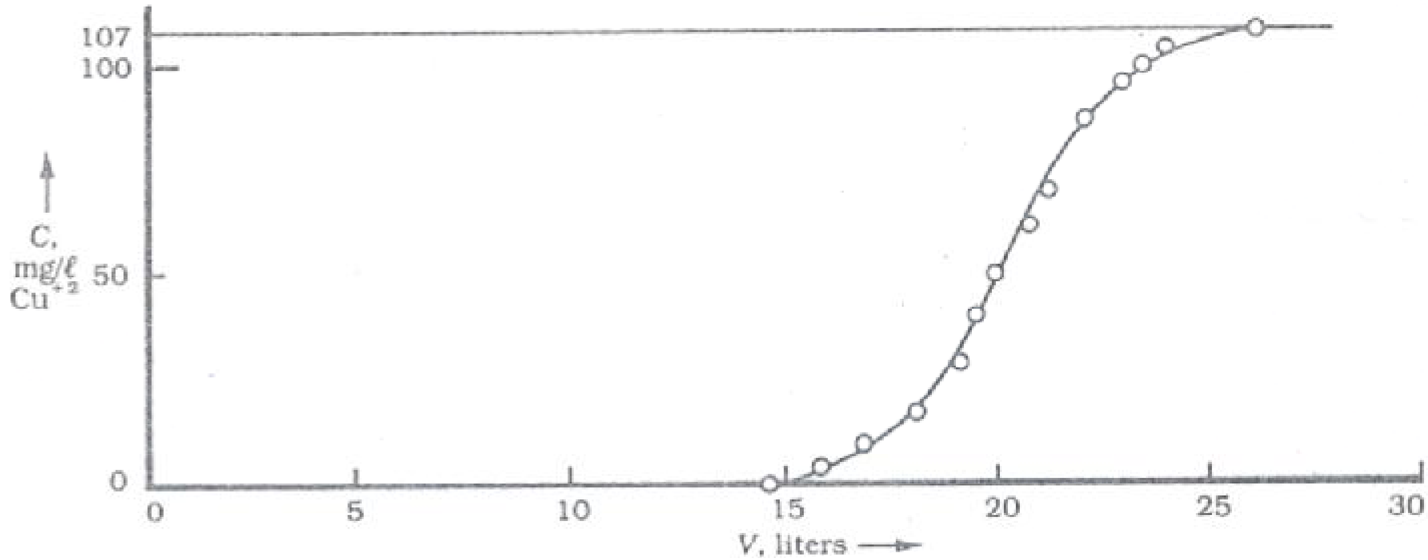

Figure 7.8

Ion Exchange

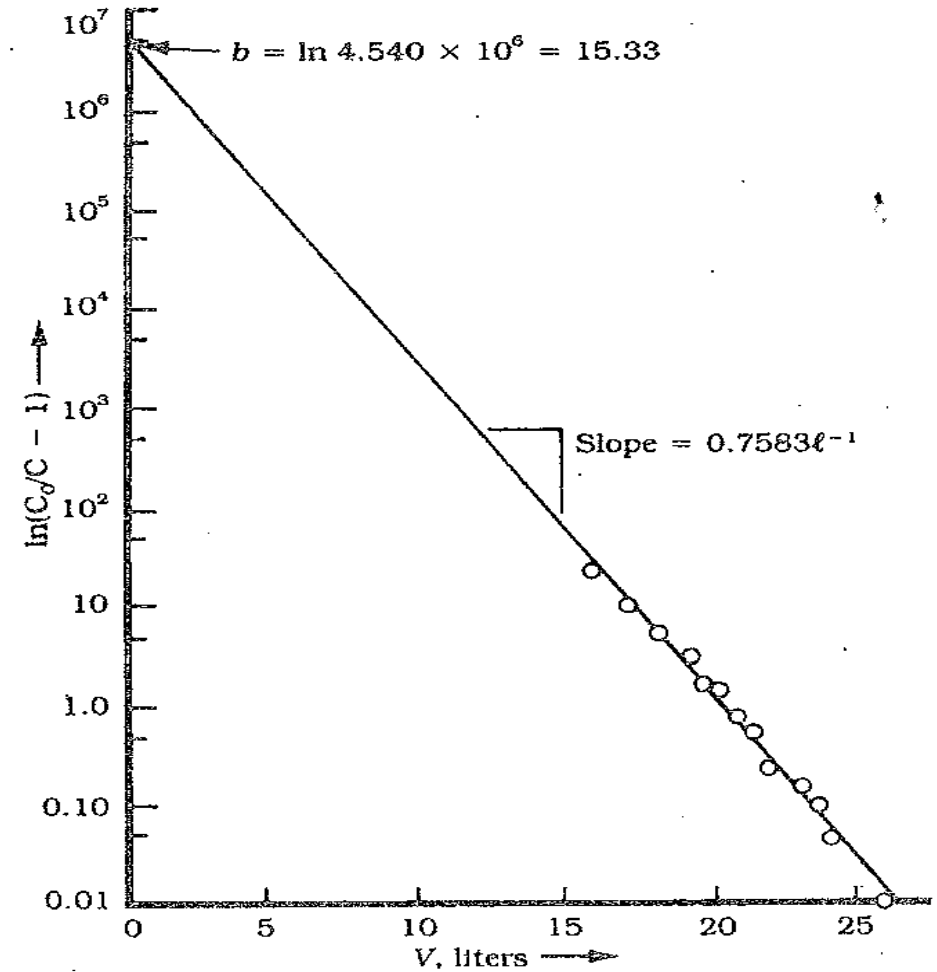

Figure 7.9

Ion Exchange

EXAMPLE 13.2 *Ion Removal*

For the test column and breakthrough curve given in Example 13.1, determine the meq of Cu^{+2} ion removed per 100 gm resin on a dry weight basis at the allowable breakthrough volume, V_B, for $C_a = 0.05C_0$. Also, determine the meq of Cu^{+2} ion removed per 100 gm resin on a dry weight basis at complete exhaustion. The dry weight of resin used was 23.24 gm.

SOLUTION The meq weight of Cu^{+2} is 63.54/2 or 31.77 mg. The area above the breakthrough curve from V = zero to V = the volume under consideration is equal to the ion content removed by the exchanger. 1 **7.10** 3.8 shows the breakthrough curve and the area above the breakthrough curve out to V_B, the allowable breakthrough volume for $C_a = 0.05C_0$. The area, A_1, is 1735 mg or 1735/31.77, which is equal to 54.61 meq. From the allowable breakthrough volume, V_B, to the volume at exhaustion, the area, A_2, is 437 mg or 437/31.77, which is equal to 13.76 meq. At exhaustion, the total area is 54.61 + 13.76 or 68.37 meq. The copper removed at $C_a = 0.05C_0$ is 54.61 meq/23.24 gm or $\boxed{\text{235 meq/100 gm dry weight.}}$ The copper removed at exhaustion is 68.37 meq/23.24 gm or $\boxed{\text{294 meq/100 gm dry weight.}}$

Ion Exchange

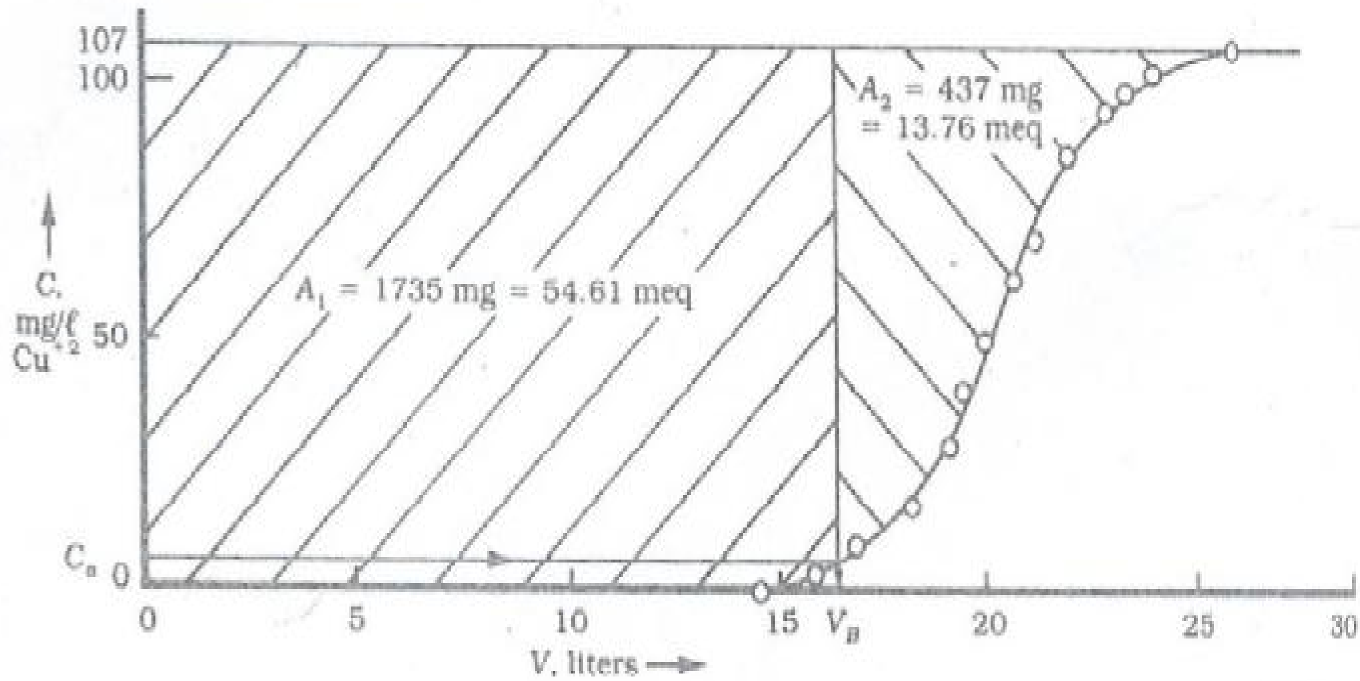

Figure 7.10

Ion Exchange

EXAMPLE 13.3 *Ion Exchange Softening*

A well water is to be softened by split-flow ion exchange with the exchanger on the sodium cycle. The flow is 50 gpm, the hardness = 225 mg/ℓ as $CaCO_3$, the desired hardness is 50 mg/ℓ as $CaCO_3$, and the moisture content of the resin is 45%. A test column has been used in the laboratory to obtain a breakthrough curve. The computed hardness removed by the resin at the allowable breakthrough concentration $C_a = 0.05C_0$ was 282 meq/100 gm resin on a dry weight basis. Determine the kilograms of resin required if the allowable breakthrough is seven days.