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## Tertiary Treatment of Wastewaters

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## 1. Introduction

Tertiary treatment (also referred as "advanced wastewater treatment") consists of processes which are designed to achieve higher effluent quality than conventional secondary treatments described in Chapters 5 and 6. The following types of tertiary treatment are described in this chapter: (1) suspended solids removal, (2) carbon adsorption (organic removal), (3) ion exchange, (4) reverse osmosis, (5) electrodialysis, (6) chemical oxidation (chlorination and ozonation), (7) nutrient removal methods (nitrogen and phosphorus removal), and (8) sonozone wastewater purification process. These processes are not utilized extensively in wastewater treatment today, but their use on an increasingly larger scale is anticipated as effluent quality requirements become more stringent in the future.

## 2. Suspended Solids Removal

Suspended solids which have not been removed by conventional primary and secondary operations may constitute a major part of the BOD of effluents from wastewater treatment plants. The following removal processes for these suspended solids are available: (1) microscreening, (2) filtration, and (3) coagulation.

Microscreens are wound around rotating drums. Wastewater is fed continuously to the inside of the drum, flowing to a clear water storage chamber on the outside. Cleaning of the inner surface of the drum is performed by sprays of clear water, washing requirements usually being about 5% of feed volume. Microscreening results in 70-90% removal of suspended solids. Filtration is commonly used for suspended solids removal yielding removal efficiencies up to 99%. Sand, anthracite, and diatomaceous earth are the most commonly employed filter media. Coagulation is performed utilizing alum, polyelectrolytes, lime, and other chemical agents.

## 3. Carbon Adsorption

### 3.1. INTRODUCTION

Adsorption is the concentration of a solute at the surface of a solid. This phenomenon takes place when such a surface is placed in contact with a solution. A layer of molecules of solute accumulates at the surface of the solid due to imbalance of surface forces (Fig. 8.1).

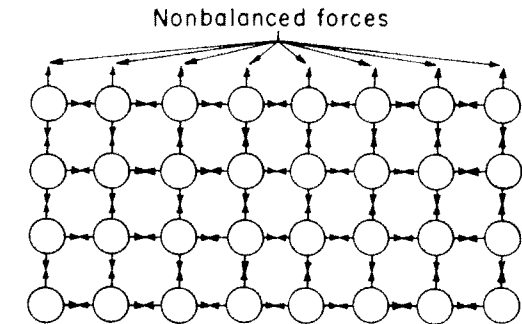


Fig. 8.1. Representation of forces in a solid.

In the interior of the solid, molecules are completely surrounded by similar molecules and therefore subjected to balanced forces, as indicated by the arrows in Fig. 8.1. Molecules at the surface are subjected to nonbalanced forces. Because these residual forces are sufficiently strong, they may imprison molecules of a solute with which the solid is in contact. This phenomenon is called physical (or van der Waals) adsorption. The solid (e.g., activated carbon) is termed the adsorbent and the solute being adsorbed is the adsorbate. Adsorption capacity is directly related to the total surface of adsorbent since the larger this surface is, the more residual (unbalanced) forces are available for adsorption.

### 3.2. ACTIVATED CARBONS AS ADSORBENTS

Activated carbons have been widely used as adsorbents in water treatment plants to remove taste and odor causing organics. It is expected that with the emphasis being placed on higher quality effluents, use of activated carbons in tertiary treatment of wastewaters will increase considerably in the future.

*Preparation of activated carbons.* Activated carbons are prepared from carbonaceous raw materials such as wood, lignite, coal, and nut shells by a process of thermal activation which yields a very porous structure with large surface areas (as high as 1000 m<sup>2</sup>/g). Adsorption equilibrium is established when the concentration of contaminant remaining in solution is in dynamic balance with that at the surface of the solid.

*Reactivation of activated carbons.* The great advantage of activated carbon as an adsorbent lies in the possibility of reactivation (up to 30 or more times) without appreciable loss of adsorptive power. Usually, reactivation is done by heating spent carbon to about 1700°F in a steam-air atmosphere (thermal reactivation). This operation can be performed in multiple hearth furnaces or rotary kilns. Adsorbed organics are burned off, and activated carbon is restored basically to its initial adsorption capacity.

### 3.3. ADSORPTION ISOTHERMS

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. In this section only the Langmuir and Freundlich isotherms are mentioned.

#### 3.3.1. Langmuir Isotherm

In the development of the Langmuir isotherm it is assumed that the solute is adsorbed as a monomolecular layer at the surface of the adsorbent. This is the most often used adsorption isotherm, being given by the relationship

$$X/M = Kbc/(1 + Kc) \quad (8.1)$$

where  $X$  is the weight of solute adsorbed (adsorbate) (mg);  $M$  the weight of adsorbent (g);  $K$  the equilibrium constant ( $\text{cm}^3$  of adsorbent/mg of adsorbate);  $C$  the equilibrium concentration of solute (mg/liter); and  $b$  a constant which represents the monolayer coverage per unit weight of adsorbent (mg of adsorbate/g of adsorbent). A typical plot of  $X/M$  vs.  $C$  based on Eq. (8.1) is shown in Fig. 8.2.

Equation (8.1) is rewritten in linear form by taking the reciprocal of both members.

$$1/(X/M) = (1/Kb)(1/C) + (1/b) \quad (8.2)$$

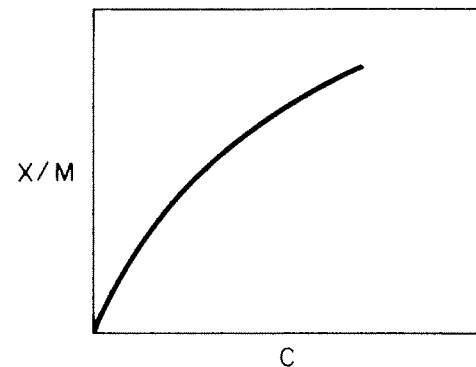


Fig. 8.2. Langmuir isotherm.

From Eq. (8.2) a plot of  $1/(X/M)$  vs.  $1/C$  yields a straight line, which permits determination of parameters  $K$  and  $b$  from its slope and intercept, respectively.

#### 3.3.2. Freundlich Isotherm

The Freundlich isotherm is expressed by the equation

$$X/M = kC^{1/n} \quad (8.3)$$

$X/M$  and  $C$  have the same meaning as in Langmuir's isotherm, and  $k$  and  $n$  are constants dependent on several environmental factors. Equation (8.3) is rewritten in linear form by taking logarithms of both members.

$$\log(X/M) = (1/n) \log C + \log k \quad (8.4)$$

Equation (8.4) reveals that a logarithmic plot of  $X/M$  vs.  $C$  yields a straight line which permits determination of parameters  $n$  and  $k$  from its slope and intercept.

### 3.4. ADSORPTION OPERATION

In practice, adsorption of organics in activated carbon is conducted either as a batch or continuous operation. In batch operation, powdered activated carbon is mixed with the wastewater and allowed to settle. Continuous operation is performed in columns containing granular carbon (40–80 mesh). It is more economical than batch operation and has found the widest application.

Removal of organics in activated carbon columns occurs by three mechanisms: (1) adsorption of organic molecules, (2) filtration of large particles, and (3) partial deposition of colloidal material. Percent removal depends primarily on contact time between wastewater and activated carbon.

As wastewater flows through the bed, carbon nearest to the feed point becomes saturated and must be replaced with fresh carbon. This is done by operating several suitably valved columns in series. The first column is replaced when exhausted, and the flow of wastewater is switched to make that column the last one in the series. In large installations regeneration of spent carbon is essential for economic feasibility.

### 3.5. DESIGN PROCEDURE FOR ACTIVATED CARBON ADSORPTION COLUMNS

The design procedure described is recommended by Eckenfelder and Ford [5] and is based on an equation derived by Bohart and Adams [1]. The following topics are discussed: (1) Bohart and Adams' equation for performance of activated carbon adsorption columns (Section 3.5.1); (2) laboratory tests with bench scale columns to obtain the necessary design parameters (Section 3.5.2); (3) "scale-up" of laboratory data and design of a plant scale unit (Section 3.5.3); and (4) derivation of Bohart and Adams' equation (Section 3.5.4).

### 3.5.1. Bohart and Adams' Equation

In the operation of an activated carbon adsorption column, wastewater with an influent solute concentration  $C_0$  (mg/liter) is fed into the column. It is desired to reduce solute concentration in the effluent to a value not exceeding  $C_E$  (mg/liter), as determined by water quality requirements.

At the beginning of the operation, when activated carbon is fresh, effluent concentration is actually *lower* than allowable concentration  $C_E$ . As the operation proceeds and activated carbon approaches saturation, effluent concentration reaches value  $C_E$ . This condition is called the break point. Let  $t$  be the time elapsed to reach the break point (service time, hours). At time  $t$ , operation is discontinued and activated carbon is regenerated.

At time zero ( $t = 0$ ), the theoretical depth of carbon which is sufficient to prevent effluent solute concentration from exceeding value  $C_E$  is called the critical bed depth  $D_0$  (ft). Evidently,  $D_0 < D$ , where  $D$  is the actual bed depth (ft) (Fig. 8.3).

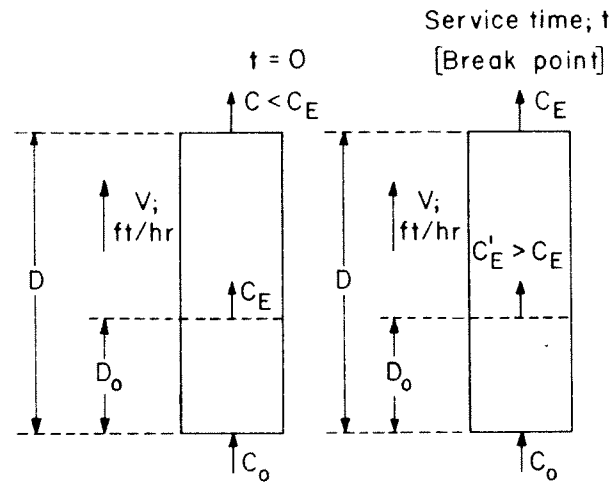


Fig. 8.3. Concept of critical bed depth ( $D_0$ ).

Adsorptive capacity ( $N_0$ ) is another important design variable. It is the maximum amount of contaminant solute that can be adsorbed by the carbon (lb solute/ft<sup>3</sup> of carbon) when saturation occurs. The break point is usually taken *before* saturation occurs. Another parameter which enters in Bohart and Adams' equation is the rate constant  $K$ . This assumes a first-order adsorption rate

$$r = Kc \quad (8.5)$$

### 3. Carbon Adsorption

mg of solute/(g of carbon)(hr) =  $K$  mg of solute/liter of solution

$$\therefore K = \text{liter of solution}/(\text{g of carbon})(\text{hr})$$

or in English units

$$K = \text{ft}^3 \text{ of solution}/(\text{lb of carbon})(\text{hr})$$

Performance of continuous activated carbon columns may be evaluated by Eq. (8.6), which was developed by Bohart and Adams [1].

$$\ln[(C_0/C_E) - 1] = \ln(e^{KN_0D/V} - 1) - KC_0t \quad (8.6)$$

where  $C_0$  is the influent solute concentration (mg/liter);  $C_E$  the allowable effluent solute concentration (mg/liter);  $K$  the rate constant [ft<sup>3</sup>/(lb of carbon)(hr)];  $N_0$  the adsorptive capacity (lb of solute/ft<sup>3</sup> of carbon);  $D$  the depth of carbon bed (ft);  $V$  the linear flow rate (ft/hr); and  $t$  the service time (hr).

An equation for  $D_0$  is written from Eq. (8.6).  $D_0$  (critical depth of carbon bed, ft) is the theoretical depth of carbon sufficient to prevent effluent solute concentration from exceeding value  $C_E$  at  $t = 0$ .  $D_0$  is obtained from Eq. (8.6) by letting  $t = 0$  and solving for  $D$  (which equals  $D_0$  in this case). Since the exponential term  $e^{KN_0D/V}$  is usually much larger than unity, the unity term within brackets in the right-hand member of Eq. (8.6) is neglected. The final result is

$$D_0 = (V/KN_0) \ln[(C_0/C_E) - 1] \quad (8.7)$$

*Expression for service time  $t$ .* Solving Eq. (8.6) for  $t$  and neglecting the unity term within brackets in the right-hand member as compared to the exponential term.

$$t = (N_0/C_0V)D - \ln[(C_0/C_E) - 1]/KC_0 \quad (8.8)$$

Equation (8.8) is the basis for experimental determination of parameters  $N_0$  and  $K$  from bench scale columns. The procedure followed is described in Section 3.5.2.

### 3.5.2. Determination of Parameters $N_0$ , $K$ , and $D_0$ from Laboratory Data

Laboratory equipment recommended by Eckenfelder and Ford [5] is shown in Fig. 8.4. Required data for removal of organics are obtained by passing wastewater containing a known concentration of organic material ( $C_0$ ) through a series of columns (e.g., three columns in Fig. 8.4) and recording the times  $t$  ( $t_1$ ,  $t_2$ , and  $t_3$ ) at which concentrations of effluents from columns #1, #2, and #3 reach the allowable effluent solute concentration ( $C_E$ ). Each set of experiments is performed at constant flow rate [gal/(min)(ft<sup>2</sup>)], therefore linear velocity  $V$  (ft/sec) is held constant. Effluent from column #1 is the first to reach value  $C_E$  (record this time  $t_1$ ); some time after, effluent from column #2 reaches value  $C_E$ , this time also being recorded ( $t_2$ ). Finally,

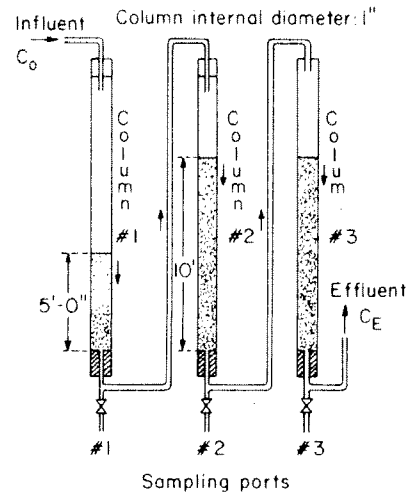


Fig. 8.4. Activated carbon columns (bench scale).

effluent from column #3 reaches concentration  $C_E$ . This time is also recorded ( $t_3$ ) and the experiment discontinued. Consequently, the experiment is carried out until the break point of the last column is reached.

Table 8.1 shows a typical tabulation of  $t$  vs.  $D$  values at four different flow rates. For Experiment no. 1, three columns of 2.5 ft of carbon depth each are utilized, corresponding to total depths of 2.5, 5.0, and 7.5 ft at sampling ports. Flow rate is 2.0 gal/(min)(ft<sup>2</sup>).

For Experiment no. 2, the first two columns contain a depth of 2.5 ft of carbon each, and the third 5 ft. Total depths corresponding to sampling ports are 2.5, 5.0, and 10 ft. Flow rate is 4.0 gal/(min)(ft<sup>2</sup>).

For experiments no. 3 and 4, carbon depths are, respectively, 5-5-5 ft and 5-10-10 ft for the three columns, corresponding to total depths at sampling ports of 5-10-15 ft and 5-15-25 ft. Flow rates are 8 and 16 gal/(min)(ft<sup>2</sup>), respectively. Equation (8.8) reveals that a plot of  $t$  vs.  $D$  yields a straight line for which slope ( $s$ ) and intercept ( $i$ ) are

$$s = N_0/C_0V$$

$$\therefore N_0 = C_0Vs \tag{8.9}$$

$$i = \ln[(C_0/C_E) - 1]/KC_0$$

$$\therefore K = \ln[(C_0/C_E) - 1]/iC_0 \tag{8.10}$$

Values of parameters  $N_0$  and  $K$  are determined from Eqs. (8.9) and (8.10), respectively. Figure 8.5 shows four straight lines corresponding to the four experiments for which data are presented in Table 8.1. Critical depth  $D_0$  is calculated from Eq. (8.7).

TABLE 8.1  
Data for Example 8.1

Experiment no.	(1) Flow rate [gal/(min)(ft <sup>2</sup> )]	(2) Bed depth (ft)	(3) Time, $t$ (hr)	(4) Throughput volume (gal) <sup>a</sup>
1	2.0	$D_1 = 2.5$	740	484
		$D_2 = 5.0$	1780	1164
		$D_3 = 7.5$	2780	1818
2	4.0	$D_1 = 2.5$	180	235
		$D_2 = 5.0$	560	732
		$D_3 = 10.0$	1330	1740
3	8.0	$D_1 = 5.0$	170	445
		$D_2 = 10.0$	500	1308
		$D_3 = 15.0$	830	2171
4	16.0	$D_1 = 5.0$	60	314
		$D_2 = 15.0$	390	2040
		$D_3 = 25.0$	730	3819

<sup>a</sup>Calculation procedure for column (4) of Table 8.1. Cross-sectional area is

$$A = \left(\frac{1}{4}\right)\pi\left(\frac{1}{12}\right)^2 = 0.00545 \text{ ft}^2$$

$$\text{Throughput volume} = \text{gal}/(\text{min})(\text{ft}^2) \times 0.00545 \text{ ft}^2 \times (t60) \text{ min}$$

or

$$(4) = (1) \times (3) \times 0.327$$

**Example 8.1**

Data in Table 8.1 are obtained by using continuous bench scale activated carbon adsorption columns with 1-in. inside diameter. Four sets of experiments are performed. The wastewater contains 20 mg/liter of an organic solute removable by carbon adsorption. Experiments are carried out recording the time taken for effluents from the first, second, and third adsorption columns to reach a concentration  $C_E = 1.0$  mg/liter of solute [column (3) of Table 8.1]. Prepare a plot of parameters  $N_0$ ,  $K$ , and  $D_0$  vs. flow rate [gal/(min)(ft<sup>2</sup>)].

**SOLUTION** A plot of  $t$  vs.  $D$  [column (3) vs. column (2) of Table 8.1] is presented in Fig. 8.5. Adsorptive capacity  $N_0$  is calculated from Eq. (8.9), where (20 mg/liter =  $20 \times 10^{-6}$  lb solute/lb liquor)

$$C_0 = 20 \times 10^{-6} \text{ lb solute/lb liquor} \times 62.4 \text{ lb liquor/ft}^3 \text{ liquor}$$

$$= 1.248 \times 10^{-3} \text{ lb solute/ft}^3 \text{ liquor}$$

Values of  $V$  (ft/hr) are

$$\text{Exp. no. 1} \quad 2.0 \text{ gal}/(\text{min})(\text{ft}^2) \times \text{ft}^3/7.48 \text{ gal} \times 60 \text{ min/hr} = 16 \text{ ft/hr}$$

- Exp. no. 2  $4.0 \text{ gal}/(\text{min})(\text{ft}^2) \times \text{ft}^3/7.48 \text{ gal} \times 60 \text{ min}/\text{hr} = 32 \text{ ft}/\text{hr}$
- Exp. no. 3  $8.0 \text{ gal}/(\text{min})(\text{ft}^2) \times \text{ft}^3/7.48 \text{ gal} \times 60 \text{ min}/\text{hr} = 64 \text{ ft}/\text{hr}$
- Exp. no. 4  $16.0 \text{ gal}/(\text{min})(\text{ft}^2) \times \text{ft}^3/7.48 \text{ gal} \times 60 \text{ min}/\text{hr} = 128 \text{ ft}/\text{hr}$

The calculation of  $N_0$  is presented in Table 8.2.

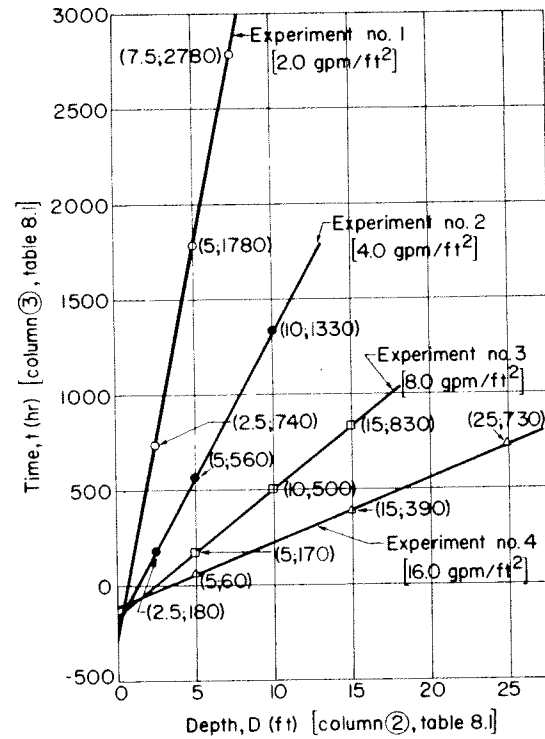


Fig. 8.5. Plots of  $t$  vs.  $D$  for Example 8.1.

TABLE 8.2  
Calculation of  $N_0$  (Example 8.1)

Exp. no.	Flow rate [gal/(min)(ft <sup>2</sup> )]	$V$ (ft/hr)	Slope (Fig. 8.5) (hr/ft)	$N_0 = C_0 V s$ Eq. (8.9) $(N_0 = \frac{\text{lb}}{\text{ft}^3} \cdot \frac{\text{ft}}{\text{hr}} \cdot \frac{\text{hr}}{\text{ft}} = \text{lb}/\text{ft}^3)$ ( $C_0 = 1.248 \times 10^{-3} \text{ lb}/\text{ft}^3$ )
1	2.0	16	408	8.15
2	4.0	32	153	6.11
3	8.0	64	66	5.27
4	16.0	128	33	5.27

TABLE 8.3  
Calculations of  $K$  and  $D_0$  (Example 8.1)<sup>a</sup>

Exp. no.	Flow rate [gal/(min)(ft <sup>2</sup> )]	$V$ (ft/hr) (Table 8.2)	$N_0$ (lb/ft <sup>3</sup> ) (Table 8.2)	$i$ (absolute value of intercept) (Fig. 8.5)	$K$ , Eq. (8.10) [ft <sup>3</sup> /(lb)(hr)]	$D_0$ , Eq. (8.7) (ft)
1	2.0	16	8.15	283	8.3	0.695
2	4.0	32	6.11	203	11.6	1.33
3	8.0	64	5.27	151	15.6	2.29
4	16.0	128	5.27	112	21.1	3.31

<sup>a</sup>  $C_0 = 1.248 \times 10^{-3} \text{ lb}/\text{ft}^3$ .

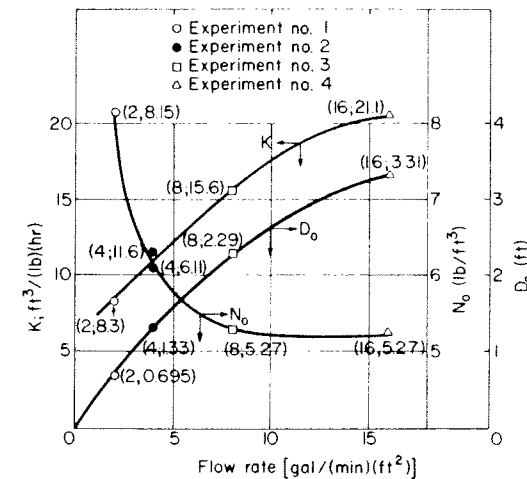


Fig. 8.6. Plots of  $N_0$ ,  $K$ , and  $D_0$  vs. flow rate (Example 8.1).

Values of  $K$  are calculated from Eq. (8.10), where  $\ln[(C_0/C_E - 1)] = \ln[(20/1) - 1] = 2.94$ . Values of  $D_0$  are calculated from Eq. (8.7). Calculations of  $K$  and  $D_0$  are presented in Table 8.3. Values of  $N_0$ ,  $K$ , and  $D_0$  are plotted vs. flow rate in Fig. 8.6.

### 3.5.3. Scale-Up of Laboratory Data and Design of a Plant Scale Unit

Plant scale design is illustrated by Example 8.2.

#### Example 8.2

Wastewater utilized in laboratory experiments (Example 8.1) is treated for removal of solute (concentration = 20 mg/liter) to a residual value of 1 mg/liter in an activated carbon bed 2.5 ft in diameter and 6 ft deep. Flow is 25,000 gal/day.

1. Calculate service time (hours per cycle).
  2. Calculate number of carbon changes required per year and annual carbon volume (ft<sup>3</sup>).
  3. Estimate solute removal (lb/year).
  4. Calculate adsorption efficiency based on  $N_0$  and  $D_0$ .
  5. Estimate % error in neglecting unity factor in term  $(e^{KN_0D_0/V} - 1)$ .
- This approximation is utilized in arriving at Eqs. (8.7)–(8.10).

**SOLUTION** Part 1. Calculation of service time

*Step 1.* Flow rate in gal/min is  $(25,000)/(24)(60) = 17.4$  gal/min. Cross-sectional area of column is  $A = (\frac{1}{4})\pi(2.5)^2 = 4.9$  ft<sup>2</sup>. Flow rate in gal/(min)(ft<sup>2</sup>) is  $17.4/4.9 = 3.6$  gal/(min)(ft<sup>2</sup>), or

$$V = 3.6 \text{ gal}/(\text{min})(\text{ft}^2) \times 60 \text{ min}/\text{hr} \times \text{ft}^3/7.48 \text{ gal} = 28.9 \text{ ft}^3/\text{hr}$$

*Step 2.* From Fig. 8.6, for flow rate 3.6 gal/(min)(ft<sup>2</sup>), one reads

$$K = 10.7 \text{ ft}^3/(\text{lb})(\text{hr})$$

and

$$N_0 = 6.35 \text{ lb}/\text{ft}^3$$

*Step 3.* Service time is calculated from Eq. (8.8).

$$t = [6.35/(1.248 \times 10^{-3} \times 28.9)]6 - 2.94/(10.7 \times 1.248 \times 10^{-3}) = 836 \text{ hr}/\text{cycle}$$

**SOLUTION** Part 2. Number of carbon changes per year and annual carbon volume

$$\text{No. carbon changes/year} = (365 \times 24)/836 = 10.5$$

$$\text{Annual carbon volume} = (6 \times 4.9)10.5 = 309 \text{ ft}^3$$

**SOLUTION** Part 3. Estimation of solute removal (lb/year)

Solute removed per cycle is calculated from

$$\begin{aligned} \text{lb solute removed per cycle} \\ = \text{lb solute in influent per cycle} - \text{lb solute in effluent per cycle} \end{aligned}$$

Since

$$\begin{aligned} \text{Volume of wastewater per cycle} \\ = 25,000 \text{ gal}/\text{day} \times 836 \text{ hr}/\text{cycle} \times \text{day}/24 \text{ hr} \times \text{ft}^3/7.48 \text{ gal} \\ = 1.16 \times 10^5 \text{ ft}^3/\text{cycle} \end{aligned}$$

and

$$C_0 = 20 \text{ mg}/\text{liter} = 1.248 \times 10^{-3} \text{ lb}/\text{ft}^3$$

then

$$\begin{aligned} \text{lb solute in influent per cycle} &= 1.248 \times 10^{-3} \text{ lb}/\text{ft}^3 \times 1.16 \times 10^5 \text{ ft}^3/\text{cycle} \\ &= 144.8 \text{ lb}/\text{cycle} \end{aligned}$$

Residual solute leaving with effluent per cycle is calculated from

$$\begin{aligned} (\text{lb solute in effluent per cycle}) &= (1.16 \times 10^5) \text{ ft}^3/\text{cycle} \times C_{\text{ave}} \text{ lb}/\text{ft}^3 \\ &= 1.16 \times 10^5 C_{\text{ave}} \text{ (lb)/cycle} \end{aligned}$$

$C_{\text{ave}}$  is given by

$$C_{\text{ave}} = (1/836) \int_{t=0}^{t=836 \text{ hr}} C dt$$

$C$  stands for a series of effluent concentrations (increasing values), the highest one being that corresponding to  $C_E = 1$  mg/liter (or  $6.24 \times 10^{-5}$  lb/ft<sup>3</sup>), which occurs after 836 hr of operation. If intermediate values of effluent concentrations from time zero (start of cycle) to  $t = 836$  hr (end of cycle) are recorded, one can evaluate the integral by graphical or numerical methods. In the absence of these values one can make a conservative (low) estimate of solute removed based on the  $C_E$  value of 1 mg/liter ( $6.24 \times 10^{-5}$  lb/ft<sup>3</sup>). The error in such an estimate is less than 5% (since in this case  $C_0/C_E = 20$ ). Thus,

High estimate of lb solute in effluent per cycle

$$= 1.16 \times 10^5 \text{ ft}^3/\text{cycle} \times 6.24 \times 10^{-5} \text{ lb}/\text{ft}^3 = 7.2 \text{ lb}/\text{cycle}$$

and

$$\text{Low estimate of lb solute removed per cycle} = 144.8 - 7.2 = 137.6 \text{ lb}/\text{cycle}$$

or

$$137.6 \text{ lb}/\text{cycle} \times 10.5 \text{ cycle}/\text{year} = 1445 \text{ lb}/\text{year}$$

**SOLUTION** Part 4. Adsorption efficiency

Based on  $N_0$ :

Total solute adsorbed: 1445 lb/year (Solution, Part 3)

Total adsorptive capacity:  $(N_0)(\text{annual carbon volume}) = 6.35 \text{ lb}/\text{ft}^3 \times 309 \text{ ft}^3 = 1962 \text{ lb}$

Efficiency:  $(1445/1962) \times 100 = 73.6\%$

Based on  $D_0$ : from Fig. 8.6 for flow rate 3.6 gal/(min)(ft<sup>2</sup>), one reads  $D_0 = 1.23$  ft.

Efficiency:  $[(D - D_0)/D] 100 = [(6 - 1.23)/6] 100 = 79.5\%$

**SOLUTION** Part 5. Error in neglecting factor of unity

$$KN_0D/V = (10.7 \times 6.35 \times 6.0)/28.9 = 14.11$$

$$e^{14.11} = 1,342,441$$

$$e^{14.11} - 1 = 1,342,440$$

$$\text{Error \%} = (1/1,342,440) 100 = 7.45 \times 10^{-5} \%$$

### 3.5.4. Derivation of the Bohart and Adams Equation [1]

Consider a mass of adsorbent. Its residual capacity ( $N$ ) diminishes at a rate given by Eq. (8.11).

$$\partial N / \partial t = -KNC \quad (8.11)$$

where  $N$  is the residual adsorbing capacity [at  $t = 0$ ,  $N = N_0 =$  adsorptive capacity (lb/ft<sup>3</sup>)];  $C$  the solute concentration (lb/ft<sup>3</sup>);  $t$  the time (hr); and  $K$  the rate constant [ft<sup>3</sup>/(lb)(hr)].

Consider now the solution from which solute is removed by adsorption. Solute concentration diminishes at a rate given by

$$\partial C / \partial D = -KNC/V \quad (8.12)$$

where  $D$  is the depth of adsorbent (total depth,  $D = D_0$ ) (ft); and  $V$  the flow velocity of solution past the adsorbent (ft/hr).

The following boundary conditions (BC) apply: For BC-1 at  $t = 0$ ,  $N = N_0$  (initial solute capacity of adsorbent). For BC-2 at  $D = 0$ ,  $C = C_0$  (inlet concentration).

Perform the following changes of variable. Let

$$N' = N/N_0 \quad (8.13)$$

$$\therefore N = N_0 N' \quad (8.14)$$

$$C' = C/C_0 \quad (8.15)$$

$$\therefore C = C_0 C' \quad (8.16)$$

$$D' = KN_0 D/V \quad (8.17)$$

$$\therefore D = D'V/KN_0 \quad (8.18)$$

$$t' = KC_0 t \quad (8.19)$$

$$\therefore t = t'/KC_0 \quad (8.20)$$

With this change of variables, one writes two modified boundary conditions: For BC-1' at  $t' = 0$  (i.e.,  $t = 0$ ), since  $N = N_0$ , then  $N' = N_0/N_0 = 1$ . For BC-2' at  $D' = 0$  (i.e.,  $D = 0$ ), since  $C = C_0$ , then  $C' = C_0/C_0 = 1$ .

Equations (8.11) and (8.12) are written in terms of the new variables  $N'$ ,  $C'$ ,  $D'$ , and  $t'$ , substituting  $N$ ,  $C$ ,  $D$ , and  $t$  by their values given by Eqs. (8.14), (8.16), (8.18), and (8.20). The final result after simplification is

$$\text{From Eq. (8.11)} \quad \partial N' / \partial t' = -N'C' \quad (8.21)$$

$$\text{or} \quad \partial \ln N' / \partial t' = -C' \quad (8.22)$$

From Eq. (8.12)

$$\partial C' / \partial D' = -N'C' \quad (8.23)$$

or

$$\partial \ln C' / \partial D' = -N' \quad (8.24)$$

Differentiating Eq. (8.22) with respect to  $D'$  and Eq. (8.24) with respect to  $t'$  leads to

$$\partial^2 \ln N' / \partial D' \partial t' = -\partial C' / \partial D' = N'C' \quad (8.25)$$

$$\partial^2 \ln C' / \partial t' \partial D' = -\partial N' / \partial t' = N'C' \quad (8.26)$$

Subtracting Eq. (8.25) from Eq. (8.26),

$$\partial^2 \ln C' / \partial t' \partial D' - \partial^2 \ln N' / \partial D' \partial t' = 0$$

or

$$\partial^2 \ln(C'/N') / \partial t' \partial D' = 0 \quad (8.27)$$

Integration of Eq. (8.27) yields

$$\ln(C'/N') = f(D') + f(t') \quad (8.28)$$

where  $f(D')$  and  $f(t')$  are, respectively, functions of  $D'$  and  $t'$  alone.\* Imposing boundary conditions BC-1' and BC-2', it follows that†

$$\ln(C'/N') = t' - D' \quad (8.29)$$

or

$$C'/N' = e^{t'-D'} \quad (8.30)$$

Equation (8.23) is rewritten as  $[\partial C' / (-C')] / \partial D' = N'$ . Dividing both members by  $C'$  and employing Eq. (8.30),

$$-(\partial C' / C'^2) / \partial D' = N' / C' = e^{D'-t'} \quad (8.31)$$

\* Proof that Eq. (8.28) is a solution for differential equation (8.27): differentiating Eq. (8.28) with respect to  $D'$  and then with respect to  $t'$  yields Eq. (8.27), since

$$\partial f(t') / \partial D' = 0$$

and

$$\frac{\partial}{\partial t'} \left( \frac{\partial f(D')}{\partial D'} \right) = 0$$

[since  $f(D')$  and  $f(t')$  are, respectively, functions of  $D'$  and  $t'$  alone].

† Application of BC-1' and BC-2' to Eq. (8.29) leads to an identity

$$\ln 1/1 = 0 - 0 = 0.$$

Therefore  $f(D')$  and  $f(t')$  are satisfied by

$$f(D') = -D' \quad \text{and} \quad f(t') = t'$$



Equation (8.31) integrates to yield\*

$$1/C' = e^{D'-t'} - \psi(t') \quad (8.32)$$

where  $\psi(t')$  is a function of  $t'$  alone.

Function  $\psi(t')$  is evaluated by imposing boundary condition BC-2'.†

$$\psi(t') = e^{-t'} - 1 \quad (8.33)$$

Thus Eq. (8.32) becomes

$$1/C' = e^{D'-t'} - e^{-t'} + 1 \quad (8.34)$$

From Eq. (8.34),

$$C' = 1/(e^{D'-t'} - e^{-t'} + 1) \quad (8.35)$$

Multiplying both numerator and denominator of Eq. (8.35) by  $e^{t'}$ ,

$$C' = e^{t'}/(e^{D'} - 1 + e^{t'}) \quad (8.36)$$

Substituting in Eq. (8.36)  $C'$ ,  $D'$ , and  $t'$  by their values given by Eqs. (8.15), (8.17), and (8.19), the result is

$$C/C_0 = e^{KC_0 t}/(e^{KN_0 D/V} - 1 + e^{KC_0 t}) \quad (8.37)$$

Solving Eq. (8.37) for  $t$ , the final result is

$$t = (1/KC_0) \ln \frac{e^{KN_0 D/V} - 1}{(C_0/C) - 1} \quad (8.38)$$

Equation (8.38) is rearranged to yield Eq. (8.6). ( $t$  is taken as the service time and therefore concentration  $C$  equals  $C_E$ .)

\* Proof that Eq. (8.32) is a solution for Eq. (8.31) is obtained by differentiation of Eq. (8.32) with respect to  $D'$ . Notice that  $\partial\psi(t')/\partial D' = 0$ , and therefore

$$\partial(1/C')/\partial D' = \partial(e^{D'-t'})/\partial D'$$

or

$$-(\partial C'/\partial D')/C'^2 = e^{D'-t'}$$

and finally

$$-(\partial C'/\partial D')/C'^2 = e^{D'-t'}$$

which is Eq. (8.31).

† Application of BC-2' to Eq. (8.34) leads to an identity

$$1/1 = e^{-t'} - e^{-t'} + 1 = 1$$

Consequently,  $\psi(t')$  is satisfied by Eq. (8.33).

## 4. Ion Exchange

### 4.1. INTRODUCTION

Ion exchange is a process where ions which are held to functional groups on the surface of a solid by electrostatic forces are exchanged for ions of a different species in solution. This treatment procedure has become increasingly important in the field of wastewater treatment.

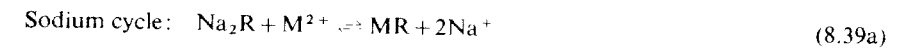
Since complete demineralization is achieved by ion exchange, it is possible to use split stream treatment processes where part of the influent wastewater is demineralized and then combined with bypassed influent to produce an effluent of specified quality (e.g., a specified hardness).

*Ion exchange resins.* Until the 1940's natural zeolites were the only ion exchange resins available. Exchange capacity was relatively low, which limited their economic feasibility in the field of wastewater treatment. Since then, natural zeolites have been replaced by synthetic resins. These are insoluble polymers to which acidic or basic groups are added by chemical reaction procedures. These groups are capable of reversible exchange with ions present in a solution. The total number of functional groups per unit weight (or unit volume) of resin determines exchange capacity, whereas the type of functional group determines ion selectivity and position of exchange equilibrium. Resin particles have diameters of approximately 0.5 mm and are employed in packed columns with wastewater flows of 5–12 gal/(min)(ft<sup>2</sup>).

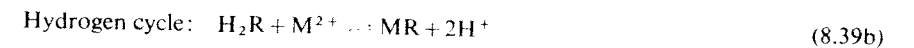
### 4.2. BASIC MECHANISM OF ION EXCHANGE: CATION AND ANION EXCHANGERS

There are two basic types of ion exchangers: (1) cation and (2) anion exchangers.

*Cation exchangers.* Cation exchange resins remove cations from a solution, exchanging them for sodium ions (sodium cycle) or hydrogen ions (hydrogen cycle). Removal is represented by Eq. (8.39). [R denotes the resin and  $M^{2+}$  the cation (e.g.,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ).]



or

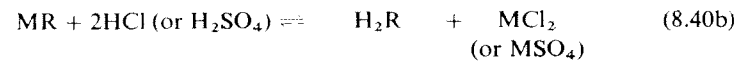
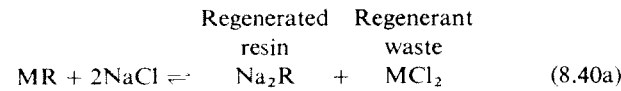


$Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  are retained on the resin and a soft effluent is produced. This soft effluent contains mainly sodium salts (if sodium cycle is employed) or acids (if hydrogen cycle is employed).

When the exchange capacity of the resin is exhausted, ionic concentration in effluent from the exchange column exceeds the specified value. This condition is called breakthrough. The resin must then be regenerated. Prior to

regeneration, the column should be backwashed to remove solid deposits. Regeneration consists of passing through the column either a brine solution (NaCl for sodium cycle) or an acid solution, usually H<sub>2</sub>SO<sub>4</sub> or HCl (for hydrogen cycle).

Regeneration reactions for the sodium and hydrogen cycles are shown below.



Typical regenerant concentrations are 2–5% by weight with flow rates of 1–2 (gal)/(min)(ft<sup>2</sup>). As indicated by Eq. (8.40), regenerant waste consists of cation salts. This waste stream amounts to 10–15% of influent volume treated before breakthrough. Following regeneration the exchanger bed is rinsed with water to remove residual regenerant.

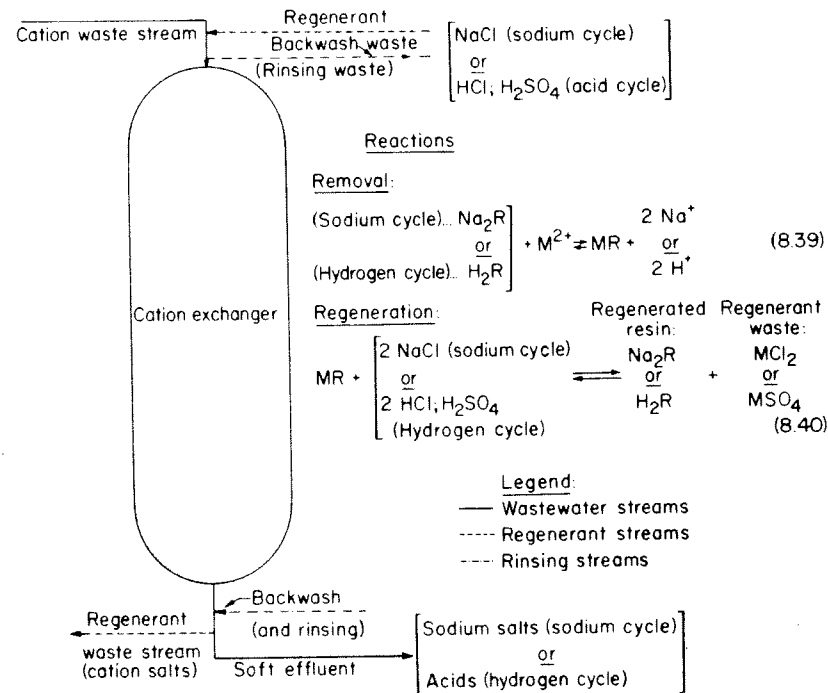
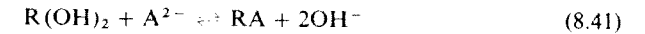


Fig. 8.7. Cation exchanger.

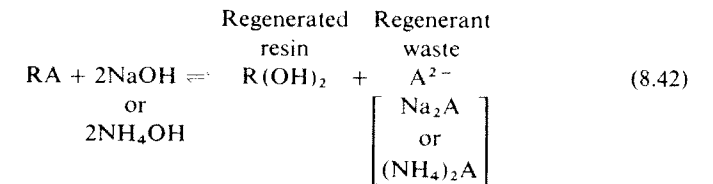
Cation exchanger reactions and directions of flow for different streams involved in the operation of a cation exchanger are indicated in Fig. 8.7. Hydrogen cycle cation exchange resins are weak or strong acids. Most acidic resins used in water pollution abatement are strong acids.

*Anion exchangers.* Anion exchange resins remove anions from a solution, exchanging them for hydroxyl ions. Removal is represented by Eq. (8.41) (where A<sup>2-</sup> represents an anion).



Anions (e.g., SO<sub>4</sub><sup>2-</sup>, CrO<sub>4</sub><sup>2-</sup>) are thus removed from solution.

Regeneration is made after breakthrough, usually preceded by backwashing to remove solid deposits. Regenerants commonly used are sodium and ammonium hydroxides. The regeneration reaction is



Typical regenerant concentrations are 5–10% by weight.

Usually, cation and anion exchangers are used in series. By adequate selection of ion exchangers, almost any wastewater problem of an inorganic nature can be handled. Basic exchange resins are either strong or weak bases. Anion exchanger reactions and direction of flow for the different streams involved in the operation of an anion exchanger are indicated in Fig. 8.8.

### 4.3. DESIGN OF ION EXCHANGE COLUMNS

The first step in designing an ion exchange system for a specific wastewater is to run a complete cation–anion analysis of the influent to be treated. In addition, data on total dissolved solids (TDS), dissolved CO<sub>2</sub>, SiO<sub>2</sub>, and pH are obtained.

Concentrations of individual ions present are expressed in either of two ways:

1. In meq/liter (milliequivalents per liter), e.g., for a solution containing 20 mg/liter of Cu<sup>2+</sup>, the concentration in terms of meq/liter is

$$20 / (63.5 / 2) = 0.63 \text{ meq/liter}$$

where 63.5 is the atomic weight of Cu and 2 is the valence.

2. In terms of calcium carbonate equivalents, e.g., for a solution containing 20 mg/liter of Cu<sup>2+</sup> and the stoichiometric amount of Cl<sup>-</sup>, the concentration of Cu<sup>2+</sup> in terms of CaCO<sub>3</sub> is calculated as

$$20(134.5/100) = 27 \text{ mg/liter of CaCO}_3$$

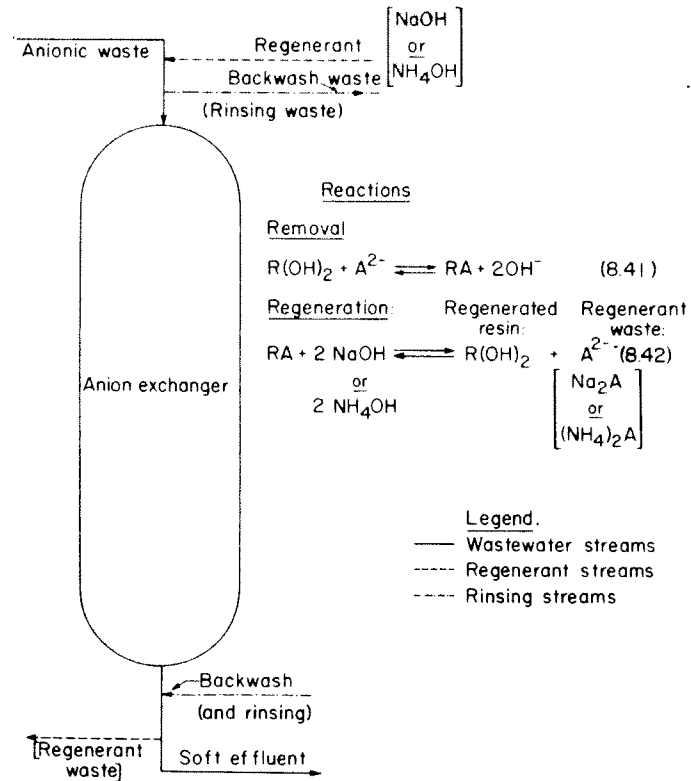


Fig. 8.8. Anion exchanger.

where 100 and 134.5 are the molecular weights of  $\text{CaCO}_3$  and  $\text{CuCl}_2$ , respectively.

Design parameters determined by laboratory tests prior to design of an ion exchange column are

1. *Exchange capacity of resin.* Cation-anion resin capacities are usually expressed as equivalents of ion removed per unit bed volume (e.g., equivalents/liter of resin or equivalents/ $\text{ft}^3$  of resin). They may be also expressed per unit weight of bed (e.g., equivalents/lb of resin). Exchange capacities are also expressed in terms of weight of  $\text{CaCO}_3$  equivalent, either per unit volume or per unit weight of bed (e.g., lb  $\text{CaCO}_3/\text{ft}^3$  of resin, lb  $\text{CaCO}_3/\text{lb}$  of resin).

2. *Regenerant requirements.* Regenerant requirements are expressed in terms of weight per unit volume of bed (e.g., lb  $\text{H}_2\text{SO}_4/\text{ft}^3$ ). The degree of theoretical capacity attained (with respect to fresh resin) depends on the weight of regenerant employed. An economic balance between degree of theoretical capacity attained and weight of regenerant (lb regenerant/ $\text{ft}^3$  of bed volume) is taken into consideration. Performance curves for regenerants

(exchange capacity of regenerated resin vs. weight of regenerant), determined from laboratory studies, are sometimes available from resin manufacturers. The exchange capacity of the column increases with weight of regenerant utilized.

3. *Rinsing water requirements.* Following regeneration, the exchanger bed is rinsed with water to remove residual regenerant. Rinsing requirements, also determined from laboratory studies, are sometimes available from resin manufacturers. They are expressed in terms of gallons of (water) per  $\text{ft}^3$  of resin (range, 100–200 gal/ $\text{ft}^3$ ). Characteristics of exchange resins are evaluated from bench scale units [5]. Plexiglass columns of 1 in. diameter are used at unit flow rates comparable to plant scale units. Table 8.4 shows typical data obtained from bench scale units.

TABLE 8.4  
Characteristics of Cation and Anion Exchange Resins Utilized in Treatment of Plating Industry Wastewater

	Cation	Anion
Exchange capacity	70 eq/ $\text{ft}^3$ of resin	3.5 lb $\text{CrO}_3/\text{ft}^3$ of resin
Regenerant	$\text{H}_2\text{SO}_4$	NaOH
Requirement (lb/ $\text{ft}^3$ of resin)	11.0 (in lb $\text{H}_2\text{SO}_4$ )	4.7 (in lb NaOH)
Concentration (%)	5.0	10.0
Flow rate [gal/(min)( $\text{ft}^2$ )]	1.0	1.0
Rinsing water requirements (gal/ $\text{ft}^3$ of resin)	130.0	100.0

Additional considerations concerning design of ion exchange systems are as follows:

1. Recovery of valuable wastewater constituents, an important factor in determining economic feasibility of ion exchange, is illustrated by Example 8.3. Chromates ( $\text{CrO}_4^{2-}$ ) from a plating plant wastewater are held by an anion exchanger and subsequently recovered as chromic acid ( $\text{H}_2\text{CrO}_4$ ) in a hydrogen cation exchanger. Nickel ions are salvaged from plating plant wastes.

2. Calculation of bed depth is illustrated in Example 8.3. Additional free height is provided to allow for expansion of the bed for backwashing and cleaning. As a rule of thumb a 50% allowance is taken.

#### 4.4. DESIGN OF AN ION EXCHANGE SYSTEM [5]

##### Example 8.3

Design an ion exchange system to treat 120,000 gal of wastewater per day from a metal-plating industry. The main metal ions present in the wastewater are chromium, equivalent to 120 mg/liter of  $\text{CrO}_3$  (present as chromate,  $\text{CrO}_4^{2-}$ );  $\text{Cu}^{2+}$ , 30 mg/liter;  $\text{Zn}^{2+}$ , 15 mg/liter; and  $\text{Ni}^{2+}$ , 20 mg/liter.

It is desired to remove  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$  in a hydrogen cycle cation exchanger (cation exchanger no. 1) and  $\text{CrO}_4^{2-}$  in an anion exchanger downstream from the cation exchanger. The hydrogen cycle cation exchanger is regenerated by a 5% solution of  $\text{H}_2\text{SO}_4$ . The anion exchanger employed to remove  $\text{CrO}_4^{2-}$  is regenerated by a 10% solution of  $\text{NaOH}$ . Effluent from this regeneration contains sodium chromate ( $\text{Na}_2\text{CrO}_4$ ). Valuable  $\text{CrO}_4^{2-}$  is recovered in another hydrogen cation exchanger (cation exchanger no. 2) as chromic acid ( $\text{H}_2\text{CrO}_4$ ). This cation exchanger is also regenerated by a 5% solution of  $\text{H}_2\text{SO}_4$ . Acid effluents from regeneration of cation exchangers no. 1 and 2 are combined, neutralized, and then discarded to a sewer. Figure 8.9 shows a flowsheet of the proposed process.

Characteristics of the cation and anion exchangers to be employed are presented in Table 8.4. Both cation and anion units operate 6 days between regenerations. Design the three ion exchangers in the system and estimate regeneration and rinse water requirements.

**SOLUTION** The flow diagram is shown in Fig. 8.9, and chemical reactions involved are

Hydrogen cycle cation—exchanger no. 1

Removal

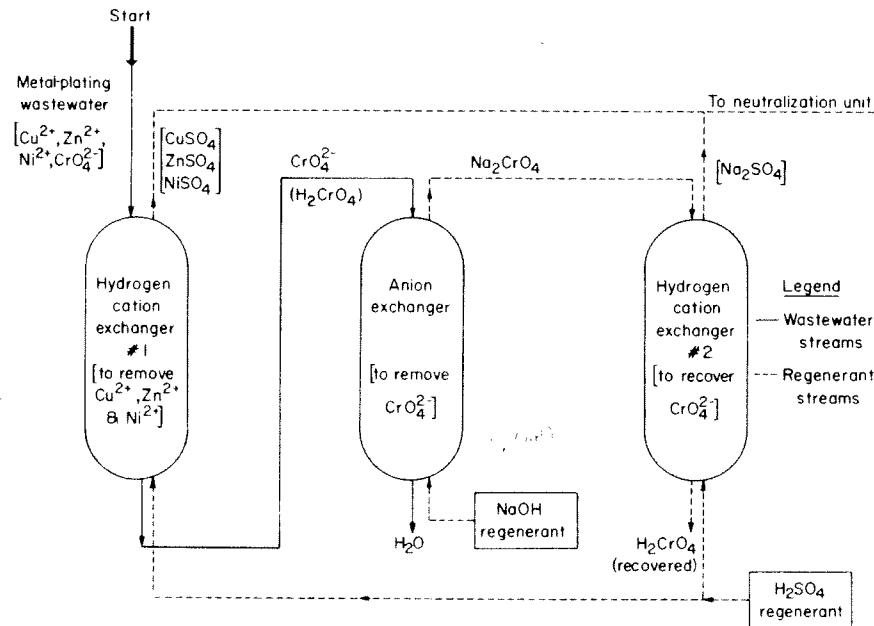
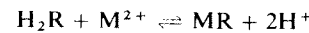
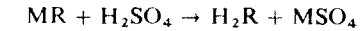


Fig. 8.9. Ion exchanger flow diagram (Example 8.3).

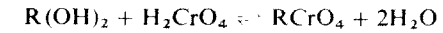
where  $\text{M}^{2+} = \text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$ .

Regeneration

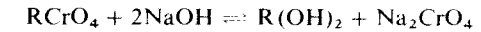


Anion exchanger

Removal

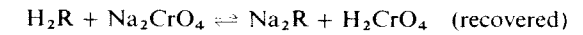


Regeneration

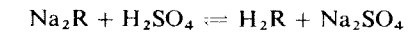


Hydrogen cycle cation—exchanger no. 2

Removal



Regeneration



*Design of hydrogen cycle cation—exchanger no. 1*

*Step 1.* Calculate equivalents of metal ions to be removed (see tabulation below).

Ion concentration	Equivalent wt	meq/liter
30 mg/liter $\text{Cu}^{2+}$	$63.5/2 = 31.7$	$30/31.7 = 0.95$
15 mg/liter $\text{Zn}^{2+}$	$65.4/2 = 32.7$	$15/32.7 = 0.46$
20 mg/liter $\text{Ni}^{2+}$	$58.7/2 = 29.4$	$20/29.4 = 0.68$
		Total = 2.09

*Step 2.* Determine the total equivalents/day to be removed.

$$2.09 \text{ meq/liter} \times 3.78 \text{ liter/gal} \times 120,000 \text{ gal/day} \times \text{eq}/1000 \text{ meq} = 948 \text{ eq/day}$$

*Step 3.* Calculate total resin requirements on the basis of 70 equivalents/ $\text{ft}^3$  of resin (Table 8.4) and 6-day operation between regenerations.

$$\text{Resin requirement} = \frac{948 \text{ eq/day} \times 6 \text{ days/cycle}}{70 \text{ eq/ft}^3} = 81 \text{ ft}^3 \text{ of resin/cycle}$$

*Step 4.* Select a column diameter of 3 ft and calculate required depth of resin bed.

$$\text{Cross section} = \left(\frac{3}{4}\right)\pi 3^2 = 7.07 \text{ ft}^2$$

$$\text{Depth} = 81/7.07 = 11.5 \text{ ft}$$

Allowing 50% free space for bed expansion for backwashing and cleaning, the height of the required column is  $(1.50)(11.5) = 17.3 \text{ ft}$ . Utilize two columns in series, each 8.5 ft in height, each containing a  $11.5/2 = 5.75\text{-ft}$  resin depth (free space, 2.75 ft for each column; ratio,  $8.5/5.75 = 1.48$ ).

*Step 5.* Calculate regenerant requirements. Regenerant is a 5% solution of  $\text{H}_2\text{SO}_4$  as indicated in Table 8.4, and 11.0 lb  $\text{H}_2\text{SO}_4/\text{ft}^3$  of resin are required. The lb of  $\text{H}_2\text{SO}_4$  required are

$$11 \text{ lb}/\text{ft}^3 \times 81 \text{ ft}^3 = 891 \text{ lb of } \text{H}_2\text{SO}_4 \text{ per cycle}$$

or

$$891(100/5) = 17,820 \text{ lb of } 5\% \text{ solution}$$

*Step 6.* Calculate rinse water requirements. From Table 8.4, 130 gal of water are required for rinsing each cubic foot of resin. Required rinse water is

$$130 \text{ gal}/\text{ft}^3 \times 81 \text{ ft}^3/\text{cycle} = 10,530 \text{ gal per cycle}$$

#### *Design of anion exchanger*

Chromic acid ( $\text{H}_2\text{CrO}_4$ ) passing through the cation unit is removed in the anion exchange unit, which is designed as follows:

*Step 1.* Total chrome removed per day (as  $\text{CrO}_3$ ) is

$$120 \text{ mg}/\text{liter} \times 3.78 \text{ liter}/\text{gal} \times \text{g}/10^3 \text{ mg} \times \text{lb}/454 \text{ g} \times 120,000 \text{ gal}/\text{day} = 120 \text{ lb}/\text{day}$$

*Step 2.* Calculate resin requirements. Basis: 3.5 lb  $\text{CrO}_3/\text{ft}^3$  of resin (Table 8.4) and 6-day operation between regenerations.

$$\text{Resin requirement} = \frac{120 \text{ lb}/\text{day} \times 6 \text{ days}/\text{cycle}}{3.5 \text{ lb}/\text{ft}^3} = 206 \text{ ft}^3 \text{ of resin}/\text{cycle}$$

*Step 3.* Select a column diameter of 3 ft and calculate required depth of resin bed.

$$\text{Cross section} = \left(\frac{1}{4}\right)\pi 3^2 = 7.07 \text{ ft}^2, \text{ depth} = 206/7.07 = 29 \text{ ft}$$

Allowing a 50% free space for bed expansion, the height of the required column is  $(1.50)(29.0) = 43.5$  ft. Utilize four columns in series, each 11 ft in height ( $11 \times 4 = 44$ ), and each containing  $29/4 = 7.25$ -ft resin depth (free space, 3.75 ft for each column; ratio,  $11/7.25 = 1.5$ ).

*Step 4.* Calculate regenerant requirements. Regenerant is a 10% solution of NaOH as indicated in Table 8.4, and 4.7 lb of NaOH solution are required per  $\text{ft}^3$  of resin. The lb of NaOH required are

$$4.7 \text{ lb}/\text{ft}^3 \times 206 \text{ ft}^3 = 968 \text{ lb of NaOH per cycle}$$

or

$$968(100/10) = 9680 \text{ lb of } 10\% \text{ solution}$$

*Step 5.* Calculate rinse water requirements. From Table 8.4, 100 gal of water are required for rinsing each cubic foot of resin. Required rinse water is

$$100 \text{ gal}/\text{ft}^3 \times 206 \text{ ft}^3 = 20,600 \text{ gal}$$

#### *Design of hydrogen cycle cation—exchanger no. 2*

Chromic acid ( $\text{H}_2\text{CrO}_4$ ) is recovered from spent regenerant leaving the anion exchanger (which contains  $\text{Na}_2\text{CrO}_4$ ) by passing it through a cation exchanger (Fig. 8.9). As calculated in Step 4 of the design for the anion exchanger, 968 lb of NaOH are required.

*Step 1.* Calculate sodium hydroxide equivalents to be removed by the cation exchanger.

$$968 \text{ lb} \times 454 \text{ g}/\text{lb} \times \text{eq}/40 \text{ g} = 10,987 \text{ eq}$$

since the equivalent weight of NaOH is 40 g.

*Step 2.* Calculate resin requirements on the basis of 70 equivalents/ $\text{ft}^3$  of resin (Table 8.4).

$$\text{Resin requirement} = \frac{10,987 \text{ eq}}{70 \text{ eq}/\text{ft}^3} = 157 \text{ ft}^3 \text{ of resin}$$

*Step 3.* Select a column diameter of 3 ft, and calculate required depth of the resin bed.

$$\text{Cross section} = \left(\frac{1}{4}\right)\pi 3^2 = 7.07 \text{ ft}^2$$

$$\text{Depth} = 157/7.07 = 22.2 \text{ ft}$$

Allowing 50% free space for bed expansion, the height of the required column is  $(1.50)(22.2) = 33.3$  ft. Utilize three columns in series, each  $33.3/3 \approx 11$  ft deep, each containing a  $22.2/3 = 7.4$ -ft resin depth (free space, 3.6 ft for each column; ratio,  $11/7.4 = 1.48$ ).

*Step 4.* Calculate regenerant requirements. Regenerant is a 5% solution of  $\text{H}_2\text{SO}_4$  as indicated in Table 8.4, and 11.0 lb of  $\text{H}_2\text{SO}_4/\text{ft}^3$  of resin are required. The lb of  $\text{H}_2\text{SO}_4$  required are

$$11 \text{ lb}/\text{ft}^3 \times 157 \text{ ft}^3 = 1727 \text{ lb } \text{H}_2\text{SO}_4$$

or

$$1727(100/5) = 34,540 \text{ lb of } 5\% \text{ solution}$$

*Step 5.* Calculate rinse water requirements. From Table 8.4, 130 gal of water are required for rinsing each cubic foot of resin. Required rinse water is therefore

$$130 \text{ gal}/\text{ft}^3 \times 157 \text{ ft}^3 = 20,410 \text{ gal}$$

## 5. Reverse Osmosis

### 5.1. OSMOSIS AND OSMOTIC PRESSURE

Although osmotic phenomena have been known for over 200 years, the first precise experiments linking osmotic pressure to temperature and solute concentration were performed in the late 1800's by Pfeffer. A typical experiment with a sucrose solution is illustrated in Fig. 8.10.

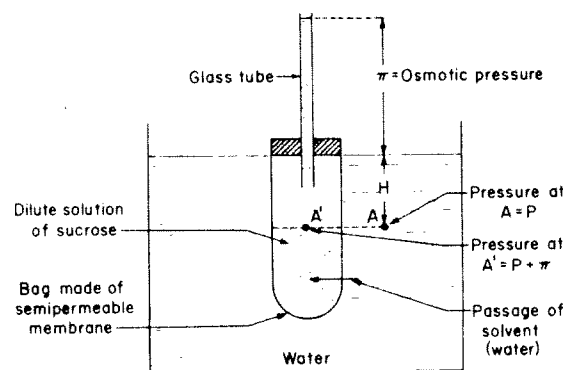


Fig. 8.10. Osmosis experiment.

The bag shown in Fig. 8.10 is made of a membrane permeable to the solvent (water in Fig. 8.10) but impermeable to the solute (sucrose). These are known as semipermeable membranes. Early semipermeable membranes utilized in osmosis were animal membranes (e.g., pig bladders). Synthetic membranes were developed later, cellulose acetate membranes now being the most widely used.

A dilute solution of sucrose (e.g., a 0.001 *M* solution) is placed inside the semipermeable bag, which is then dipped into a vat containing pure water. The water diffuses spontaneously from the vat to the interior of the semipermeable bag, as indicated by the arrow. As a result, a column of liquid rises through the glass tube connected to the dilute sucrose solution, reaching at equilibrium a height  $\pi$  above the level of water in the vat. At this moment, passage of solvent stops. Pressure exerted on points *A'* and *A* situated at the same elevation differs by the increment corresponding to height  $\pi$  of liquid. This value is called the osmotic pressure of the sucrose solution. Osmosis is defined as the spontaneous passage of a solvent from a dilute solution (pure water in the case of Fig. 8.10) to a more concentrated one through a semipermeable membrane.

Let *P* be the pressure at point *A* (atmospheric pressure plus pressure corresponding to a column of water of height *H*). The pressure at *A'* is (*P* +  $\pi$ ). Osmotic pressure  $\pi$  is a function of the concentration of the sucrose solution and temperature. The mathematical relationship for  $\pi$  as a function of concentration of solute (*c*) and absolute temperature (*T*) is given by the van't Hoff equation.

## 5.2. VAN'T HOFF EQUATION FOR OSMOTIC PRESSURE

Derivation of the van't Hoff equation is found in standard physical chemistry texts [3]. The equation is

$$\pi = nRT/V = cRT \quad (8.43)$$

where  $\pi$  is the osmotic pressure (atm); *n* the g mole of solute (e.g., sucrose); *V* the volume of the sucrose solution;  $n/V = c$  the concentration of sucrose solution (g mole/liter); *R* the ideal gas constant [0.082 (atm)(liter)/(g mole)(°K)]; and *T* the absolute temperature (°K).

The van't Hoff equation shows a startling similarity to the ideal gas law, the solvent corresponding to the empty space between gas molecules and these latter corresponding to the molecules of solute, in the case of osmosis. Thus, one could consider osmotic pressure to be the result of bombardment exerted by molecules of solute on the membrane. Despite this analogy, it is deceptive to consider osmotic pressure as a sort of pressure which is exerted by the solute. Rather osmosis is the passage of solvent through the membrane due to momentary inequality of the chemical potential on the two sides of the membrane [3.] Osmotic pressure results from this passage of solvent.

Application of Eq. (8.43) to a 0.001 *M* solution of sucrose (i.e.,  $n/V = c = 0.001$  g mole/liter) at 20°C leads to a value of the osmotic pressure calculated as

$$\begin{aligned} \pi &= cRT = 0.001 \text{ g mole/liter} \times 0.082 \text{ (atm)(liter)/(g mole)(°K)} \times 293.2^\circ\text{K} \\ &= 0.024 \text{ atm} \end{aligned}$$

Assuming the specific gravity of the dilute solution to be that of pure water, this corresponds to a height  $\pi$  (Fig. 8.10) equal to

$$\pi = 0.024 \text{ atm} \times 34 \text{ ft water/atm} = 0.82 \text{ ft} \quad (\approx 10 \text{ in.})$$

If the van't Hoff equation could be applied to relatively concentrated sucrose solutions (e.g., a 1.0 *M* solution), height  $\pi$  would be 1000 times that just calculated, i.e., 820 ft. Inasmuch as the ideal gas law does not describe accurately gas behavior at higher pressures, the van't Hoff equation is not an adequate model for osmotic pressure at higher solute concentrations.

## 5.3. PRINCIPLE OF REVERSE OSMOSIS

The principle of reverse osmosis is illustrated by Fig. 8.11. Figure 8.11(a) depicts direct osmosis [e.g., condition existing at beginning of experiment with sucrose solution (Fig. 8.10)]. Solvent flows spontaneously through the semipermeable membrane. Figure 8.11(b) illustrates the equilibrium condition. Here the liquid head which has developed as a result of solvent flow through the membrane is equal to the osmotic pressure. Solvent flow stops. Figure 8.11(c) illustrates what happens when a force *F* in excess of the value of osmotic pressure is applied to the sucrose solution. Solvent flow is reversed, i.e., from the compartment containing the sucrose solution to the water compartment. This phenomenon is called reverse osmosis (hence abbreviated as RO).

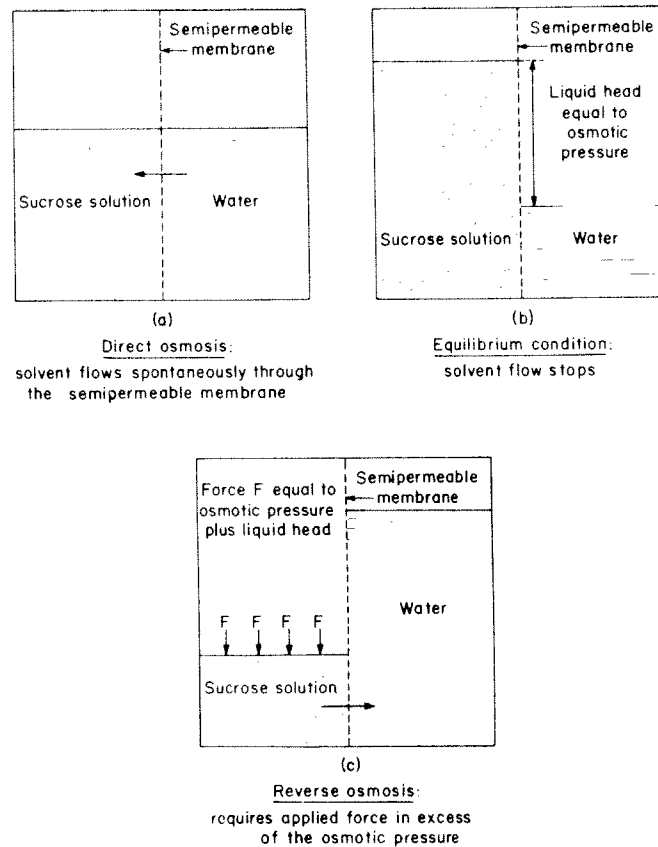


Fig. 8.11. Illustration of the principle of reverse osmosis.

In the treatment of wastewaters by reverse osmosis, contaminated influent is placed in contact with a suitable membrane at a pressure in excess of the osmotic pressure of the solution [same situation as in Fig. 8.11(c), except that the left compartment contains wastewater instead of sucrose solution]. Under these conditions, water with a very small amount of contaminants permeates the membrane. Dissolved contaminants are concentrated in the wastewater compartment. This concentrate, which hopefully is a small fraction of the total volume of wastewater to be treated, is discarded. Purified water is obtained from the other compartment.

The compartments indicated in Fig. 8.11 are a schematic representation of RO process. In practice, the RO process is conducted in a tubular configuration system (Fig. 8.12). Raw wastewater flows under high pressure (in excess of the value of its osmotic pressure) through an inner tube made of a semi-

permeable membrane material and designed for high pressure operation. Purified water is removed from the outer tube, which is at atmospheric pressure and is made of ordinary tubular material. Typical values of operating pressures, water fluxes (yield of purified water per unit area of membrane), and product quality are discussed in the following sections.

#### 5.4. PREPARATION OF RO MEMBRANES

Reverse osmosis found its earlier applications in desalination of ocean water. Considerable research and pilot-plant work are being done for utilization of RO in removal of contaminants from wastewaters. Some of these (e.g., nitrogen and phosphorus compounds, chromates, and some organic compounds) are not adequately removed by other processes. Consequently, usual processes may be complemented by RO, provided economic considerations are favorable. Research indicates that in principle, RO can be used to obtain an effluent of virtually any desired degree of purity while still maintaining reasonable flow rates.

Many natural materials have semipermeable characteristics. Animal and plant membranes are well-known examples. Collodion, cellophanes, porous glass frits, finely cracked glass, and inorganic precipitates such as copper ferrocyanide, and zinc and uranyl phosphates have been used. All these, however, have the shortcomings of developing leaks and exhibiting short-lived selectivity and poor reproducibility.

Cellulose acetate membranes (hence denoted as CA membranes) are the most successful semipermeable membranes developed. Sourirajan and Loeb [9] developed a technique for preparation of CA membranes yielding both high permeabilities and high degrees of solute separation from aqueous solutions of sodium chloride. Their technique is as follows:

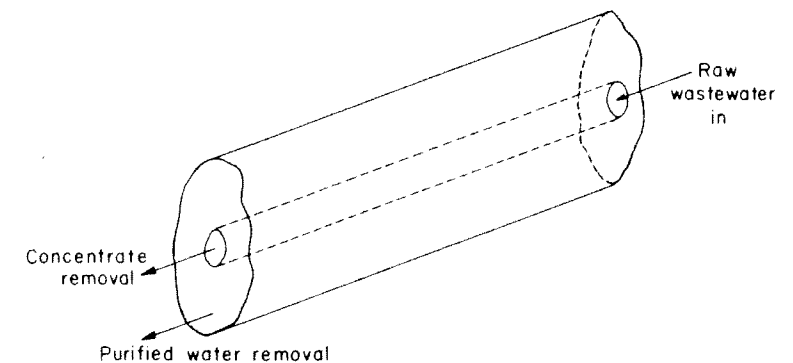


Fig. 8.12. Diagram of a tubular configuration system for wastewater treatment by reverse osmosis.

1. *Casting step.* The film-casting solution contains cellulose acetate dissolved in acetone, to which is added an additive soluble in water and not affecting the solubility of cellulose acetate in acetone (e.g., magnesium perchlorate). With this solution, membranes are cast on flat or tubular surfaces (e.g., glass plates or tubular surfaces), either at laboratory or lower temperatures ( $\approx -10^\circ\text{C}$ ). One of the most significant developments in the field of CA membrane technology is casting in tubular form. Tubular-shaped membranes are entirely lined within a porous fiberglass reinforced tube.

2. *Evaporation step.* After casting, part of the solvent (acetone) is allowed to evaporate from the surface of the membrane at casting temperature.

3. *Gelation step.* The membrane is immersed in ice-cold water for at least 1 hr. The film sets to a gel, from which the additive (e.g., magnesium perchlorate) and the solvent (acetone) are leached out, leaving a tough solid porous film on the flat or tubular surface.

4. *Shrinkage step.* Membranes from the gelation step exhibit pores which are too large to permit efficient operation (diameters  $\approx 4000 \text{ \AA}$ ). These large pores are a result of the leaching process. Consequently, the membrane receives a thermal treatment by shrinking it in hot water for about 10 min. Adjusting the hot water temperature, it is possible to obtain variable porosities, which results in different degrees of wastewater separation. Higher hot water temperatures (usual range is  $70^\circ\text{--}98^\circ\text{C}$ ) yield smaller pores.

### 5.5. PREFERENTIAL SORPTION-CAPILLARY FLOW MECHANISM FOR REVERSE OSMOSIS

Several mechanisms have been proposed by different investigators to explain reverse osmosis. Of these, only the preferential sorption-capillary flow mechanism is described here. This mechanism, proposed by Sourirajan [9], is summarized as follows: RO separation is the combined result of an interfacial phenomenon and fluid transport under pressure through capillary pores. Figure 8.13 is a conceptual model of this mechanism for recovery of fresh water from aqueous salt solutions (ocean water).

The solution is in contact with a porous membrane, the surface of which has a preferential sorption for water and/or preferential repulsion for the solute. A continuous removal of preferentially sorbed interfacial water is effected by flow under pressure through the membrane capillaries. The preferentially sorbed water layer at the interface is of a monomolecular nature (indicated in Fig. 8.13 below the single dotted line), and results from interaction between interfacial surface tension and adsorption of solute.

For a maximum separation and permeability, this model gives rise to the concept of critical pore diameter, which is equal to twice the thickness of the preferentially sorbed interfacial water layer (Fig. 8.14). From an industrial standpoint, application of the reverse osmosis technique for a given separation

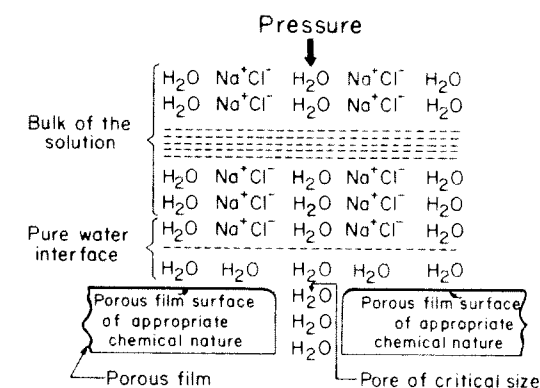


Fig. 8.13. Schematic representation of preferential sorption-capillary flow mechanism [9]. (Reprinted with permission from *Ind. Eng. Chem.* Copyright by the American Chemical Society.)

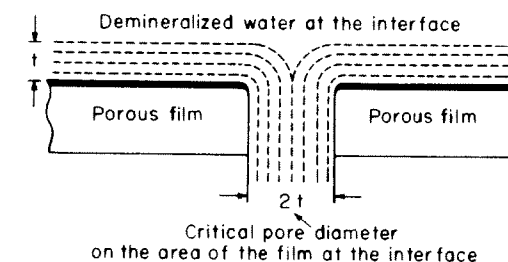


Fig. 8.14. Critical pore diameter for maximum separation and permeability [9]. (Reprinted with permission from *Ind. Eng. Chem.* Copyright by the American Chemical Society.)

problem involves the choice of the appropriate chemical nature of the film surface and development of methods for preparing films containing the largest number of pores of the required size. This approach is the basis of the successful development of the Sourirajan-Loeb type of porous CA membranes for saline water conversion and other applications.

### 5.6. CHARACTERIZATION OF MEMBRANE PERFORMANCE

The two basic parameters for characterizing RO systems are (1) production of purified water per unit area of membrane (water flux) and (2) product quality, i.e., purity of purified water (rejection factor). These parameters are discussed in Sections 5.7 and 5.8.



### 5.7. WATER FLUX

Production of purified water is measured by the water flux, defined as quantity of product recovered per day per unit area of membrane. English units are used for water flux in field work [gal/(day)(ft<sup>2</sup>)], whereas metric units [g/(sec)(cm<sup>2</sup>)] are used in laboratory tests.

Flux through a specific membrane is determined by (1) physical characteristics of the membrane, e.g., thickness, chemical composition, and porosity, and (2) system conditions, e.g., temperature, differential pressure across the membrane, salt concentration of solutions touching the membrane, and velocity of feed moving across the membrane.

In practice, physical characteristics of the membrane as well as temperature and concentrations of solute in feed and product streams are fixed for a given process. Therefore, water flux is a function of the differential pressure across the membrane, being given approximately by

$$F_{H_2O} \approx A(\Delta P - \Delta\pi) \quad (8.44)$$

where

$$\Delta P = P_F - P_P \quad (8.45)$$

$$\Delta\pi = \pi_F - \pi_P \quad (8.46)$$

and  $F_{H_2O}$  is the water flux [gal/(day)(ft<sup>2</sup>)];  $A$  the permeation coefficient for a unit area of membrane [gal/(day)(ft<sup>2</sup>)(atm)]. This term includes physical variables of the membrane and is relatively constant;  $\Delta P = (P_F - P_P)$  the pressure exerted on feed solution ( $P_F$ ) minus pressure on product ( $P_P$ ) (atm); and  $\Delta\pi = (\pi_F - \pi_P)$  the osmotic pressure of feed solution ( $\pi_F$ ) minus osmotic pressure of product ( $\pi_P$ ) (atm).

For a laboratory experiment with a feed of pure water  $\Delta\pi = 0$ , Eq. (8.44) reduces to a classical flux equation:

$$F_{H_2O} = A \Delta P \quad (8.47)$$

i.e., flux = resistance  $\times$  driving force. When wastewater feed is relatively concentrated in solute and product is a very dilute solution (nearly pure water), correction factor  $\Delta\pi$  is subtracted from differential pressure  $\Delta P$ . Actually,  $\Delta\pi$  should be equal to the difference in osmotic pressure between solutions touching the membrane on each side (i.e., feed and product sides). This is *not* exactly equal to  $\pi_F - \pi_P$  because of concentration polarization, a condition discussed in Section 5.15. This is why Eq. (8.44) is approximate. An accurate version is written in Section 5.15.

### 5.8. REJECTION FACTOR

Improvement of quality between feed and product streams is expressed quantitatively by the rejection factor, defined as

$$f = (C_F - C_P)/C_F \quad (8.48)$$

where  $f$  is the rejection factor (dimensionless);  $C_F$  the solute concentration in feed solution; and  $C_P$  the solute concentration in product.

Thus,  $f = 0.9$  means that  $C_P = 0.1C_F$ , i.e., the product contains one-tenth the concentration of solute in the feed; therefore, 90% of the solute is rejected by the membrane. Rejection factor is therefore a measure of membrane selectivity. Solute concentrations  $C_F$  and  $C_P$  are obtained by determination of total dissolved solids (evaporation to dryness). When the solute is an electrolyte (e.g., NaCl), analysis is conveniently performed by conductivity measurements.

The ability of a membrane to reject solutes is a complicated problem depending on a combination of physicochemical characteristics of solute, membrane, and water. Properties of the solute which have the most influence on rejection of individual species are (1) valence charge—rejection increases with value of charge of ion; (2) molecular size—rejection increases with molecular size of solute; and (3) hydrogen bonding tendency—permeation increases with strength of hydrogen bonding. Ability of a membrane to reject salts decreases with operating time. Variation of rejection with time is illustrated by Fig. 8.15.

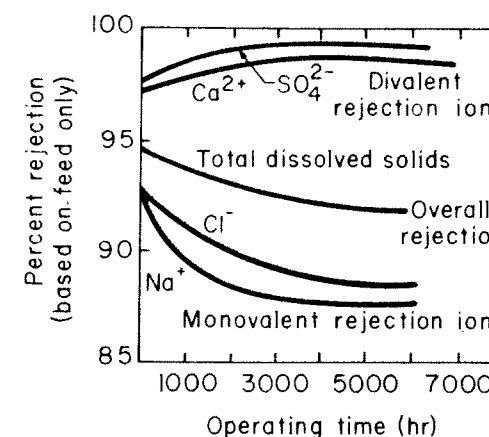


Fig. 8.15. Variation of salt rejection with operating time [6]. (Reprinted by special permission from *Chemical Engineering*, April 1973. Copyright by McGraw-Hill, Inc., New York, N.Y., 10020.)

At first, decrease is more pronounced for small, univalent ions such as sodium (Na<sup>+</sup>) and chloride (Cl<sup>-</sup>). These are normally among the most permeable, showing the lowest initial rejection and have the highest rate of decline. Divalent ions such as calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) and anions such as sulfate (SO<sub>4</sub><sup>2-</sup>) are initially rejected very well and show a very

slow rate of decline. Rejection of such ions may actually increase for a while (Fig. 8.15), becoming nearly constant after that. Overall salt rejection tends to follow the monovalent curve.

Progressive decrease in salt rejection may be caused by hydrolysis of the membrane, with subsequent loss of bonding sites. Another cause may be increase in pore size due to membrane swelling. Most probably, both effects play a part in the result.

### 5.9. EFFECT OF SHRINKAGE TEMPERATURE ON PERFORMANCE OF CA MEMBRANES

Adjusting hot water temperature in the shrinkage step for preparation of CA membranes (Section 5.4) permits control of membrane porosity, thus leading to various degrees of wastewater separation. At higher shrinkage temperatures, pore sizes obtained are smaller, leading to greater rejection. Water flux, however, decreases at higher shrinkage temperatures, as expected. For specific RO applications one seeks an economic balance between water flux and rejection. Figure 8.16 shows rejection and flux data obtained by Kopecek and Sourirajan for three types of CA membranes.

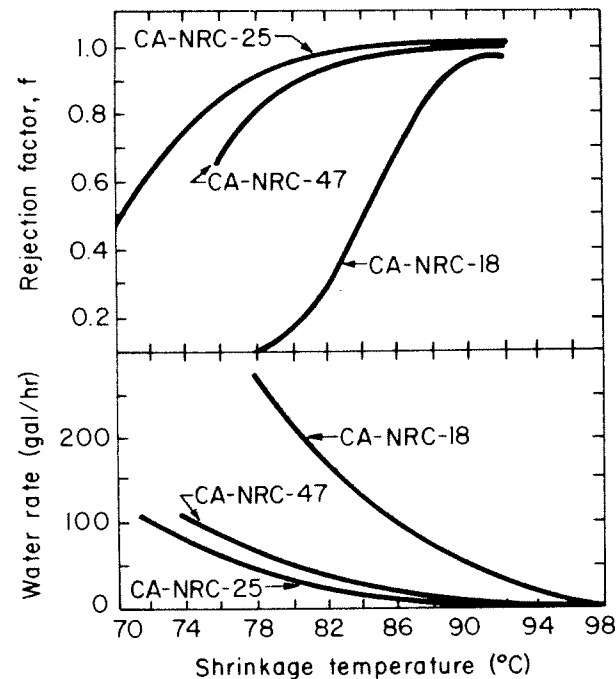


Fig. 8.16. Effect of shrinkage temperature on the performance of different CA membranes [9]. (Reprinted with permission from *Ind. Eng. Chem.* Copyright by the American Chemical Society.)

### 5.10. EFFECT OF FEED TEMPERATURE ON FLUX [6]

Flux is also affected by feed temperature. Water permeability for the membrane increases about 1.5% per °F. Flux for a membrane is usually specified at 75°–77°F, and a correction factor is applied at other temperatures. This correction factor can be derived by theoretical considerations from diffusivity and viscosity values, but experimentally determined corrections are more reliable.

A correction factor which is a multiplier of the required membrane area is presented in Fig. 8.17. This curve was developed by Gulf Environmental Systems Co. for modified cellulose acetate membranes. Application of the correction factor is illustrated in Example 8.4.

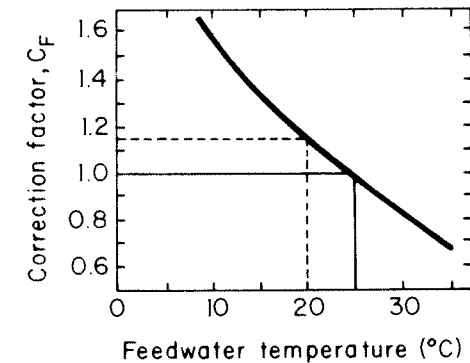


Fig. 8.17. Flux/temperature correction curve [6]. (Reprinted by special permission from *Chemical Engineering*, April 2, 1973. Copyright by McGraw-Hill, Inc., New York, N.Y., 10020.)

#### Example 8.4 [6]

It is desired to specify the membrane area for a 100,000 gal/day RO system to treat brackish water. Records indicate that the lowest water temperature expected for any prolonged period is 68°F (20°C). The cellulose acetate membrane chosen is expected to have an average flux of 15 gal/(day)(ft<sup>2</sup>) during its 2-year life, operating at 600 psig. Average flux was determined at a base temperature of 77°F. Determine required membrane area for operation at 68°F.

SOLUTION Membrane area is shown in Eq. (8.49).

$$\text{Membrane area (ft}^2\text{)} = \frac{\text{water production in gal/day}}{\text{water flux in gal/(day)(ft}^2\text{)}} \quad (8.49)$$

At 77°F the required membrane area is

$$\text{Area (77°F)} = \frac{100,000 \text{ gal/day}}{15 \text{ gal/(day)(ft}^2\text{)}} = 6667 \text{ ft}^2$$

For operation at 68°F (20°C), the correction factor  $C_F$  from Fig. 8.16 is  $C_F = 1.15$ . Therefore,

$$\text{Area (68°F)} = 1.15 \times 6667 = 7667 \text{ ft}^2$$

If additional product is not required when temperature is above 68°F, operating pressure is reduced.

### 5.11. FLUX DECLINE [6]

Application of pressure to the membrane results in compaction and consequently in a decline of flux. Compaction results from densification of the thin membrane layer and corresponds to narrowing of the pores through which water must pass. As the channels narrow, flow decreases.

Another cause of flux decline is hydrolysis of acetyl groups which takes place during the life of the membrane. Therefore, RO membranes are limited to a pH operating range of 3-7, outside of which rapid hydrolysis and membrane degradation occur. The optimum range is believed to be pH 5-6. Hydrolysis of acetyl groups results in loss of hydrogen bonding sites, which reduces the water transport. This hydrolysis is also a source of salt leakage because there are fewer water bridges blocking passage of foreign materials through the pores.

Loss in productivity happens slowly to every membrane and is permanent. Chemical rejuvenation and low pressure operation to relax and swell the matrix have been tried without success; the membrane simply ages and flux decreases until economics dictate replacement.

### 5.12. FOULING: CAUSES AND CURES [6]

Fouling, resulting in temporary flux reduction, is caused by foreign materials coating the membrane surface, as only hydrogen bonding substances (water, ammonia) pass through the discriminating pores of the membrane. Non-bonding materials are left in the quiescent film known as the liquid boundary layer.

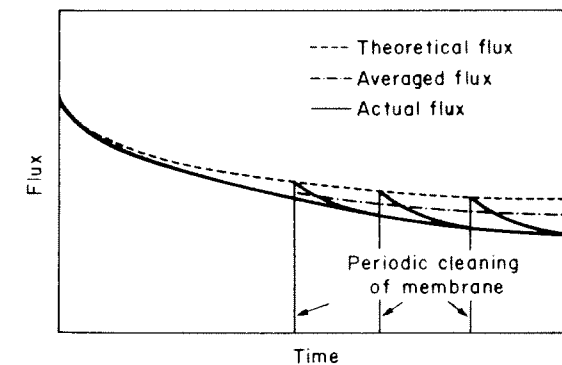
The composition of deposits in boundary layers reflects the composition of feedwater. As expected, the most common constituents are calcium carbonate, sulfate scales, hydrates of iron and aluminum oxides, silicates, miscellaneous particulates, and biological growths.

Fouling is minimized by taking the following precautions: (1) pretreating feed to remove iron and control pH, (2) limiting the process to nonscaling concentrations of wastewater, (3) filtration of wastewater feed, and (4) injection of small amounts of biocides (e.g., chlorine). Unfortunately, no matter how thorough the protection, fouling always occurs and the membranes should be periodically cleaned. The usual cleaning procedure is as follows:

1. Flush the membrane with feedwater at reduced pressure of two or three times normal velocity; the turbulent action of the fluid loosens fouling deposits and carries them away. Water flushing is the preliminary step in every cleaning operation.

2. Hardness scales (carbonates and sulfates salts of calcium and magnesium) are sometimes removed by soaking the membrane in distilled water for long periods of time. Since this is time consuming, more often a warm solution of 1-2% citric acid is vigorously circulated through the unit, dissolving large amounts of metallic ions and keeping them in solution by chelation.

3. Microbiological growths occur in most natural waters, and are a particular problem when treating effluents from biological processes. These are often removed by recirculating washes of enzyme detergents.



**Fig. 8.18. Effect of membrane cleaning on flux [6].** (Reprinted by special permission from *Chemical Engineering*, April 2, 1973. Copyright by McGraw-Hill, Inc., New York, N. Y., 10020.)

Flux degradation by fouling is an additional loss superimposed on the permanent losses discussed in Section 5.11. This is shown in Fig. 8.18, which illustrates the effect of membrane cleaning on flux. As shown in Fig. 8.18, the actual flux curve follows a declining, saw-toothed pattern when the membrane is cleaned periodically. Without cleaning, flux would follow the lowest curve, a projection of the initial smooth decline. Flux from a hypothetical

membrane that is never fouled (theoretical flux) is shown by the upper line, the theoretical flux curve which touches only the peaks of the saw-toothed curve.

### 5.13. PREDICTION OF FLUX [6]

Water output from a membrane begins to decline as soon as pressure is applied, and continues to degrade slowly thereafter. The loss is irreversible, and if more flux is required feed pressure must be increased. This alternative is self-defeating since additional pressure, while producing more water, also compresses the membrane further and hastens flux decline. Normal practice is to overspecify the membrane area slightly and to keep the operating pressure constant as long as possible, resorting to additional pressure late in the life of the membrane.

The output of a membrane is predictable because the decline per unit area of the membrane is quite uniform and can be projected. A plot of flux vs. operating time at a specified pressure (like the lower curve in Fig. 8.18) yields a curve with an initial steep descent followed by a prolonged and moderate decline. A logarithmic plot yields a straight line which is adequate for prediction purposes for 1 and probably 2 years. Thus, flux can be predicted from such plots once the initial flux and slope are known.

Manufacturers provide initial flux values and estimates of slopes at various operating pressures. Initial flux is the production for the first 24 hr divided by the membrane area in the test unit. Decline slope is computed or determined graphically from flux values taken at time intervals such as 10, 100, and 1000 hr. Time intervals in multiples of 10 are conveniently selected because computation is simplified. Decline rate is given by Eq. (8.50).

$$m = (\log F_i - \log F_x) / (\log t_i - \log t_x) = \log(F_i/F_x) / \log(t_i/t_x) \quad (8.50)$$

where  $F_i$  is the initial flux [gal/(hr)(ft<sup>2</sup>)];  $F_x$  the flux at time  $x$  [gal/(hr)(ft<sup>2</sup>)];  $t_i$  the operating time (hr) for initial flux (obtained by computing initial flux and determining from a logarithmic plot of  $F_x$  vs.  $t$  the time  $t_i$  corresponding to this calculated value); and  $t_x$  the operating time (hr).

Determination of flux over the life of the membrane is basic to the design of RO systems, because these values are used to estimate membrane area required for a desired plant capacity by utilizing Eq. (8.49). Three possible approaches are

1. Take an average of the initial and final flux as a compromise to obtain an average area. When this choice is made, it is expected that during the later life of the membrane, flux will be brought up to its initial value by increasing the operating pressure.
2. Specify membrane area from final or smallest flux value. Although fixed costs are higher, lower system pressures decrease operating costs.
3. Select initial flux as the design basis. This minimizes membrane area

and capital costs, but raises operating costs as pressures are increased to maintain production. This is a logical choice for intermittent and short-term projects in which initial costs must be minimized.

### 5.14. MEMBRANE LEAKAGE [6]

Calculated solute rejection is always higher than experimental values, even those that are determined under the most careful conditions. For example, theoretical rejection of sodium chloride from a modified CA membrane is calculated as 99.7%, but experimental results show no better than 97–99% rejection. The difference is caused by minute imperfections in the membrane through which pressurized brine can flow and contaminate the product water.

All membranes have imperfections; these are probably not manufacturing faults, but a property of the membrane that must be adjusted or optimized to suit a specific service. Hence, very porous CA membranes are used to screen out large molecules (20–500 Å diameter) and very small particles for ultrafiltration applications. Less porous membranes are selected for high water flow and moderate salt rejection service in saltless softeners, and membranes heat treated to low porosity are used for applications requiring high rejection.

Fortunately, most imperfections are small and easily plugged. Distribution runs from numerous holes with diameters 100 Å and smaller to a few of 1-μm in diameter. The major source of product contamination results from solute passage through larger holes, since from Poiseuille's law for viscous flow, salt leakage increases proportionately to the fourth power of pore diameter.

A number of techniques have been tried to reduce membrane leakage:

1. *Heat treating and modifying dope formula.* This is the only permanent way to reduce leakage. Membranes for sea water must be heat treated at high temperatures to yield a film that can reject 99.5% of the salt in the feed.
2. *Addition of certain chemicals to the feed.* Chemicals of large molecular size added to the feed are utilized to plug leaking pores. Loeb [7] discovered that trace amounts of aluminum salts occurring in Los Angeles tap water plugged leaking pores of test membranes and improved salt rejection. Zephiran (tetraalkylaluminum chloride) was used at University of California at Los Angeles (UCLA) to gain a similar and more reproducible effect. Other materials that improve rejection include polyvinyl methyl ether and Dowfax.

Unfortunately, leak-stopping additives have serious drawbacks that limit their use: (1) they are more effective on low flux than on high flux standard CA membranes, now almost exclusively used; (2) they dissipate quickly and must be regularly replenished; (3) most of them reduce water flux as they reduce solute leakage; and (4) they are expensive and therefore useful only in special situations where cost is not a factor.

### 5.15. SOLUTE PERMEABILITY AND CONCENTRATION POLARIZATION

Theoretically, solute flux is a function of membrane permeability and the difference between solute concentrations in the high and low pressure sides of the membrane, i.e.,

$$F_{\text{solute}} = \beta(C_H - C_L) = \beta \Delta C \approx \beta C_H \quad (8.51)$$

where  $F_{\text{solute}}$  is the solute flux [ $\text{g}/(\text{cm}^2)(\text{sec})$ ];  $\beta$  the solute permeability coefficient ( $\text{cm}/\text{sec}$ );  $C_H$  the concentration of solute on high pressure side of membrane, i.e., concentrate side ( $\text{g}/\text{cm}^3$ ); and  $C_L$  the concentration of solute on low pressure side of membrane, i.e., product side ( $\text{g}/\text{cm}^3$ ).

Unlike water flux [Eq. (8.44)], normal solute flux is independent of pressure [Eq. (8.51)]. Theoretically, if pressure in the RO system is increased, solute diffuses at a constant rate while water flow increases. The result is greater production of pure water.

Since  $C_L$  is usually small as compared to  $C_H$ , Eq. (8.51) is written approximately as indicated, i.e., salt flux is essentially governed by concentration of solute in the boundary layer next to the membrane on the concentrate side. Solute concentration  $C_H$  can be substantially higher than the concentration in the feed  $C_F$  owing to an effect called concentration polarization. In membrane processes solute accumulates in a relatively stable layer (boundary layer) next to the membrane. Concentration polarization is the ratio of solute concentration at this boundary layer to that in the bulk of the solution. Initially, solute concentration at the boundary layer is the same as in the bulk of the solution. However, since the membrane is permeable to solvent and impermeable to solute, the boundary layer becomes heavily populated with solute as solvent leaves through the channels of the membrane. The boundary layer grows thicker and more concentrated, because the rate of solute diffusion away from the membrane cannot keep pace with solvent flow through the membrane.

The result of concentration polarization follows from Eq. (8.51). Write  $C_H = C_{\text{BL}}$ , where  $C_{\text{BL}}$  stands for the progressively increasing solute concentration at the boundary layer. Therefore

$$F_{\text{solute}} \approx \beta C_{\text{BL}} \quad (8.52)$$

Consequently, concentration polarization results in an increased solute flux or a lower product quality. This is undesirable, so one strives to reduce the concentration polarization effect. This is accomplished in two ways:

1. *Higher feed velocity.* This reduces thickness and concentration of the boundary layer as it is scoured away by the feed stream at high velocity. The extra flow through the unit results in an overall lower product recovery, i.e., smaller ratio of product to feed. This increases power consumption and amount of concentrate (waste) produced.

2. *Addition of turbulence promoters.* This is a more efficient way to reduce the boundary layer. Tubular membrane units are provided with plastic balls on the high pressure side to break up the smooth flow of feed solution. Turbulence promoters may require prefiltration of the feed so that particulates or precipitates do not get lodged in narrow flow spaces and plug the membrane. The usual concentration polarization ratio is 1.2–2.0, which means that solute concentration at the boundary layer is 1.2–2.0 times that in the bulk of the feed.

The approximate equation for water flux, Eq. (8.44), is rewritten taking into account the concentration polarization effect, in which case  $\Delta\pi$  is

$$\Delta\pi = \pi_{\text{BL}} - \pi_P \quad (8.53)$$

where  $\pi_{\text{BL}}$  is the osmotic pressure of the concentrated solution at the boundary layer ( $\pi_{\text{BL}} > \pi_F$ ). Since  $\Delta\pi$ , given by Eq. (8.53), is higher than the value calculated from Eq. (8.46), this implies from Eq. (8.44) a decreased water flux owing to the concentration polarization effect. Substitution of Eqs. (8.53) and (8.45) in Eq. (8.44) yields

$$F_{\text{H}_2\text{O}} = A[(P_F - P_P) - (\pi_{\text{BL}} - \pi_P)] \quad (8.54)$$

There is no simple experimental technique available to determine solute concentration at the boundary layer (and therefore  $\pi_{\text{BL}}$ ). An indirect approach consists of determining experimentally water flux,  $F_{\text{H}_2\text{O}}$ , and permeation coefficient  $A$  (Section 5.16). Then  $\pi_{\text{BL}}$  is the only unknown in Eq. (8.54), and therefore

$$\pi_{\text{BL}} = \pi_P + (P_F - P_P) - (F_{\text{H}_2\text{O}}/A) \quad (8.55)$$

The concentration of solute at the boundary layer is then obtained from a previously prepared plot of osmotic pressure vs. solute concentration [ $\pi = f(c)$ ].

### 5.16. EXPERIMENTAL TECHNIQUE FOR LABORATORY PREDICTION OF MEMBRANE PERFORMANCE

A laboratory apparatus for the prediction of membrane performance in reverse osmosis is described by Sourirajan and Agrawal [9], and a schematic flow diagram is shown in Fig. 8.19. Feed solution is pumped through a surge tank into the cell containing the membrane. Pressure is controlled by a pressure regulator operating on a nitrogen back pressure system.

Experimentally determined variables at a specific pressure are (1) rejection factor [Eq. (8.48)]; (2) product recovery, i.e., ratio of product to feed; and (3) permeation coefficient  $A$ . Permeation coefficient  $A$ , which includes physical variables of the membrane, is relatively constant (Section 5.7). Therefore, it

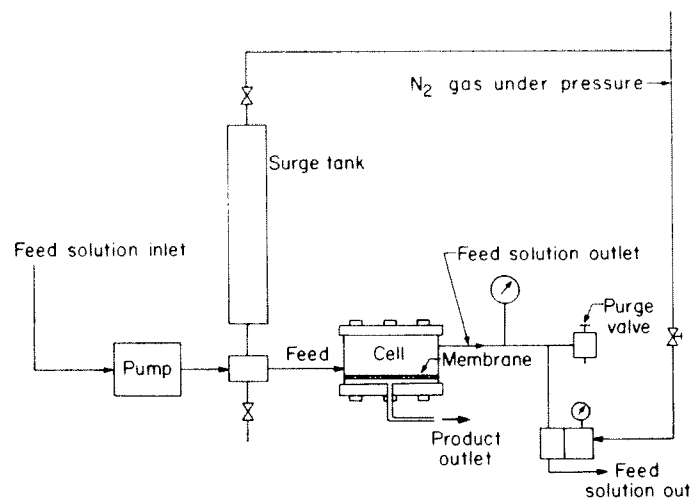


Fig. 8.19. Schematic flow diagram of RO laboratory unit [9]. (Reprinted with permission from *Ind. Eng. Chem.* Copyright by the American Chemical Society.)

can be determined once and for all by operating the system at a specific pressure with pure water and measuring the rate at which it permeates through the membrane. Equation (8.53) for pure water operation yields

$$\Delta\pi = \pi_{HL} - \pi_P = 0$$

From Eq. (8.54),

$$A = F_{H_2O}/\Delta P \quad (8.56)$$

where

$$\Delta P = P_F - P_P$$

and  $F_{H_2O}$  is the pure water flux [g/(hr) (cm<sup>2</sup>)]. Product flow (g/hr) in this case is called pure water permeability (*PWP*). Therefore from Eq. (8.56),

$$A = PWP/(M \times S \times 3600\Delta P) \quad (8.57)$$

where  $A$  is the permeation coefficient [g mole of water/(sec)(cm<sup>2</sup>)(atm)];  $PWP$  the pure water permeability (g/hr);  $M$  the molecular weight of water (18);  $S$  the effective membrane area (cm<sup>2</sup>) (7.6 cm<sup>2</sup> for Sourirajan's apparatus in Fig. 8.19); and  $\Delta P$  the differential pressure (atm).

### 5.17. FINAL REMARKS ON REVERSE OSMOSIS

Reverse osmosis is still too expensive for widespread utilization in wastewater treatment. It is also limited to treating soluble wastes since suspended solids clog the membranes. Consequently, pretreatment of the feed is required whenever there are suspended solids, thus raising costs.

Operating pressures employed vary from 600 up to 1500 psig. One of the main goals in current research is to develop better membranes that can operate at lower pressures (around 250 psig) and still yield relatively high product rates, of the order of 40 gal/(day)(ft<sup>2</sup>). Once these difficulties are overcome, RO could become a process of widespread application in the field of wastewater treatment.

## 6. Electrodialysis

### 6.1. INTRODUCTION

Electrodialysis was originally developed for desalination of ocean water. It is a promising method for removal of inorganic nutrients (phosphorus and nitrogen) from wastewaters, and thus it is a possible final stage in wastewater treatment processes.

A diagram of an electrodialysis cell is shown in Fig. 8.20. The basic components of the cell are a series of membranes made of ion exchange resins. These membranes are permeable only to ionic species and are selective to a specific type of ion. There are two types of membranes utilized in an electrodialysis cell: (1) cation membranes, which possess a fixed negative charge, allowing cations (positive ions) to pass through them but repelling anions (negative ions); and (2) anion membranes, which possess a fixed positive charge, allowing anions (negative ions) to pass through them but repelling cations (positive ions).

Passage of ions through the membranes is accelerated by application of a constant voltage across a series of cation- and anion-permeable membranes, as indicated in Fig. 8.20. The cathode and anode are located at two extremes of the cell, so that the membrane closest to the cathode is cation permeable and that closest to the anode is anion permeable. Raw wastewater is fed continuously into the concentrating compartments, and treated wastewater is withdrawn continuously from the diluting compartments.

### 6.2. VOLTAGE REQUIRED FOR ELECTRODIALYSIS

Voltage required is calculated from Ohm's law [Eq. (8.58)].

$$E = IR \quad (8.58)$$

where  $E$  is the applied voltage (V),  $I$  the current (A), and  $R$  the total electrical resistance of membranes and solutions in cells (ohms).

### 6.3. CURRENT REQUIRED FOR ELECTRODIALYSIS

The current required is proportional to the ionic strength of solution (expressed in terms of normality), and the number of cells. It is calculated

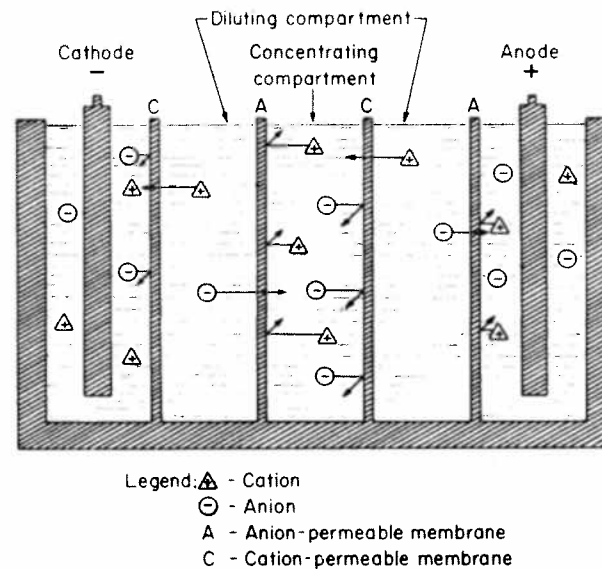


Fig. 8.20. Diagram of an electro dialysis cell.

from Faraday's law:  $96,500 \text{ A} \times \text{sec}$  of electricity transfer one gram-equivalent weight of an electrolyte from one electrode to another. Thus, current required for electro dialysis for a fixed applied voltage  $E$  is given in Eq. (8.59).

$$I = FqNe/n\varepsilon \quad (8.59)$$

where  $I$  is the current (A),  $F$  the Faraday constant ( $96,500 \text{ A} \times \text{sec/g}$  equivalent),  $q$  the flow rate (liters/sec),  $N$  the normality of solution (g equivalents/liter),  $e$  the removal efficiency ( $0 < e < 1.0$ ),  $n$  the number of cells between electrodes, and  $\varepsilon$  the current efficiency ( $0 < \varepsilon < 1.0$ ).

Increasing the number of cells for a fixed applied voltage  $E$  results in an increase of the total electrical resistance  $R$ . Consequently, from Ohm's law the current  $I$  decreases.

#### 6.4. PRETREATMENT OF WASTEWATERS IN ELECTRODIALYSIS

For proper operation of the electro dialysis cell, particulate matter, large organic ions, and colloidal matter must be removed prior to the process. If this is not done, these materials cause fouling of membranes, which results in an increase of total electrical resistance. For a constant applied voltage, the current passing through the cell is thus lowered. Therefore, demineralizing capacity of the equipment is lowered.

Fouling of membranes is the greatest problem to be overcome in order to achieve economic operation of electro dialysis in treatment of wastewaters. Fouling is minimized by

1. Pretreatment of raw wastewater in order to remove particulate and colloidal matter and large organic ions. This is done by addition of coagulants, filtration through microscreens, and/or adsorption in activated carbon columns. Cost of pretreatment may render the process uneconomical.
2. Fouling is minimized by periodic plant shutdown for cleaning.
3. Frequent current reversals tend to minimize the effects of fouling.

## 7. Chemical Oxidation Processes (Chlorination and Ozonation)

### 7.1. CHLORINATION OF WASTEWATERS

#### 7.1.1. Utilization and Purposes of Chlorination

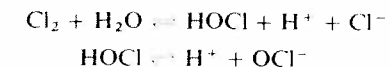
Chlorination is a widely used process in the treatment of domestic and industrial wastewaters. Some industrial effluents which are commonly chlorinated prior to discharge into receiving waters are those from beet sugar, cannery, dairy, pulp and paper, textile, tanning, petrochemical, pharmaceutical, and metal processing (chromium, electroplating) plants.

Purposes of chlorination are summarized as follows:

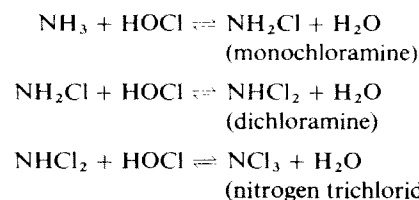
1. *Disinfection.* Primarily a disinfectant owing to its strong oxidizing capacity, chlorine destroys or inhibits growth of bacteria and algae.
2. *BOD reduction.* Chlorine accomplishes BOD reduction by oxidation of organic compounds present in wastewaters.
3. *Elimination or reduction of colors and odors.* Color and odor-producing substances present in wastewaters are oxidized by chlorine. The oxidizing ability of chlorine is employed for odor control and color removal in treatment of many industrial effluents (beet sugar, cannery, dairy, pulp and paper, textiles).
4. *Oxidation of metal ions.* Metal ions which are in a reduced state are oxidized by chlorine (e.g., ferrous to ferric ion and manganous to manganic ions).
5. *Oxidation of cyanides to innocuous products.* This application is described in Section 7.1.4.

#### 7.1.2. Reactions of Chlorine in Water

Added to water as either a gas or solution, chlorine reacts to form hypochlorous acid (HOCl), which subsequently dissociates according to the following chemical equations:



In the presence of ammonia, hypochlorous acid reacts to form monochloramine, dichloramine, and nitrogen trichloride. Relative proportions of these products depend on pH and concentration of ammonia present. Corresponding chemical equations are



Reactions of chlorine in water are illustrated by Fig. 8.21, which shows the relationship between chlorine added and chlorine residual.

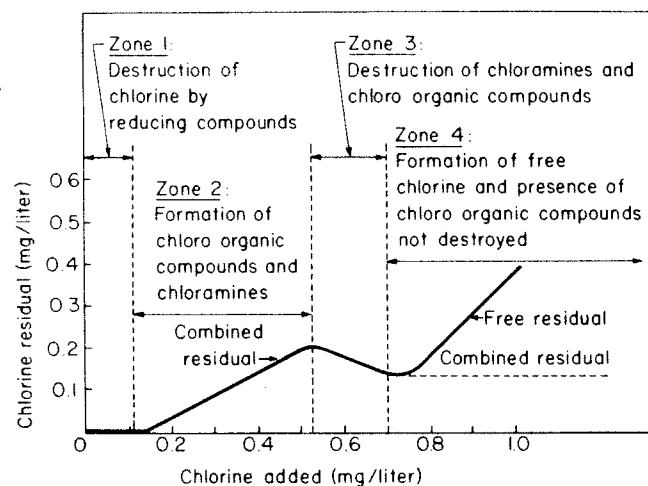


Fig. 8.21. Reactions of chlorine in water [8].

The initial amount of chlorine added is reduced by compounds which react rapidly with chlorine (e.g.,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ ). This corresponds to Zone 1 for which residual chlorine is nearly zero. Continued addition of chlorine results in residual chlorine in the form of chloro organic compounds or chloramines (combined residual). Chlorine residual is always less than the chlorine added. This corresponds to Zone 2 of the curve in Fig. 8.21. By adding more chlorine, chloro organic compounds are frequently oxidized: the molecule is broken down and chlorine is liberated. This results in a decrease of residual chlorine (Zone 3 in Fig. 8.21). Finally, when all reducing compounds have been oxidized, the additional quantity of chlorine added to the

water results in an equivalent residual chlorine. This corresponds to Zone 4 in Fig. 8.21, which displays a 45° straight line for the free residual, and a straight line parallel to the abscissa for the constant combined residual.

### 7.1.3. Chlorine as a Disinfectant

Typical chlorine dosages required for disinfection are shown in Table 8.5. The effectiveness of chlorine for killing bacteria is given by Chick's law [4], which is written in differential form as Eq. (8.60).

$$dN/dt = -kN \quad (8.60)$$

TABLE 8.5  
Typical Chlorine Dosages for Disinfection [8]

Effluent from	Dosage range (mg/liter)
Untreated wastewater (prechlorination)	6-25
Primary sedimentation	5-20
Chemical precipitation plant	2-6
Trickling filter plant	3-15
Activated sludge plant	2-8
Multimedia filter following activated sludge plant	1-5

where  $N$  is the bacteria count,  $t$  the time,  $dN/dt$  the rate of bacteria kill, and  $k$  the rate of kill constant.

Separating the variables and integrating from time  $t = 0$  to any time  $t$ ,

$$N/N_0 = e^{-kt} \quad (8.61)$$

where  $N_0$  is the bacteria count at  $t = 0$  and  $N$  the bacteria count at time  $t$ . The rate of kill constant  $k$  is a function of pH, temperature, and applied concentration of chlorine. It is estimated from the slope of a straight line plot of  $\ln N/N_0$  vs.  $t$  based on Eq. (8.61), which written in logarithmic form is

$$\ln(N/N_0) = -kt \quad (8.62)$$

The effectiveness of chlorination for destruction of various organisms corresponds to values of  $k$  from 0.24 to 6.3 for 99% kill (i.e.,  $N/N_0 = 1/100 = 0.01$ ) at 0°-6°C.

Chick's law is an idealized portrayal of the situation. Usually, ideal conditions do not exist owing to variations in cell resistance, decrease in chlorine concentration, etc. Rates of kill sometimes increase or decrease with time. Consequently, a modified form of Eq. (8.61) containing an extra constant  $m$  to be determined from experimental data is written as

$$N/N_0 = e^{-kt^m} \quad (8.63)$$



If  $m$  is less than 1, the rate of kill decreases with time, and if  $m$  is greater than 1, it increases. Constants in Eq. (8.63) are determined by plotting  $-\ln(N/N_0)$  vs. contact time  $t$  on logarithmic paper. The linear relationship is

$$\log[-\ln(N/N_0)] = \log k + m \log t \quad (8.64)$$

The effect of chlorine concentration is defined by the relationship

$$C^n t_p = \text{constant} = K \quad (8.65)$$

where  $C$  is the chlorine concentration (mg/liter);  $t_p$  the time required for a given percentage kill; and  $n$  the constant to be evaluated from the experimental data.

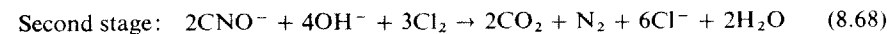
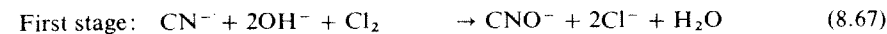
Constants in Eq. (8.65) are determined by plotting on logarithmic paper the concentration of chlorine vs. time for a given percentage kill. The linear form of Eq. (8.65) is

$$\log C = -(1/n) \log t_p + (1/n) \log K \quad (8.66)$$

The slope of this line corresponds to value of  $-(1/n)$ .

#### 7.1.4. Utilization of Chlorine for Destruction of Cyanides

Chlorine is utilized to oxidize cyanide to innocuous products. This is done in an alkaline media at values of pH greater than 8.5. Oxidation takes place in two stages according to Eqs. (8.67) and (8.68).



From Eqs. (8.67) and (8.68) the theoretical stoichiometric ratio is  $5\text{Cl}_2/2\text{CN}^-$  or  $2.5\text{Cl}_2/1\text{CN}^-$ . In practice, a large excess of chlorine is utilized, of the order of 7.5 parts chlorine per one part  $\text{CN}^-$ .

#### 7.1.5. Economics of Chlorination of Wastewaters

Although the use of chlorination is widespread, it should be pointed out that chlorine is a relatively expensive chemical. If economics is a consideration for a given application, other methods should be evaluated. Chlorine oxides ( $\text{Cl}_2\text{O}$ ,  $\text{Cl}_2\text{O}_5$ ,  $\text{Cl}_2\text{O}_7$ ) have been used in the disinfection of waters. A mixture of  $\text{Cl}_2\text{O}_5/\text{Cl}_2\text{O}_7$  is available commercially.

### 7.2. OZONATION OF WASTEWATERS

Chemical oxidation with ozone is an effective method for treating wastewaters, based on the following factors [5]:

1. Ozone reacts readily with unsaturated organics in wastewaters.

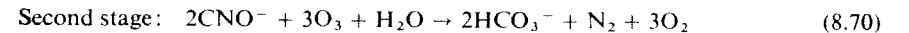
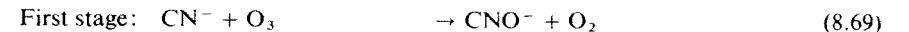
2. Foaming characteristics of wastewaters are reduced following ozone treatment.

3. Ring opening and partial oxidation of aromatics renders the wastewater more susceptible to conventional biological treatment.

4. Ozone in the effluent quickly reverts to oxygen once it has served its purpose. This dissolved oxygen is beneficial to the receiving stream and helps support aquatic life. In contrast, chlorine (which is the most widely used bacteria kill agent) lingers in the effluent and becomes a pollutant itself).

Laboratory scale ozonation equipment for evaluating amenability of wastewater to ozone oxidation is described by Eckenfelder and Ford [5].

Ozone may replace chlorine in treatment of cyanide wastewaters. Oxidation takes place in two stages according to Eqs. (8.69) and (8.70).



## 8. Nutrient Removal

### 8.1. INTRODUCTION

Removal of nutrients (phosphorus and nitrogen compounds) from wastewaters is an important operation, because these compounds play a critical role in lake eutrophication (Chapter 1, Section 7). Emphasis has been given to phosphorus removal for two reasons: (1) phosphorus is the most critical nutrient, and (2) nitrogen removal processes are less efficient and more expensive. Most nutrient removal treatment processes in operation today are designed for phosphorus removal alone.

### 8.2. PHOSPHORUS REMOVAL

#### 8.2.1. Processes for Phosphorus Removal

Processes for phosphorus removal include (1) chemical precipitation, (2) activated sludge process (Chapter 5), (3) stabilization ponds (Chapter 6, Section 6), (4) reverse osmosis (Chapter 8, Section 5), and (5) electrodialysis (Chapter 8, Section 6).

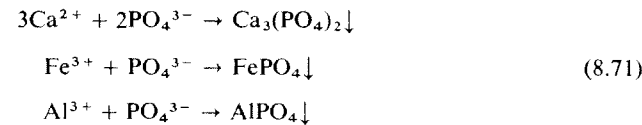
The activated sludge process, although primarily intended for removal of organic contaminants, removes both phosphorus and nitrogen, since biological cells contain approximately 2.0% phosphorus and 12% nitrogen by weight. For domestic sewage this amounts to a phosphorus removal rate of 20–40% (or 1–2 mg/liter).

Stabilization ponds yield relatively high phosphorus and nitrogen removal, provided light and temperature conditions are favorable to the growth of algae. During the summer, removal of about 80% of the nutrients may be

obtained, whereas during the winter it may drop to 20% or less. Reverse osmosis and electrodialysis are still too costly for generalized use. The discussion of phosphorus removal in this section is exclusively concerned with chemical precipitation processes.

### 8.2.2. Chemical Precipitation Processes for Phosphorus Removal

Precipitants which have been mainly employed in phosphorus removal are  $\text{Fe}^{3+}$  (as  $\text{FeCl}_3$ ),  $\text{Ca}^{2+}$  (as lime),  $\text{Al}^{3+}$  [as alum,  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ ], and combinations of  $\text{Fe}^{3+}$  and lime. The mechanism of phosphorus removal is mostly precipitation in the form of phosphates of  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$ .



Adsorption also plays a role in the removal of some phosphates which are adsorbed on the precipitating floc. Considerations on utilization of different precipitants are as follows:

1.  $\text{Fe}^{3+}$  (as  $\text{FeCl}_3$ ).  $\text{FeCl}_3$  (in dosages of 10 mg/liter) is the most commonly employed precipitating agent for phosphorus, yielding around 90% removal.

2.  $\text{Ca}^{2+}$  (as lime). Lime is less efficient than  $\text{FeCl}_3$ . Utilized in dosages of 500–700 mg/liter yields removal of at most 80% at pH values of 10.5–11. Another drawback of lime utilization resides in the large volumes of sludge produced, which causes a disposal problem. Recovery of lime by calcination of this sludge may be performed. Because of the presence of organic materials, the sludge may be capable of supporting its own combustion.

3.  $\text{Al}^{3+}$  [as alum,  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ ]. Although alum precipitation yields approximately 95% phosphorus removal at dosages of 200–250 mg/liter, it is less frequently applied owing to the high cost of alum. Removal of 50–60% of organic materials (carbonaceous and nitrogenous) is obtained simultaneously with phosphorus removal.

4. Combination of  $\text{Fe}^{3+}$  and lime. Combinations of  $\text{FeCl}_3$  solutions and lime in respective proportions of 100–150 mg/liter and 2–5 mg/liter have been used, yielding phosphorus removal of approximately 95%.

The precipitation operation is usually carried out within a treatment process. Figure 8.22 summarizes three alternative precipitation operations for phosphorus removal within an activated sludge plant.

*Alternative No. 1—precipitation in primary clarifier.* The precipitant, usually a combination of  $\text{FeCl}_3$  and lime with typical dosages indicated previously, is added to raw sewage, phosphates being precipitated and removed in

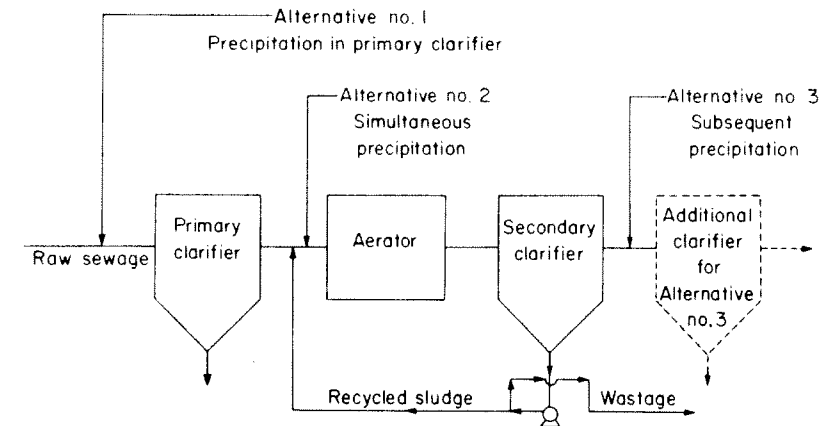


Fig. 8.22. Alternative precipitation operations for phosphorus removal.

the primary clarifier. Phosphorus removal is 90–95%, and a considerable amount of sludge is obtained. The addition of lime in this process raises the pH of the effluent from the primary clarifier to nearly 10.0. This is not an obstacle to the proper operation of the biological process in the aerator, which requires a pH near neutrality. The natural buffering capacity of the activated sludge process is sufficient to provide the required neutralization, owing to production of carbon dioxide.

*Alternative No. 2—simultaneous precipitation.* Precipitant is added directly to the aeration tank. The precipitate settles in the secondary clarifier together with the activated sludge. It seems that the chemicals do long-term damage to the biological cells, and that their organic removal efficiency is impaired to some extent. On the other hand, addition of chemicals aids settling and compaction of the activated sludge in the secondary clarifier.

*Alternative No. 3—subsequent precipitation.* Precipitating chemicals are added to the effluent from the secondary clarifier. An additional clarifier is required to remove precipitated phosphates, thereby increasing capital costs. On the other hand, the phosphorus removal efficiencies obtained are somewhat higher than those for the two previous alternatives.

Estimating chemical requirements for phosphorus removal cannot be done from simple stoichiometric relationships, because the actual mechanism of phosphorus removal is not known. Empirical relationships have been developed for estimating chemical requirements, and two of these are mentioned next.

1. For estimating  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  requirements,

$$\varepsilon = C_1 + 0.5 \log(m/P_i) \quad (8.72)$$

where  $\varepsilon$  is the efficiency of phosphorus removal [ $\varepsilon = (P_i - P_f)/P_i$ ], where  $P_i$

is the initial phosphorus concentration in wastewater (moles of  $P$ /liter);  $P_f$  the final phosphorus concentration after precipitation operation (moles of  $P$ /liter)];  $C_1$  a constant with a value of 0.614 for  $\text{FeCl}_3$  and 0.662 for alum; and  $m$  the required molality of precipitant (moles  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ /liter).

Solving for  $m$ ,

$$m = P_i 10^{(e-C_1)/0.5} \quad (8.73)$$

Equations (8.72) and (8.73) apply for a range  $0.45 < \varepsilon < 0.95$ .

2. For estimating lime requirements, a rule of thumb consists in utilizing a quantity of lime (moles/liter of  $\text{Ca}^{2+}$ ) equal to 1.5 times the carbonate hardness of the wastewater.

Laboratory evaluation of phosphorus removal can be performed. These tests not only permit plotting curves of phosphorus removal efficiency vs. dosage of precipitant, but also evaluation of effects of pH and temperature. Curves of phosphorus removal efficiency vs. dosage of precipitant are exponential. They reach a plateau beyond a certain concentration of chemical added. It is usually uneconomical, therefore, to attempt reducing phosphorus concentration below 0.10 mg/liter owing to extremely high chemical requirements.

### 8.3. NITROGEN REMOVAL

#### 8.3.1. Introduction

Nitrogen together with phosphorus contributes to the process of lake eutrophication. Also, nitrogen in the form of  $\text{NH}_4^+$  or nitrites ( $\text{NO}_2^-$ ) exerts an oxygen demand because of its oxidation to nitrates ( $\text{NO}_3^-$ ).



These facts justify the desirability of nitrogen removal from wastewaters prior to discharge into receiving waters.

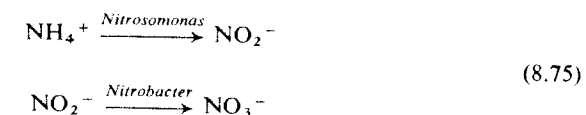
For domestic wastewaters the split among the various forms of nitrogen is relatively constant:  $\text{NH}_4^+$  nitrogen, 50–60%; organic nitrogen, 40–59%; and nitrites and nitrates, 0–5%. In the effluent from activated sludge treatment, most nitrogen is present either as nitrites or nitrates, owing to the occurrence of nitrification. Nitrification invariably occurs during activated sludge treatment at values of  $F/M$  ratio less than 1.0. (Optimum range of  $F/M$  ratios for the activated sludge process is from 0.3 to 0.7; see Chapter 5, Section 5.)

#### 8.3.2. Processes for Nitrogen Removal

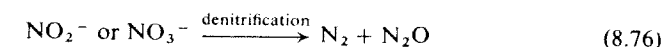
Processes for nitrogen removal include (1) nitrification–denitrification process; (2) ammonia stripping; (3) ion exchange; (4) biological processes such as activated sludge and stabilization ponds; and (5) precipitation processes.

1. *Nitrification–denitrification.* The main process geared specifically for nitrogen removal is nitrification–denitrification, which is a modification of the activated sludge process and takes place in two steps:

(a) Nitrification consists in aeration employing  $F/M$  ratios less than 1.0, usually  $F/M \approx 0.3$ , and a longer aeration period than for the conventional activated sludge process. Nitrogen compounds are converted to nitrites ( $\text{NO}_2^-$ ) and nitrates ( $\text{NO}_3^-$ ) in the presence of *Nitrosomonas* and *Nitrobacter* microorganisms.



(b) Denitrification is an anaerobic step which takes place in the secondary clarifier by extending residence time and adding an organic carbon source, usually methanol. Nitrites and nitrates are converted to nitrogen gas and nitrogen oxide, which are vented out.



Sludge age in secondary clarifier is at least 2–3 days, higher values being required at lower operating temperatures. Denitrification is performed even without addition of the organic carbon source to help meet denitrifying bacteria requirements. Endogenous respiration provides these requirements, but addition of the carbon source is helpful. A two-step nitrification–denitrification process is shown in Fig. 8.23.

A more sophisticated *three-step nitrification–denitrification process* is shown in Fig. 8.24. The first step is a high rate activated sludge process where 75–85% of the carbonaceous material is removed. Residence time in the aerator is approximately 2 hr. The second step is nitrification in the presence of an

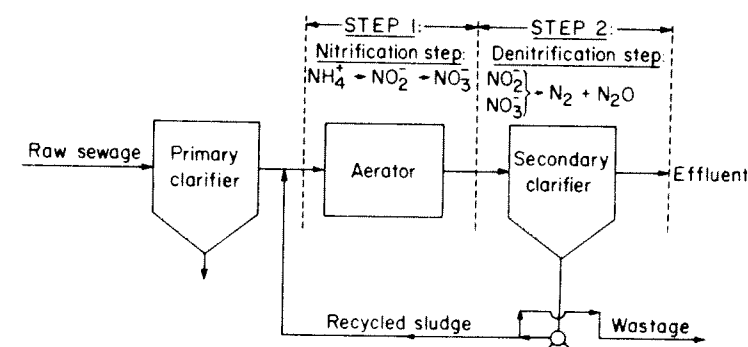


Fig. 8.23. Two-step nitrification–denitrification process.

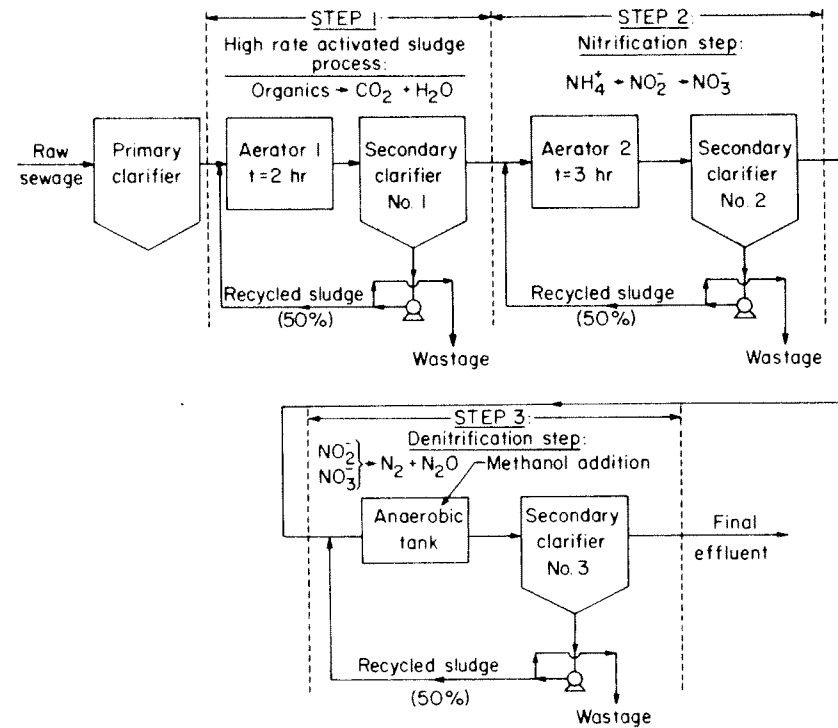


Fig. 8.24. Three-step nitrification-denitrification process.

enriched culture of nitrifying bacteria. Residence time in the aerator is approximately 3 hr. The third step is denitrification, which is an anaerobic operation, methanol being added to provide an adequate  $C/N$  ratio.

2. *Ammonia stripping.* This process consists of adjusting pH of the wastewater to a value above 10 (lime is utilized for this purpose), and then air-stripping the ammonia (at  $\text{pH} > 10$  nitrogen is present as  $\text{NH}_3$ ) in a stripping tower. Nitrogen removal efficiencies of approximately 90% are obtained at air/liquid ratios of  $350 \text{ ft}^3/\text{gal}$  and liquid rates of about  $3.0 \text{ gal}/(\text{min})(\text{ft}^2)$ . Removal efficiency is increased close to 98% with an air/liquid ratio of  $800 \text{ ft}^3/\text{gal}$ . However, removal efficiency drops considerably in cold weather.

Ammonia stripping is employed either before or after secondary treatment. If the stripping operation is followed by biological treatment, it is necessary to lower the pH to a value near the neutral point. This is usually done by recarbonation, i.e., bubbling through flue gas containing carbon dioxide. It is important to leave enough nitrogen unremoved to satisfy nutritional requirements for the biological process.

Simultaneously with nitrogen removal, air-stripping accomplishes phosphorus removal, BOD reduction, and removal of suspended solids. The primary variables involved in the ammonia-stripping process are pH, air/liquid ratio, hydraulic loading [ $\text{gal}/(\text{min})(\text{ft}^2)$ ], packed height, and characteristics of the packing elements.

3. *Ion exchange.* A cation exchange resin (clinoptilolite) which is selective for  $\text{NH}_4^+$  is utilized in treatment of activated sludge effluents from the secondary clarifier. This resin is regenerated with lime, and the regenerant is reused after being air-stripped of ammonia in a stripping tower. The cost of operation is high, and usually, this process is not economically feasible. Anion exchange resins are used for removal of nitrates ( $\text{NO}_3^-$ ). Phosphates and other anions are simultaneously removed. The resin is regenerated with brine and restored by treatment with acid and methanol. Pretreatment by filtration may be required in ion exchange processes, thereby increasing costs.

4. *Biological processes,* i.e., activated sludge and stabilization ponds, have already been mentioned in Section 8.2.1 in connection with phosphorus removal.

5. *Precipitation processes.* Section 8.2.2 describes these processes in connection with phosphorus removal. As far as nitrogen removal is concerned, precipitation methods are rather inefficient, accounting for less than 30% removal of total nitrogen.

#### 8.4. ADDED BENEFITS IN NUTRIENT REMOVAL

Although initial costs in the processes studied are high, there are added benefits in nutrient removal processes which in some cases justify the costs. Among these are (1) BOD reduction, (2) suspended solids removal, (3) bacterial and viral removal, and (4) removal of volatile organics.

## 9. Sonozone Wastewater Purification Process

This tertiary treatment process has been developed at the University of Notre Dame (Lobund Laboratory), and sonozone plants are commercially available from the Ecology Division of Telecommunications Industries, Inc. (Lindenhurst, New York). A pilot plant at the University of Indiana with a capacity of  $20,000 \text{ gal}/\text{day}$  is being used as a research model, treating on-campus sewage. A full-size plant (capacity,  $570,000 \text{ gal}/\text{day}$ ) is in operation at Indiantown, Florida.

Telecommunications Industries, Inc. claims that the sonozone process provides tertiary treatment at costs comparable to secondary treatment. The sonozone process combines ultrahigh frequency sound and ozone treat-

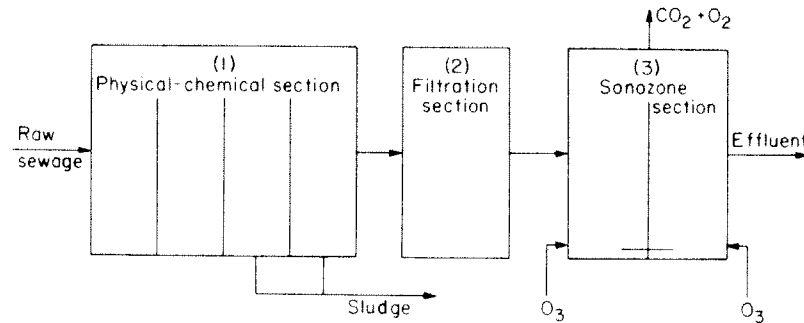


Fig. 8.25. Flow diagram of sonozone process [10]. (Courtesy of Telecommunications Industries, Inc.)

ment. A simplified flow diagram is shown in Fig. 8.25. Treatment involves three stages, of which the two initial ones are pretreatment units.

1. *Physical-chemical section.* Sludge is removed by a series of primary treatment contacts utilizing coagulation followed by clarification.

2. *Filtration section.* The filtration system is designed to remove micro-sized solids and organics from clarified wastewater.

3. *Sonozone section.* The central unit is the ozone and sonics unit. It consists of a small vibrating metal disk at the bottom of a tank through which wastewater flows. A steady stream of ultrasonic waves is sent out by the vibrating disk, and simultaneously ozone is bubbled into the tank from a nearby generator, which produces ozone by shooting electric arcs through the air.

The exact mechanism for the phenomena taking place when wastewater is subjected to a combination of ozone and ultrasonic waves is still under investigation. High frequency sound waves rattle bacteria and dissolved particles, breaking them into submicron size. In this form, they become highly susceptible to the strong oxidizing effect of ozone, so less of it is required. Carbonaceous materials are oxidized, yielding  $CO_2$  and  $O_2$ . This corresponds to the simplified equation [Eq. (8.77)]



In tests conducted at the 20,000-gal/day pilot unit at the University of Notre Dame, less than 60 sec of sonozone treatment destroyed 100% of fecal bacteria and viruses, 93% of phosphates, and 72% of nitrogen compounds. Effluent purity was just short of that obtained by distillation.

In the effluent, ozone quickly reverts to oxygen. This dissolved oxygen is beneficial to the receiving stream and helps support aquatic life. In contrast, chlorine, the most largely used bacteria kill, lingers in the effluent and becomes a pollutant itself.

Sludge from the physical-chemical section of the sonozone system is processed by any of the standard methods such as sand bed drying, vacuum filtration, centrifugation, or incineration. The Indiantown plant uses sand bed drying, with liquid waste from the sludge reprocessed through the sonozone system. Sludge is collected and periodically transported to a sludge disposal area.

One important characteristic of the process is its compactness. It is estimated that the sonozone system requires approximately 20% of the land area of conventional systems; thus real estate acquisition costs are considerably reduced. In addition, the smaller housing of the plant is more attractive than the large horizontal aeration and sedimentation tanks of conventional systems.

### Problems

I. For the activated carbon column in Example 8.2, calculate the residual concentration ( $C_E$ ) if depth is increased to 10 ft, keeping the same service time. Prepare a plot of  $C_E$  vs. depth utilizing depths of 5, 10, 15, and 20 ft.

II. Verify if the carbon adsorption data in the tabulation below are fit by the Langmuir isotherm. If so, determine constants  $K$  and  $b$ .

$C$ (mg/liter)	$X/M$ (g/g)
10	0.20
20	0.28
30	0.33

III. The wastewater stream from a plating industry has the following characteristics: flow rate, 50 gal/min for 12 hr a day; chemical composition: copper, 30 mg/liter as  $Cu^{2+}$ ; zinc, 12 mg/liter as  $Zn^{2+}$ ; nickel, 20 mg/liter as  $Ni^{2+}$ ; and chromate, 125 mg/liter as  $CrO_3$ . Characteristics of cation and anion exchange resins used are as given in the tabulation below.

	Cation	Anion
Regenerant	$H_2SO_4$	NaOH
Dosage (lb/ft <sup>3</sup> )	11.0	4.7
Concentration (%)	5	10.0
Flow rate [gal/(min)(ft <sup>2</sup> )]	0.5	0.5
Exchange capacity	1.5 eq/liter	3.8 lb $CrO_3$ /ft <sup>3</sup>
Rinsing water (gal/ft <sup>3</sup> of resin)	130	100

1. Design an anion exchange system to remove chromate. Calculate volume of resin required, NaOH for daily regeneration, and rinsing water requirements.

2. Design a cation exchanger to remove  $Cu^{2+}$ ,  $Zn^{2+}$ , and  $Ni^{2+}$ . Calculate volume of resin required,  $H_2SO_4$  for daily regeneration, and rinsing water requirements.

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# Appendix

## Conversion Factors from English to Metric Units

### LENGTH

$$\begin{aligned} \text{in.} \times 2.54 &= \text{cm} \\ \text{ft} \times 30.48 &= \text{cm} \\ \text{ft} \times 0.3048 &= \text{m} \end{aligned}$$

### AREA

$$\begin{aligned} \text{in.}^2 \times 6.4516 &= \text{cm}^2 \\ \text{ft}^2 \times 929.03 &= \text{cm}^2 \\ \text{ft}^2 \times 0.092903 &= \text{m}^2 \\ \text{acre} \times 4046.8 &= \text{m}^2 \quad (1 \text{ acre} = 43,560 \text{ ft}^2) \end{aligned}$$

### VOLUME (U.S. GAL UTILIZED)

$$\begin{aligned} \text{in.}^3 \times 0.01638 &= \text{liter} \\ \text{in.}^3 \times 16.386 &= \text{cm}^3 \\ \text{ft}^3 \times 28.316 &= \text{liter} \\ \text{ft}^3 \times 0.02831 &= \text{m}^3 \\ \text{ft}^3 \times 2.8316 \times 10^4 &= \text{cm}^3 \\ \text{gal} \times 3.7854 &= \text{liter} \\ \text{gal} \times 3785.4 &= \text{cm}^3 \end{aligned}$$

### FLOW RATE (U.S. GAL UTILIZED)

$$\begin{aligned} \text{gal/min} \times 0.0631 &= \text{liter/sec} \\ \text{gal/hr} \times 1.052 \times 10^{-3} &= \text{liter/sec} \\ \text{gal/day} \times 4.381 \times 10^{-5} &= \text{liter/sec} \\ \text{MGD} \times 43.81 &= \text{liter/sec} \quad (\text{Note: MGD} = \text{million gallons/day}) \end{aligned}$$

### FLOW RATE PER UNIT AREA (U.S. GAL UTILIZED)

$$\begin{aligned} \text{gal/(min)(ft}^2) \times 40.75 &= \text{liter/(min)(m}^2) \\ \text{gal/(min)(ft}^2) \times 0.679 &= \text{liter/(sec)(m}^2) \\ \text{gal/(min)(ft}^2) \times 0.004075 &= \text{liter} \\ \text{gal/(min)(ft}^2) \times 0.2445 &= \text{liter/(hr)(cm}^2) \\ \text{gal/(min)(ft}^2) \times 2445 &= \text{liter/(hr)(m}^2) \\ \text{gal/(hr)(ft}^2) \times 2445 &= \text{liter/(min)(m}^2) \\ \text{gal/(hr)(ft}^2) \times 40.75 &= \text{liter/(sec)(m}^2) \\ \text{gal/(hr)(ft}^2) \times 0.2445 &= \text{liter/(min)(cm}^2) \\ \text{gal/(hr)(ft}^2) \times 14.67 &= \text{liter/(hr)(cm}^2) \\ \text{gal/(hr)(ft}^2) \times 146,700 &= \text{liter/(hr)(m}^2) \end{aligned}$$

### FLOW RATE PER UNIT VOLUME (U.S. GAL UTILIZED)

$$\begin{aligned} \text{gal/(hr)(ft}^3) \times 2.2285 &= \text{liter/(min)(m}^3) \\ \text{gal/(hr)(ft}^3) \times 0.0371 &= \text{liter/(sec)(m}^3) \end{aligned}$$

**MASS**

$$\text{lb} \times 453.59 = \text{g}$$

$$\text{lb} \times 0.045359 = \text{kg}$$

**QUANTITY OF HEAT**

$$\text{BTU} \times 0.25198 = \text{kg calorie}$$

$$\text{BTU} \times 251.98 = \text{g calorie}$$

**TEMPERATURE**

$$^{\circ}\text{C} = (1/1.8)(^{\circ}\text{F} - 32)$$

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