13.1 PRINCIPLES OF ION EXCHANGE

13.1-1 Ion-Exchange Resins

All modern resins are polymeric structures, generally based on either a styrene or an acrylic matrix.

**POLYSTYRENE SULFONIC ACID CATION RESINS**

Styrene (vinylbenzene) is polymerized readily, using an organic peroxide catalyst, to form linear polystyrene. If divinylbenzene (DVB) (usually about 8% of the total) is mixed with the styrene, a three-dimensional polymer network is formed. The DVB cross-links give a three-dimensional structure that renders the polymer insoluble. The characteristic spherical ion-exchange beads therefore are made by suspension polymerization. The catalyzed monomer mixture is stirred into water under conditions designed to give the desired droplet size which, after several hours heating, will yield solid spherical beads.

At this stage, the beads are hydrophobic but can absorb some organic liquids such as toluene, swelling as a result. The extent of swelling is used in fact as a measure of the crosslinking of the polymer. The beads are converted into an ion-exchange resin, by first swelling the polymer with an inert solvent such as ethylene dichloride. They are then treated with concentrated sulfuric acid, at about 80°C, to make a cation exchanger. The cation exchanger is totally insoluble but is freely permeable by water and contains about 50% H₂O by weight in an apparently dry state. The final material is sulfonated crosslinked polystyrene which is the most widely used cation-exchange resin in commercial use. The total capacity of the resin for sorbing any ion is about 0.00525 equivalent per gram, normally expressed as 5.25 meq/g, calculated on oven-dried resin.

**ACRYLIC CATION RESINS**

These materials are made usually by copolymerizing acrylic or methacrylic acid with DVB. The total capacity is extremely high, at 13.0 meq/dry gram, corresponding with about 6.5 meq/wet gram, or 4500
meq/L. Polyacrylics, with lower molecular weight and high capacity, have replaced almost entirely the methacrylics. The manufacture is a little more complex, since acrylic acid is fairly soluble in water and cannot be polymerized in suspension. Thus, the procedure is to make crosslinked poly ethyl acrylate, or acrylonitrile, which is then hydrolyzed to give the final product.

**POLYSTYRENE ANION EXCHANGERS**

The basic polymer is exactly as for the polystyrene cation exchangers, but the introduction of the active group requires two steps. A chloromethyl group is introduced into each benzene ring, after which any amine group can be introduced by a simple addition reaction with chloromethyl ether.

If a tertiary amine such as trimethylamine is used, the product is a strong base quaternary ammonium compound. This resin is the anionic equivalent of the sulfonic cation materials. The capacity of a typical strong base resin is 3.9-4.2 meq/dry gram. The use of a secondary amine, such as dimethylamine, gives a tertiary amine product, which is more weakly basic. However, whereas there are only two acidic groups readily available for cation resins, very large numbers of amines can be used to produce anion-exchange materials for different characteristics. This fact is used to produce special resins for uranium and gold recovery.

**ACRYLIC ANION EXCHANGERS**

A range of polyacrylic anion-exchange resins has been produced in recent years. The exact structure and method of manufacture have not been published, but it is clear that they contain quaternary ammonium groups (or in the case of the weakly basic materials, amino groups) attached to an acrylic skeleton. They are physically robust materials, with good operating characteristics, and are serious competitors to the polystyrene resins.

**MODIFIED RESIN SKELETONS**

The polystyrene resins have an extremely irregular structure, owing to the fact that DVB polymerizes with itself more rapidly than with styrene. Consequently, the first polymer formed is highly crosslinked, and the liquid mixture is depleted in DVB. During the progress of polymerization, which takes several hours, the product becomes progressively less crosslinked, and, ultimately, some linear polymer is formed, attached to the copolymer matrix. The final resin, while having an average crosslinking of say 8%, contains tightly knotted regions in which crosslinking may be up to 25%, and the intermolecular distance is correspondingly reduced.

This heterogeneous structure has two results. First, in the case of simple, relatively small, inorganic ions, it is found that the law of mass action is not wholly obeyed, and the defined equilibrium "constants" are not fixed. As an ion enters the resin, the process becomes progressively more difficult as the concentration in the resin approaches the total capacity, and the less accessible active groups come into use.

A second, and more important, problem occurs with large ions such as the natural humic and fulvic acids occurring in the surface-water supplies. These are large polycarboxylic molecules, which diffuse freely through the less crosslinked regions of anion resins but become trapped in the tightly crosslinked regions. As a result, resins can become poisoned, losing capacity and giving inferior treated-water quality. New types of resin, which are referred to as "macroporous" or "macroreticular," overcome this problem. On the molecular scale these resins have a sintered structure that gives free water channels (in contrast to bound gel water) of about 1000 Å diameter. Large molecules travel freely through these channels and have only short distances to travel through the resin itself. Therefore, these materials have a high resistance to organic poisoning. They take up and release natural organic matter freely. Macroporous resins, anion or cation, generally have greater osmotic shock stability than the standard gel resins, but not necessarily greater compressive strength or attrition resistance. Their use in anion form has become very widespread.

Macroporous cation resins are also available but are less widely used than the anion materials. This is because the standard gel cation resins are themselves very strong and also because the poisoning of cation resins by large organic cations is virtually unknown.

**INORGANIC ION EXCHANGE MATERIALS**

The earliest ion-exchange phenomena were discovered using naturally occurring ion-exchange materials, especially zeolites consisting mainly of an aluminosilicate structure. Interest in the application of inorganic materials for ion exchange has continued with considerable vigor and in some instances these materials are preferred to synthetic polymeric ion-exchange resins.

Important materials that have found widespread application in the process industries fall under the following general headings:

- Natural and synthetic zeolites
- Insoluble salts, for example, hydrous zirconium phosphate
- Heteropolyacids, for example, ammonium phosphomolybdate
- Complex ferrocyanides, for example, sodium copper cyanoferrate (II)
- Clays, for example, montmorillonite
Zeolites, whose use as molecular sieve adsorbents is discussed in Chapter 12, possess well-defined crystal structures composed of an aluminosilicate lattice containing Si, Al, and O atoms in a cage-type structure. The matrix is capable of exchanging cations, usually alkali or alkaline earth ions in aqueous solution. There is considerable affinity for divalent ions such as Ca\(^{2+}\) and Mg\(^{2+}\) as well as for Sr\(^{2+}\). The latter renders zeolites of exceptional importance in the removal of strontium (and cesium) from low- and intermediate-level nuclear waste solutions. Naturally occurring zeolites, such as clinoptilolite, have found extensive use in the nuclear industry for this and related applications. Zeolites offer other important advantages over polymeric materials since they can withstand higher operating temperatures, are resistant to ionizing radiation, and are generally more chemically stable. The advantage of naturally occurring materials is their relative cheapness if they are used on a once-through basis. It is common practice in the nuclear industry to extract traces of radioactive strontium and cesium onto zeolites and subsequently immobilize the exhausted ion-exchange material in concrete or cement for permanent storage. Naturally occurring clays, such as montmorillonite, have also been considered for this application but are less favored.

The use of finely divided zeolites in detergents for water softening will lead undoubtedly to large-scale use in the future. Most inorganic ion-exchange materials are cationic, although a few synthetic materials are amphoteric in character. The most interesting salt is hydrous zirconium phosphate, which acts as a cation exchanger in alkaline solution and as an anion exchanger in acid. Other insoluble salts of zirconium can be prepared in crystalline form and exhibit ion-exchange properties, for example, zirconium tungstate, zirconium molybdate, and zirconium arsenate. These compounds hydrolyze above pH 6 and therefore are of more limited use.

Complex transition metal ferrocyanide salts can be produced in crystalline and powdered forms and possess a very high selectivity for cesium in solutions having high salt concentrations. Potassium cobalt cyanoferrate (II) and sodium copper cyanoferrate (II) have been identified as useful reagents for cesium removal from radioactive waste streams and other cyanoferrates are capable of separating Cs from Rb and from a fission product mixture.

13.1-2 Ion-Exchange Selectivity

Ion-exchange equilibria in cation- and anion-exchange resins depend largely on the type of functional group and the degree of crosslinking. The degree of crosslinking determines the tightness of the matrix structure and thus its porosity. It cannot be measured directly and is rarely homogeneous.

Crosslinking varies from the outer shell to the center of a bead and is usually quoted by the manufacturers as the "nominal DVB content." Modern ion-exchange resins contain a more rigid and well-defined structure and are referred to as "macroreticular" or "isoporous" materials. These are composed of highly crosslinked microspheres with a macrospHERical structure. However, the laws governing equilibria are essentially the same for these materials.

The important properties of ion exchange materials are briefly given below:

1. To preserve electroneutrality, (a) ion exchange is stoichiometric and (b) capacity is independent of the nature of the counterion.
2. Ion exchange is nearly always a reversible process;
3. Ion exchange is a rate-controlled process, usually governed by diffusion in the bead or the surrounding stagnant liquid film.

**Simple Binary Systems**

The most widely employed method for expression of ion-exchange equilibria has been developed from the law of mass action or the Donnan membrane theory. Consider the exchange of cations A and B between a cation-exchange resin and a solution containing no other cations. Assume that the ion exchanger is initially in the B from and that the solution contains ions A. The mass action expression for cation exchange can be written

\[
\zeta_A B^{z_B} + \zeta_B A^{z_A} = \zeta_B A^{z_B} + \zeta_A B^{z_A}
\]

(13.1-1)

Here, overbars denote the ionic species in the resin phase, \(z_A\) and \(z_B\) denote the valency and charge of counterions A and B. We can define the thermodynamic equilibrium constant \(K_a\) as follows:

\[
K_a = \frac{\left(\frac{\zeta_A}{\zeta_B}\right)^{z_B}}{\left(\frac{\zeta_B}{\zeta_A}\right)^{z_A}}
\]

(13.1-2)

The difficulty in the evaluation of the activity coefficients and therefore activities in the resin phase is great. For most practical applications it is usually satisfactory to assume that the solution-phase activity coefficients are almost unity, which is particularly valid in dilute solutions. Therefore, the resin-phase activity coefficients usually are combined into the equilibrium constant \(K_a\), to provide a new pseudoconstant, that is, the selectivity coefficient \(K_{se}\). Thus.
Often it is desirable to use equivalent ionic fractions to represent concentrations in the solution and resin phases. Thus, in a binary system,

\[ (K_c)_B^A = \frac{(C_A)^{z_A} (C_B)^{z_B}}{(C_B)^{z_A} (C_A)^{z_B}} \]  

(13.1-3)

The distribution coefficient \( m_A \) is defined as

\[ m_A = \frac{C_A}{C_A} = \frac{y_A C}{x_A C} \]  

(13.1-5)

the separation factor \( \alpha \) is defined as

\[ \alpha_B^A = \frac{y_A/x_A}{y_B/x_B} = \frac{y_A}{y_B} \frac{x_B}{x_A} \]  

(13.1-6)

**Univalent Exchange.** If we consider the exchange of univalent ions, that is, \( z_A = z_B = 1 \), then the selectivity coefficient becomes

\[ (K_c)_B^A = \frac{y_A y_B}{y_B x_A} = \frac{y_A (1 - x_A)}{x_A (1 - y_A)} = \alpha_B^A \]  

(13.1-7)

A typical plot of \( K_c \) for univalent exchange is given in Fig. 13.1-1. The equilibrium data are plotted with respect to species A and show that if \( K_c > 1 \), species A is preferred by the exchanger; the preferential attraction becomes more pronounced as \( K_c \) increases. If, \( K_c < 1 \) then species A is less preferred and the ion exchange preferentially sorbs species B. The selectivity of an ion-exchange resin is affected greatly by the degree of crosslinking. Slightly crosslinked and highly swollen resins exhibit reduced selectivity for one small ion over another. With increase in crosslinking, selectivity is increased (see Table 13.1-3). Gregor\(^3\) indicates that swelling of resins during the exchange process is a result of an osmotic process during which the osmotic pressure of the resin gel is opposed by tension in the resin structure.
Table 13.1-1 Calculated Values of $K_c$ for Sodium-Hydrogen Exchange for Sulfonated Polystyrene-DVB

<table>
<thead>
<tr>
<th>DVB (%)</th>
<th>$K_c$ Calculated</th>
<th>$K_c$ Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.18</td>
<td>1.06</td>
</tr>
<tr>
<td>5</td>
<td>1.49</td>
<td>1.25</td>
</tr>
<tr>
<td>10</td>
<td>2.2</td>
<td>1.75</td>
</tr>
<tr>
<td>17</td>
<td>3.2</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Source: Reichenberg et al.¹

Table 13.1-2 Calculated Values of $K_c$ for Sodium-Hydrogen Exchange for Varying Degrees of Saturation

<table>
<thead>
<tr>
<th>Fractional Saturation with Sodium</th>
<th>DVB (%)</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
<th>0.7</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$K_c$ (calc.)</td>
<td>1.18</td>
<td>1.23</td>
<td>1.27</td>
<td>1.29</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>$K_c$ (obs.)</td>
<td>1.06</td>
<td>1.10</td>
<td>1.11</td>
<td>1.14</td>
<td>1.16</td>
</tr>
<tr>
<td>5</td>
<td>$K_c$ (calc.)</td>
<td>1.49</td>
<td>1.59</td>
<td>1.68</td>
<td>1.77</td>
<td>1.86</td>
</tr>
<tr>
<td></td>
<td>$K_c$ (obs.)</td>
<td>1.25</td>
<td>1.40</td>
<td>1.45</td>
<td>1.41</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Source: Gluekauf and Duncan.²

Table 13.1-3 Selectivity ($K_a$) Scale for Univalent Ions in Sulfonic Acid Resins Using the Lithium Ion as Reference

<table>
<thead>
<tr>
<th></th>
<th>4% DVB</th>
<th>8% DVB</th>
<th>16% DVB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>H</td>
<td>1.32</td>
<td>1.27</td>
<td>1.47</td>
</tr>
<tr>
<td>Na</td>
<td>1.58</td>
<td>1.98</td>
<td>2.37</td>
</tr>
<tr>
<td>NH₄</td>
<td>1.90</td>
<td>2.55</td>
<td>3.34</td>
</tr>
<tr>
<td>K</td>
<td>2.27</td>
<td>2.90</td>
<td>4.50</td>
</tr>
<tr>
<td>Rb</td>
<td>2.46</td>
<td>3.16</td>
<td>4.62</td>
</tr>
<tr>
<td>Cs</td>
<td>2.67</td>
<td>3.25</td>
<td>4.66</td>
</tr>
<tr>
<td>Ag</td>
<td>4.73</td>
<td>8.51</td>
<td>22.9</td>
</tr>
<tr>
<td>Tl</td>
<td>6.71</td>
<td>12.4</td>
<td>28.5</td>
</tr>
</tbody>
</table>

Source: Bonner and Smith.³

Conditions of equal valency, large hydrated ions are less favored since they require expansion of the network. Tables 13.1-1 and 13.1-2 show the predicted values of $K_c$ as a function of degree of crosslinking for the exchange of sodium and hydrogen. Increased selectivity with increasing crosslinking is observed and can be predicted from theory.⁴ ⁵

Bonner and Smith⁶ have given the selectivity of univalent ions in sequence with lithium as the reference ion. The selectivity scale (see Table 13.1-3) is based on the parameter $K_a$ and similarly shows the improved selectivity with decrease in hydrated ion size and with increase in the degree of crosslinking.

Divalent-Univalent Exchange. In the industrially important case of divalent-univalent exchange, that is, $z_A = 2$, $z_B = 1$, the expression for the selectivity coefficient becomes

$$ (K_d) \frac{y_A(1 - y_A)}{C} = \frac{y_A(1 - y_A)^2}{x_A(1 - y_A)^2} \quad (13.1-8) $$

Here the relationship between $y_A$ and $x_A$ becomes greatly dependent on the value of $C$, the solution-phase concentration. A typical equilibrium plot is shown in Fig. 13.1-2 and it is obvious that the preference for
A is enhanced greatly as the solution concentration is decreased. Increasing the concentration results in a lowering of the selectivity of the divalent ion over the univalent ion. A selectivity scale for divalent cations is given in Table 13.1-4. Again the arbitrary value of unity is given to the lithium ion. Bonner and Smith corrected their value of the equilibrium constant by allowing for activity coefficients by using the method developed by Argersinger and Davidson. Thus, 

$$\log K = \int_0^1 \log \left( \frac{K}{y_A} \right) dC_A$$  \hspace{1cm} (13.1-9)

which is the result of the Gibbs-Duhem relationship.

**Anion Exchange.** Extensive values of the selectivity coefficients for strongly basic anion resins of the quaternary ammonium types have been tabulated by Bauman and Wheaton, \(^8\) Kunin and McGarvey, \(^9\) and Gregor et al. \(^10\) Gregor and coworkers have shown two classes of ions: those that exhibit little change in selectivity coefficient with resin composition, and those with composition-dependent selectivity coefficients. The latter presumably form clusters within the resin phase while the former are distributed randomly at equilibrium.

<table>
<thead>
<tr>
<th></th>
<th>4% DVB</th>
<th>8% DVB</th>
<th>16% DVB</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO(_2)</td>
<td>2.36</td>
<td>2.45</td>
<td>3.34</td>
</tr>
<tr>
<td>Mg</td>
<td>2.95</td>
<td>3.29</td>
<td>3.51</td>
</tr>
<tr>
<td>Zn</td>
<td>3.13</td>
<td>3.47</td>
<td>3.78</td>
</tr>
<tr>
<td>Co</td>
<td>3.23</td>
<td>3.74</td>
<td>3.81</td>
</tr>
<tr>
<td>Cu</td>
<td>3.29</td>
<td>3.85</td>
<td>4.46</td>
</tr>
<tr>
<td>Cd</td>
<td>3.37</td>
<td>3.88</td>
<td>4.95</td>
</tr>
<tr>
<td>Ni</td>
<td>3.45</td>
<td>3.93</td>
<td>4.06</td>
</tr>
<tr>
<td>Ca</td>
<td>4.15</td>
<td>5.16</td>
<td>7.27</td>
</tr>
<tr>
<td>Sr</td>
<td>4.70</td>
<td>6.51</td>
<td>10.1</td>
</tr>
<tr>
<td>Pd</td>
<td>6.56</td>
<td>9.91</td>
<td>18.0</td>
</tr>
<tr>
<td>Ba</td>
<td>7.47</td>
<td>11.5</td>
<td>20.8</td>
</tr>
</tbody>
</table>

**Source:** Bonner and Smith. \(^6\)
MULTICOMPONENT ION EXCHANGE

The theoretical treatment of multicomponent ion exchange is quite complex, especially if it involves species of different valency. The treatment of ion-exchange equilibria involving only ions of the same valence is quite straightforward since it can be assumed that the selectivity coefficient or separation factor is constant over the complete range of ionic concentration.

Consider any two species, \( i \) and \( j \); the separation factor is defined as

\[
\alpha_j = \frac{y_i x_j}{x_i y_j}
\]  

(13.1-10)

(even for ions of different valencies, the assumption of constant \( \alpha \)'s may be a good approximation). If the total number of exchangeable ions is \( n \), there are \( n - 1 \) independent equations of this type. To find the liquid-phase concentrations from given solid-phase concentrations, the above equations can be combined to yield

\[
x_i = \frac{y_i}{\sum_j \alpha_j x_j} = \frac{\alpha_j y_i}{\sum_j \alpha_j y_j}
\]  

(13.1-11)

where the summation is carried out over all the components and \( k \) designates an arbitrarily chosen component, \( \alpha_k \), \( \alpha'_k \), and \( \alpha''_k \) are equal to 1. An analogous equation can be obtained for \( y_i \) in terms of the \( x \)'s:

\[
y_i = \frac{x_i}{\sum_j \alpha'_j x_j} = \frac{\alpha'_j x_i}{\sum_j \alpha'_j x_j}
\]  

(13.1-12)

If \( x \) is constant, \( y \) becomes a linear function of the other \( y \)'s. Similarly, if \( y \) is constant, \( x \) becomes a linear function of the other \( x \)'s. Consider a ternary system involving three components A, B, and C. Assuming univalent ions, then \( (K_A)_B = \alpha_B \), \( (K_B)_C = \alpha_C \), and \( (K_C)_A = \alpha_A \). It follows that

\[
\alpha_A \alpha_B \alpha_C = 1
\]  

(13.1-13)

Three-component equilibrium data can be represented on a triangular diagram. The regular grid of the diagram is used to represent the composition of one of the phases (usually the resin phase): the composition of the other phase is given by a set of contour lines, each corresponding to a constant concentration of one of the components. Figure 13.1-3 shows the triangular composition diagram for a hypothetical system having \( \alpha_A = 2 \) and \( \alpha_B = 2 \). A contour line (which is straight in this case) for \( x_A = 0.1 \) is constructed by connecting its intercepts with the lines \( y_B = 0 \) and \( y_C = 0 \). The intercepts are obtained directly from the binary A–C and A–B equilibrium relationships. For the case of a divalent-univalent system, the separation factor (expressed as \( \alpha_A^* \)) will vary with composition. Thus, the effect of concentration must be taken into account.
account in presentation of equilibrium data. In such a case, it is still possible to draw the appropriate ternary diagram and an example of variable-separation factor equilibria is shown in Fig. 13.1-4. The contour lines are now curved so that a variable-separation factor system may be viewed as a distorted constant-separation factor system that exhibits identical properties over an infinitesimal composition change. Qualitatively, the behavior over finite composition change is similar to the univalent system.

For ternary systems, the theory is tidy and quite precise, although the representation relies heavily on the constancy of the relevant separation factors. Regrettably, the values of the selectivity coefficients and separation factors are not constant in practice. There is much experimental evidence to show that these parameters are far from constant even in the simplest cases. Figures 13.1-5, 13.1-6, and 13.1-7 show experimentally determined values of the binary separation factors in the K-Na-H system. Note the significant decrease in $\alpha_{\text{K}}$ as a function of $x_{\text{K}}$. The deviation of the experimental points from the derived contour lines is shown in Figs. 13.1-8 and 13.1-9. A method of qualitative representation and interpretation of multicomponent ion-exchange equilibria has been published by Brignal et al. and this paper should be consulted for a rational procedure. A general method for the prediction of multicomponent ion-exchange equilibria from the data of relevant binary systems has emerged in recent years. This requires the calculation of thermodynamic equilibrium constants for the reaction and parameters to calculate activity coefficients of the exchanging species in both phases. Two parameters for each ionic component are required in the solution phase to calculate the activity coefficients by the extended Debye-Hückel equation. Two interaction coefficients are required in the resin phase by analogy with vapor-liquid equilibrium data and the Wilson method has been successfully applied. If a multicomponent system can be resolved into a set of binary equilibria, then it is necessary only to characterize the binary data. If the equilibrium constants constants and the interaction parameters are applied, then the multicomponent data can be obtained by solving the resulting binary-exchange equations simultaneously.

13.1-3 Ion Exchange Kinetics

General Introduction

The kinetics of ion exchange may be divided into five steps:

1. Diffusion of the counterions through the bulk solution to the surface of the ion exchanger.
FIGURE 13.1-5 The effect of solution concentration on the separation factor in the Na\(^+\)-H\(^+\) system. For the 8% DVB resin; ○, 0.01 \(N\) Cl\(^-\); ×, 0.1 \(N\) Cl\(^-\); and +, 1.0 \(N\) Cl\(^-\).

FIGURE 13.1-6 The effect of solution concentration on the separation factor in the K-H system. For the 8% DVB resin: ○, 0.01 \(N\) Cl\(^-\); ×, 0.1 \(N\) Cl\(^-\); and +, 1.0 \(N\) Cl\(^-\).
FIGURE 13.1-7 The effect of solution concentration on the separation factor in the $K^+ - Na^+$ system. For the 8% DVB resin: $\bigcirc$, 0.01 $N$ Cl$^-$; $\times$, 0.1 $N$ Cl$^-$; $+$, 1.0 $N$ Cl$^-$. 

FIGURE 13.1-8 Ternary equilibria for the system $H^+ - Na^+ - K^+$: 1.0 $N$ Cl$^-$, 8% DVB resin. The curves are estimated from binary data and solid circles (•) represent experimental points.
FIGURE 13.1-9 Ternary equilibria for the system H⁺–Na⁺–K⁺: 0.01 N Cl⁻, 8% DVB resin. The curves are estimated from binary data and the solid circles (●) represent experimental points.

2. Diffusion of the counterions within the solid phase.
3. Chemical reaction between the counterions and the ion exchanger.
4. Diffusion of the displaced ions out of the ion exchanger.
5. Diffusion of the displaced ions from the exchanger surface into the bulk solution.

Steps 4 and 5 are the reverse processes of steps 2 and 1, respectively. The kinetics of ion exchange are governed by either a diffusion or mass action mechanism, depending on which is the slowest step. In general, the diffusion of ions in the external solution is termed film diffusion control. This is a useful concept but hydrodynamically it is ill defined. The diffusion or transport of ions within the exchanger phase is commonly termed particle diffusion control. Chemical reaction at the exchanger sites can be rate controlling in certain cases.

DIFFUSIONAL PROCESSES
It should be stated that simple diffusion-based kinetic treatments are idealized cases of ion exchange. They are only strictly valid for systems undergoing isotopic redistribution where precise boundary conditions can be described. Usually, it is assumed that all ion-exchange particles are spherical and of uniform size. In this case, diffusional processes are fundamentally described by Fick’s First Law:

\[ J_i = D \text{ grad } C_i \]  

Here \( J_i \) is the flux of the diffusing species \( i \) of concentration \( C_i \), and \( D \) is the diffusion coefficient. Fundamental treatment of the rate laws of ion exchange is given by Helfferich.\(^{15}\)

The nature of the rate-determining step can be predicted by use of the simple dimensionless criterion given by Helfferich:\(^{15}\)

\[ \frac{CD_i}{CD_i} (5 + 2\alpha_i^p) \ll 1 \text{ particle diffusion control} \]

\[ \frac{CD_i}{CD_i} (5 + 2\alpha_i^p) \gg 1 \text{ film diffusion control} \]
where the variables are defined in the Notation section. If film diffusion is much faster than diffusion within the ion-exchange particles, then concentration differences in the liquid film level out instantaneously (see Fig. 13.1-10). Concentration gradients exist within the exchanger, and particle diffusion is the rate-controlling step. The quantitative aspects of particle diffusion are more complex since the internal solid phase is only partially available as a diffusion medium. A large fraction of the interior of a bead is occupied by the exchanger matrix and this leads to steric hindrance and tortuous diffusion paths. Furthermore, migration of counterions is confined to the array of fixed ionic groups on the matrix of the exchanger. Thus, steric hindrance and ionic interactions result in slower diffusion kinetics within the particle.

Under the infinite solution volume condition, fractional conversion or attainment of equilibrium is given by the expression

$$X = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \exp \left( - \frac{Dn^2t}{r_0^2} \right)$$  \hspace{1cm} (13.1-16)

In actual ion exchange, the counterdiffusing ions possess different mobilities. For a quantitative treatment, Fick's Law has to be replaced by the Nernst-Planck equation which allows both particle and film diffusion kinetics in exchanging ideal systems to be described:

$$J_i = -D_i \left( \text{grad} C_i + \frac{z_iF}{RT} \text{grad} \phi \right)$$  \hspace{1cm} (13.1-17)

where $\phi$ is the electrical potential. The Nernst-Planck theory predicts that the forward and reverse rates of ion exchange should differ markedly with different mobilities of the counterions concerned (Fig. 13.1-11). A striking feature is the behavior of the concentration profiles within the beads. If the ion initially present in the bead is the much faster one, then a comparatively sharp boundary moves toward the center of the particle (see Fig. 13.1-12). This is a result of the great dependence of the interdiffusion coefficient on ionic composition. Hence, in this case, the concentration of the faster-moving ion is low in the outer shells and high at the center of the bead. Therefore, the interdiffusion coefficient decreases toward the center of the bead, and the edge is converted quickly. This behavior is similar to the proposed shell progressive or ash-layer diffusion model for interacting species.

**Chemical Reaction Kinetics.** The possibility of a chemical reaction between the counterions and the fixed exchange sites is also recognized as one of the general ion-exchange mechanisms in certain cases.
The rate-controlling step is no longer a conventional diffusional process but chemical reaction kinetics are assumed. The rate of ion exchange is governed by the rate constant of the corresponding chemical reaction. Basic laws of chemical kinetics can be used in the mathematical treatment.

**Homogeneous Reaction Kinetics.** Rate laws that describe bimolecular second-order chemical reactions can be treated as an analogue of the ion-exchange process. Although ion exchange involves a heterogeneous system, homogeneous chemical kinetics may be applied if one assumes that the exchanger phase is a fully dissolved reactant. The rate of ion exchange is now represented by the following rate equation:

\[
\frac{dC}{dt} = k_2(C_A - C)(C_B - C)
\]  

(13.1-18)

which is integrated to give

\[
t = \frac{1}{k_2(C_A - C_B)} \ln \frac{C_B(C_A - C)}{C_A(C_B - C)}
\]  

(13.1-19)

**FIGURE 13.1-11** Comparisons of forward and reverse exchange rates of two given counterions. The exchange is faster when the faster ion (H\(^+\) in H\(^+\)-Na\(^+\) exchange, Na\(^+\) in Na\(^+\)-Sr\(^{2+}\) exchange) is initially in the resin. Figure reproduced from F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962. Available from University Microfilms International, Ann Arbor, MI.

where $C_A$ and $C_B$ are the initial concentrations of counterions in the exchanger and external solution, respectively. The coefficient $k_2$ is the second-order rate constant and $C$ represents the external ionic concentration of the counterion originally in the solid phase at time $t$. Equation (13.1-19) can be arranged to a more appropriate form:

$$
t = \frac{1}{k_2(C_A - C_B)} \ln \left[ \frac{C_B(1 - X)}{C_A(C_B/C_A - X)} \right]
$$

Equation (13.1-20)

It must be noted that in this case there are no concentration gradients within the ion exchanger and no dependence on particle size.

**Heterogeneous Reaction Systems** The mathematical treatment is quite different if the exchanger is treated as a solid phase. The conceptual models are then similar to those developed for noncatalytic fluid-solid reactions. These kinetic models have been applied successfully to some ion-exchange processes.

The "shell progressive" or "shrinking-core" model assumes that a liquid reactant containing counterions $A$ is advancing into a spherical ion-exchange bead (unreacted core); see Fig. 13.1-13. The chemical reaction between the counterions and the exchanger sites progresses in shells or layers and produces a solid product layer that is often called the ash layer. Initially, the reaction takes place at the outer surface of the bead, and as the reaction proceeds, the interface between the reacted and unreacted core moves gradually into the interior of the bead, leaving behind an envelope of reacted material. During this process, a sharp inward-moving reaction boundary is formed, resulting in an unreacted core that shrinks with time.

The shell progressive mechanism can be applied to some ion-exchange processes. Any of the three subsequent steps, that is, film diffusion, ash-layer diffusion, and chemical reaction control, can be rate determining, depending on the prevailing conditions. The following relationships have been obtained for the indicated conditions.

**Liquid Film Diffusion Control**

$$
t = \frac{ar_0C_0}{3C_Ak_{ma}} X
$$

Equation (13.1-21)

**Ash-Layer Diffusion Control**

$$
t = \frac{ar_0C_0}{2D_lC_A} \left[ \frac{1}{2} - \frac{1}{2} (1 - X)^{2/3} - \frac{1}{3} X \right]
$$

Equation (13.1-22)
Chemical Reaction Control

\[ t = \frac{r_0}{C_{A0}K_s} [1 - (1 - X)^{1/3}] \]  

(13.1-23)

It must be noted that the above derivations are confined to cases involving a large excess of liquid reactant. However, other authors have achieved the above relationships with different conceptual approaches.\textsuperscript{25,26}

CONCLUSIONS

Conventional ion-exchange reactions often can be explained by homogeneous diffusional kinetics. For example, simple ion-exchange reactions encountered in water treatment, such as \( \text{Na}^+ - \text{H}^+ \) of \( \text{Cl}^- - \text{OH}^- \) exchange with polyelectrolyte gels or macroreticular resins, can be fitted by diffusional theory. However, more complex ion-exchange reactions involving complex ions or chelating ion-exchange materials are not satisfied so easily by these relationships. For example, the sorption and desorption or uranium or plutonium from acid solutions or the sorption of copper with an amino-diacectic acid exchanger are better fitted by chemical reaction-based models. Also, sorption into inorganic exchangers can be fitted better by chemical reaction rates. The field of mass transfer and ion-exchange kinetics is in a period of transition owing to the development of new resin products and new industrial applications.

13.2 APPLICATIONS OF ION EXCHANGE

13.2-1 Introduction

The industrial applications of ion exchange are extremely widespread and range from the purification of low-cost commodities such as water to the purification and treatment of high-cost pharmaceutical derivatives as well as precious metals such as gold and platinum. The largest single application, measured in terms of ion-exchange resin usage is water treatment, that is, water softening, water demineralization for high-pressure boilers, and dealkalization. Indeed, enormous advances in ion-exchange technology have occurred because of the relentless requirement for pure and ultrapure water. Other major industrial applications are the processing and decolorization of sugar solutions and the recovery of uranium from relatively low-grade mineral acid leach solutions.

Examples of major ion-exchange applications are listed in Table 13.2-1. The fields of water treatment, effluent treatment, and pollution control are predominant and there have been many recent advances. For example, the partial demineralization of brackish water using the Sirotherm process has been developed in Australia and this is probably one of the most innovative developments in recent years. \textsuperscript{1} Important applications in the fields of medicine, pharmacology, chemical processing, catalysis, and analytical techniques are also mentioned. The remainder of this section describes some important applications in detail.

13.2-2 Water Treatment

The removal of hardness from water by ion exchange has been carried out since the beginning of this century and represents the first major application of ion exchange in the water industry. Softening has been used extensively in domestic water supplies in the United States, although the practice is less common in the United Kingdom. In essence, the hardness present in water is removed by passing the water over a cation-exchange column in the sodium form. A typical reaction is as follows:

\[ 2\text{R}^-\text{Na}^+ + \text{Ca}^{2+} = \text{R}_2\text{Ca}^{2+} + 2\text{Na}^+ \]

Practically all modern cation-exchange materials are effective for this reaction. The equilibrium coefficient of the above reaction favors calcium sorption (or any other diveralent ion, such as magnesium) at low concentrations. At total hardness of about 500 ppm, the equilibrium diagram is similar to Fig. 13.1-2. Since the overall selectivity of the cation exchangers for most common diveralent ions decreases with concentration, the resin may be regenerated conveniently with concentrated sodium chloride solutions. Because of the change in selectivity with concentration, the efficiency of the cation-exchange softening process decreases with increasing salinity of the water. It is possible nevertheless to soften water up to concentrations of about 5000 ppm and ion exchange has even been suggested for the pretreatment of seawater prior to multistage flash evaporation provided that blowdown can be used as a regenerant.

The removal of salts and other ionic impurities from water by means of ion-exchange resins is based primarily on the exchange of cations (\( \text{Na}^+ \), \( \text{K}^+ \), \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), etc.) with the hydrogen form of a cation-exchange resin and the exchange of anions (\( \text{Cl}^- \), \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), etc.) with the hydroxide form of an anion-exchange resin. Usually, deionization of water is achieved by using a mixed bed of both cation- and anion-exchange resins and this is the classical method of producing ultrapure water for boiler feed, electronics,
and for more general use in the chemical and allied industries. A mixed bed uses a cation-exchange resin in the hydrogen form intimately mixed with an anion-exchange resin in the hydroxide form. The passage of a salt solution, for example, CaSO\(_4\), leads to the following irreversible reaction within the bed:

\[
2\text{H}^+ + 2\text{OH}^- + \text{Ca}^{2+} + \text{SO}_4^{2-} \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O}
\]

Under these conditions, the selectivity coefficient for impurities is infinite and therefore the efficiency of sorption is substantially better than if two columns of cation and anion resins are used in series. Regeneration requires separation of the resin prior to treatment with acid and alkali. It is quite difficult to obtain complete regeneration of each resin and therefore some cation and anion contamination of the treated water will occur. Natural groundwaters contain appreciable amounts of long-chain aliphatic acids, for example, humic and fulvic acid, and these are known to foul conventional strong base anion-exchange resins. In recent years, anion-exchange resin synthesis methods have been improved and more modern materials possess a structured matrix rather than a polyelectrolyte gel backbone. The advantage of "macroporous" and "isoporour" anion resins lies in the relative ease of regeneration of associated organic pollutants.

Ion-exchange is used widely in condensate polishing, and the application of mixed-bed ion-exchange columns in high-pressure boilers (conventional and nuclear) is now widespread. Sorption of impurities at concentrations of 50 ppb and less is customary and this can be achieved with considerable elegance. The

<table>
<thead>
<tr>
<th>Water Treatment</th>
<th>Reagent Purification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water softening</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>Dealkalization</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>Deionization</td>
<td>Phenol</td>
</tr>
<tr>
<td>Fluoride removal</td>
<td>Acrylates</td>
</tr>
<tr>
<td>Color removal</td>
<td>Inorganic Sol (Preparation)</td>
</tr>
<tr>
<td>Oxygen removal</td>
<td></td>
</tr>
<tr>
<td>Iron and manganese removal</td>
<td>SiO(_2)</td>
</tr>
<tr>
<td>Nitrate removal</td>
<td>Fe(OH)(_3)</td>
</tr>
<tr>
<td>Ammonia removal</td>
<td>Al(OH)(_3)</td>
</tr>
<tr>
<td>Sugars and Polyhydric Alcohols</td>
<td>Thoria</td>
</tr>
<tr>
<td>Purification of cane, corn, and beet sugars</td>
<td>Zirconia</td>
</tr>
<tr>
<td>Glycerine purification</td>
<td>Catalysis</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>Sucrose inversion</td>
</tr>
<tr>
<td>Biological Recovery and Purification</td>
<td>Esterification</td>
</tr>
<tr>
<td>Antibiotics</td>
<td>Condensation</td>
</tr>
<tr>
<td>Vitamins</td>
<td>Medicine</td>
</tr>
<tr>
<td>Amino acids</td>
<td>Antacids</td>
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<tr>
<td>Proteins</td>
<td>Sodium reduction</td>
</tr>
<tr>
<td>Enzymes</td>
<td>Taste masking</td>
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<td>Plasma</td>
<td>Sustained release</td>
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<td>Blood</td>
<td>Diagnostic</td>
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<td>Viruses</td>
<td>Tablet disintegration</td>
</tr>
<tr>
<td>Hydrometallurgy (Recovery and Purification)</td>
<td>pH control</td>
</tr>
<tr>
<td>Uranium</td>
<td>Potassium removal</td>
</tr>
<tr>
<td>Thorium</td>
<td>Skin treatment</td>
</tr>
<tr>
<td>Rare earths</td>
<td>Toxin removal</td>
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<td>Transition metals</td>
<td>Analysis</td>
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<td>Separation</td>
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<tr>
<td>Gold, silver, platinum</td>
<td>Concentration</td>
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<tr>
<td>Chromium</td>
<td>Purification</td>
</tr>
<tr>
<td>Solvent Purification</td>
<td>Alcohols</td>
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<td>Alcohols</td>
<td>Benzene</td>
</tr>
<tr>
<td>Benzene</td>
<td>Chlorinated hydrocarbons</td>
</tr>
<tr>
<td>Chlorinated hydrocarbons</td>
<td>Acetone</td>
</tr>
<tr>
<td>Acetone</td>
<td>Carbon tetrachloride</td>
</tr>
</tbody>
</table>

### Table 13.2-1: Examples of Major Ion-Exchange Applications

- Water Treatment
- Reagent Purification
- Water softening, Hydrochloric acid
- Dealkalization, Formaldehyde
- Deionization, Phenol
- Fluoride removal, Acrylates
- Color removal, Inorganic Sol (Preparation)
- Oxygen removal
- Iron and manganese removal, SiO\(_2\)
- Nitrate removal, Fe(OH)\(_3\)
- Ammonia removal, Al(OH)\(_3\)
- Sugars and Polyhydric Alcohols
- Purification of cane, corn, and beet sugars, Zirconia
- Glycerine purification, Catalysis
- Sorbitol, Sucrose inversion
- Biological Recovery and Purification
- Antibiotics, Esterification
- Vitamins, Condensation
- Amino acids, Medicine
- Proteins, Antacids
- Enzymes, Sodium reduction
- Plasma, Taste masking
- Blood, Sustained release
- Viruses, Diagnostic
- Hydrometallurgy (Recovery and Purification)
- Uranium, Tablet disintegration
- Thorium, pH control
- Rare earths, Potassium removal
- Transition metals, Skin treatment
- Transuranic elements, Toxin removal
- Gold, silver, platinum, Analysis
- Chromium, Separation
- Solvent Purification
- Alcohol, Concentration
- Benzene, Purification
- Chlorinated hydrocarbons, Alcohols
- Acetone, Benzene
- Carbon tetrachloride, Chlorinated hydrocarbons
use of powdered ion-exchange materials as precoats on conventional candle filters enables condensate treatment to be performed at high flow rate and high efficiency.\(^2\)

Ion-exchange resins also are used widely in effluent treatment and pollution control. Process strategy depends entirely on the waste to be treated, concentration of pollutants, flow rate, and so on, and applications are extremely diverse. The treatment of drainage water from mines, removal of ammonia and nitrates from groundwater, and the treatment of nuclear waste solutions are some typical examples of present-day processes. The efficiency of waste treatment is strongly dependent on the regenerant consumption and thus it is usual to attempt treatment processes with either weak acid or weak base exchangers. Success is likely if the process solutions are either acidic or alkaline. Ion-exchange resins can be used for the removal of noxious gases from gas streams. For example, H\(_2\)S and NH\(_3\) have been removed using macroteticular carboxylic acid resins and quaternary ammonium anion-exchange resins, respectively. The selective removal of these two impurities in hydrogen-cycle gas streams from oil refinery processes and their subsequent recovery by thermal elution using an inert gas are of particular value.

### 13.2-3 Sugar Processing

Practically all sugar that is milled and refined is produced from either sugar cane or sugar beet. The term sugar is used generally as a synonym for the crystalline sucrose derived from either cane or beet. However, other sugars are used in the food and beverage industry and the most widely used alternative is glucose (dextrose), a monosaccharide derived from corn starch.

The principal applications of ion exchange in the purification and treatment of sugar solutions, juices, and syrups are as follows:

1. Softening and demineralization of sugar juices to remove scale-forming elements prior to evaporation.
2. Decolorization using anion-exchange resins.
3. Catalytic inversion of sucrose to fructose and glucose.

In general, the largest field of application for ion exchange in sugar processing is in the sugar beet industry. Sugar syrup contains significant amounts of calcium and magnesium salts, and these can be exchanged with a conventional cation-exchange resin in the sodium form. This prevents scale formation in pipelines and evaporators. Deionization of the sugar syrups using both cation- and anion-exchange resins also reduces the molasses, and thus the sugar yield is increased. Ion-exchange resins are used for decolorizing sugar solutions on a wide scale. Generally, an ion-exchange resin column follows an alternative adsorption column, for example, granular carbon, powdered carbon or bone char. Rarely are resins used exclusively for decolorizing due to irreversible fouling, although in recent years, macroreticular and isotropic strong base anion-exchange resins have been used without prefilters. Resins have several advantages over granular carbonaceous adsorbents as decolorizing agents. High capacity for color retention, rapid equilibration, low rinse water requirement, and in situ regeneration are some of the important factors.

The inversion of sucrose can be catalyzed by a cation-exchange resin in the hydrogen form. The resin acts as a heterogeneous catalyst and its effectiveness depends on the chemical nature, degree of crosslinking, and particle size of the ion exchanger, reaction temperature, and contact time. A strong acid cation-exchange resin containing sulfonic acid groups in the hydrogen form and possessing a relatively low degree of crosslinking is a more effective catalyst than, for example, a weak carboxylic acid type exchanger.

### 13.2-4 Pharmaceutical and Medical Applications

Ion exchange is used extensively in the fields of pharmaceutical manufacture and medicine. Some of the more important applications are (1) processing of pharmaceuticals, (2) use of ion exchangers in pharmaceutical formulations, (3) use of ion exchangers and related materials in artificial organs, and (4) analytical uses in medicine.

The separation of antibiotics from fermentation broths is an interesting application for ion exchange. Streptomycin is a high-molecular-weight, water-soluble organic base containing two guanidine groups and a glucose amine group. The former are strongly basic and the latter is a weakly basic group. Therefore, streptomycin is susceptible to ion exchange with cation-exchange materials and can be sorbed from solution under neutral pH conditions:

$$2 \text{R} \cdot \text{COO}^- \cdot \text{Na}^+ + (\text{streptomycin})^{2+} \rightarrow (\text{R} \cdot \text{COO})_2 (\text{streptomycin}) + 2\text{Na}^+$$

It is customary to use a weak acid ion-exchange resin in the sodium form (e.g., a polyacrylic carboxylic resin) and regenerate with hydrochloric acid. Neomycin, a related antibiotic, is also recovered with a carboxylic acid ion exchanger. However, since the basic amine groups in neomycin are considerably weaker
than the guanidine groups in streptomycin, it is possible to elute the neomycin with ammonia solutions at pH values high enough to suppress completely the ionization of the neomycin.

Vitamin B\textsubscript{12} is produced by microbial fermentation and can also be separated from the broth using a carboxylic acid exchanger. It is adsorbed and eluted by a different mechanism, since vitamin B\textsubscript{12} is essentially a nonionic compound. It does sorb onto the acid form of the ion-exchange resin at pH 3, and after treatment with HCl to remove impurities the vitamin B\textsubscript{12} product is eluted with an acid-acetone-water solution. Various polymeric adsorbents, that is, macroreticular structured hydrocarbons containing no ionogenic functional groups, have also been found to be effective for the separation of vitamin B\textsubscript{12} from fermentation broths.

In medicine, ion-exchange materials have found use as preparative media and for various clinical treatments. In the collection of blood, citrate and dextrose solutions are added to prevent coagulation. However, these substances do not influence long-term stability. If the blood is passed over the sodium form of a cation-exchange resin to remove calcium and magnesium, then coagulation can be prevented. Treatment of blood to remove intentional or accidental overdoses of drugs can be effected by hemodialysis. Traditional hemodialysis treatment involves the use of selective membranes, although ion-exchange resins offer the advantage of rapid kinetics and high surface area. It is obvious that the treatment of blood over ion-exchange resins and polymeric adsorbents (hemoperfusion) has considerable advantages. Medical applications are too extensive to be reviewed here and exhaustive detail can be found elsewhere.

### 13.2.5 Hydrometallurgy

A list of metals that have been recovered and purified commercially by ion exchange is given in Table 13.2.1. In some cases the scale of operation is relatively small, for example, the rare earth elements, the transuranic elements, and the platinum group metals, although the intrinsic value of metal recovered is usually extremely high. Ion exchange is particularly suitable for high-cost, low-throughput purification processes. Separately, the recovery of trace amounts of metal from effluent and waste streams accounts for many applications, for example, chromium from spent metal plating solutions and copper and zinc from wastes arising in the rayon and synthetic fiber industry. However, the largest single application in hydrometallurgy is the recovery and concentration of uranium from naturally occurring mineral ore bodies. At the present time there is a recession in uranium demand and worldwide production is at a low level. About 20,000 tonnes/year of uranium concentrate are produced as yellow cake (ammonium diuranate) in the Western World. Principal producers are the United States, Canada, and South Africa. The most cost-effective recovery processes involve the separation of uranium as a by-product of other minerals or metals. Typical examples are the recovery of by-product uranium from gold and the recovery of uranium during the refining of wet process phosphoric acid. Fixed-bed ion-exchange plants were installed to meet the early demand for uranium in the nuclear industry, although more recently liquid extraction using liquid ion-exchange reagents has found acceptance in some mining locations. Uranium plants are typically capable of processing 100-1000 m\textsuperscript{3}/h of pregnant solution and it is the uranium industry that has been responsible for many innovations that have occurred in the development of ion-exchange technology in recent years. The foremost equipment development is continuous countercurrent ion exchange in multistage fluidized beds. This novel technology has been advanced most vigorously in South Africa and several large plants have already been erected.

Ion exchange is particularly advantageous for the treatment of low-grade uranium ore deposits. A typical example of one such application is the Rossing uranium mine in Namibia. Here, the mineral contains about 0.035 wt.\% U\textsubscript{3}O\textsubscript{8} on average. The Rossing flowsheet is given in Fig. 13.2-1 and incorporates both ion exchange and liquid extraction and employs the considerable advantages of both techniques. Continuous ion exchange is used to upgrade the low concentration feed (0.15 g/L U\textsubscript{3}O\textsubscript{8}) and to produce an eluate feed of constant composition containing 3-4 g/L U\textsubscript{3}O\textsubscript{8}. This eluate is the feed solution to a liquid-liquid extraction plant that performs the effective separation of uranium from trace impurities. The final strip solution contains about 10 g/L U\textsubscript{3}O\textsubscript{8} and after precipitation and calcination produces a product containing approximately 97\% U\textsubscript{3}O\textsubscript{8} by weight.

The combination of ion exchange and liquid extraction is not new in the uranium industry and many early plants in the United States have used this technique. Merritt\textsuperscript{5} has written a comprehensive review of the extractive metallurgy of uranium with particular reference to North America. The Eluex plants operated in the United States were essentially similar to the Rossing plant described above, but the ion-exchange equipment was far less elegant.

Continuous ion exchange also facilitates the separation of metals in high-concentration aqueous solutions. A process was developed in South Africa to recover spent hydrochloric acid from pickle liquors. The Metsep process used three continuous countercurrent fluidized-bed columns to separate zinc and iron (Fe\textsuperscript{2+}) in hydrochloric acid prior to recovery in a pyrohydrolysis reactor.\textsuperscript{6} The flowsheet for the process is given in Figs. 13.2-2 and 13.2-3. Separation is possible with feed streams containing about 20 g/L zinc, 120 g/L iron, and 30 g/L hydrochloric acid. A special weak base anion-exchange resin was used with a specific gravity of about 1.2 g/cm\textsuperscript{3}. This was vital, since the feed solution density was about 1.1 g/cm\textsuperscript{3}. Selective separation of the chloride complexes of Zn\textsuperscript{2+} and Fe\textsuperscript{3+} is relatively easy since the latter does not
FIGURE 13.2-1 Simplified flowsheet of the uranium recovery circuit at the Rossing Uranium Mine in Namibia.
form stable anion complexes at low acid concentration. The removal of zinc from the acid stream is achieved by ion exchange and this can be recovered subsequently by liquid extraction using a cationic extractant (di-2-ethyl hexyl phosphoric acid), thereby converting zinc chloride to zinc sulfate as a fertilizer additive.

It has become common practice to recover gold from low-concentration side-streams with activated carbon. Conventional multistage fluidized-bed columns are used for the sorption process, although the regeneration step is more difficult and requires high-temperature elution and thermal reactivation of the adsorber. Recently, there has been renewed interest in the application of ion-exchange resins for gold recovery from cyanide liquors. Resins are less susceptible to poisoning by calcium or organic impurities and possess higher sorption capacity and selectivity for gold. Pilot-plant work has been performed at MINTEK (Council for Mineral Technology, Randburg, South Africa) using a continuous countercurrent
fluidized-bed column to recover gold from clarified leach liquors with a feed concentration of about 2 ppm and to yield a barren solution containing less than 2 ppb gold. This is achieved with both weak and strong base resins, although the former will probably prove easier to elute in practice and thus provide a cheaper recovery process.

13.3 EQUIPMENT FOR ION EXCHANGE

13.3-1 Principles of Equipment Design

The main variable in the design of an ion-exchange plant is the configuration of the resin while it reacts with the aqueous feed solution. In the past, only fixed beds were considered for most ion-exchange processes, whereas modern technology allows the designer to choose between fixed beds, moving packed beds, fluidized beds, and stirred tanks. The amount of suspended solids in the feed solution determines which of these possibilities are feasible. Packed beds of resin act as efficient filters and rapidly block if suspended solids are present, whereas fluidized beds can handle up to several hundred parts per million of fine solids. Stirred tanks can handle slurries containing up to 20 wt. % solids provided that no particles are larger than the resin beads.

The size of the plant is a further factor that may lead the designer to consider other options besides the conventional fixed bed. A very small plant may be comprised of overdesigned fixed beds to simplify operation and require no instrumentation. On the other hand, the use of continuous ion exchange may significantly reduce the capital cost of a large plant.

The above mentioned factors, combined with the fact that high flow rates obtainable in packed beds give faster reaction rates, have led to the development of present-day plants. In general, clear dilute solutions are treated in fixed or moving packed beds while turbid effluents and ore slurries are handled in fluidized beds or stirred tanks.

PLANT DESIGN PROCEDURE

The basis of ion-exchange plant design is the superficial velocity of liquid feed passing through the vessels, sometimes termed the "empty-bed velocity". Once the type of resin bed—either fixed, fluidized, or stirred—has been selected, a design velocity from the feasible range for that type must be assumed.

The cross-sectional area of the vessels is calculated directly from the specified total throughput and the superficial velocity. If this is larger than current practice, then parallel streams must be considered.

The pressure drop over the resin bed may be an important variable in fixed beds while in other techniques it is not relevant in comparison with pressure losses incurred in pumping liquid through the pipework. The superficial velocity is one of the main variables in the pressure-drop and bed-expansion calculations.

The change in concentration of the solution passing through a resin bed fluidized at the velocity assumed above can be calculated from correlations of reaction rate or mass transfer coefficient. The number of beds and bed depth can be derived.

The type of resin pumping or transfer system to be used is a major decision in ion exchange since resin is both fragile and expensive. Other auxiliary systems such as methods of detecting resin levels and flows, materials of construction and control systems must also be selected.

13.3-2 Flow Through Fixed Beds of Resin

The size of resin beads and the pressure drop generally used in industrial applications result in laminar flow conditions in fixed beds of resin. The characteristic of such flow is that the pressure drop varies linearly with flow rate. Actual measurements of pressure drop over beds of resin include the effect of flow distribution manifolds which may show quadratic dependence of pressure drop against flow rate.

The two most important factors influencing the pressure drop over a bed of resin are the size distribution of the beads and the voidage of the bed. Modern resins are spherical in shape due to their method of manufacture, but older resins were sometimes granular. Many manufacturers publish data on pressure drop as a function of flow rate for their resins at stated water temperatures. These data can also be obtained readily in laboratory experiments or estimated from the particle size distribution of resin and the appropriate solution properties.

The pressure drop for laminar flow through a fixed bed of particles can be predicted by the Carman-Kozeny equation as expressed in the following form:

\[
\frac{\Delta P}{L} = k_r \frac{S^2 \mu (1 - \varepsilon)^2}{\varepsilon^3} U
\]  

(13.3-1)

where \( U \) is the superficial or empty-bed velocity and is equal to the volumetric flow rate divided by the cross-sectional area without resin present, and \( L \) is the depth of the bed. The fraction of bed volume
TABLE 13.3-1 Typical Data for Pressure Drop over Packed Beds of Resin

<table>
<thead>
<tr>
<th>Type of Resin</th>
<th>Amberlite IR-120 Cation</th>
<th>Amberlite IRA-420 Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure drop e $\Delta P/L$ (kPa/m)</td>
<td>22.62</td>
<td>5.66</td>
</tr>
<tr>
<td>Flow rate e $U$ (m/h)</td>
<td>20.78</td>
<td>24.45</td>
</tr>
<tr>
<td>Water temperature (°C)</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>Water viscosity $\mu$ (Pa·s)</td>
<td>$1.5 \times 10^{-3}$</td>
<td>$0.29 \times 10^{-3}$</td>
</tr>
<tr>
<td>Constant f $K_2$ (kPa·h/m²)</td>
<td>1.09</td>
<td>0.232</td>
</tr>
</tbody>
</table>

eResin manufacturers usually give their data as graphs of pressure drop (psi/ft) against flow rate (gal/min·ft²) for various temperatures. The conversion factors are: (psi/ft) × 22.62 = (kPa/m): kilopascal per meter of bed depth (gal/min·ft²) × 2.445 = (m/h): superficial bed velocity in meters per hour

fPressure drop is correlated by $\Delta P/L = K_2 U$.

The constant $K_2$ may be estimated at another temperature by multiplication of the ratio of water viscosities at the two temperatures.

occupied by voids between resin particles is given by $\varepsilon$ and $S$ is the specific surface area of the resin beads and is equal to the total surface of the beads divided by their volume. The dynamic viscosity of the liquid, $\mu$, will change with the temperature and nature of the dissolved solids. The constant $K_1$ is equal to $S$.

Equation (13.3-1) reduces to the very simple form below for any given bed of resin and liquid viscosity:

$$\frac{\Delta P}{L} = K_2 U$$

(13.3-2)

Therefore, a single measurement of pressure drop $\Delta P$ for a bed of depth $L$ with a flow rate $U$ of liquid having a known viscosity enables one to calculate the appropriate value of $K_2$. The value of $K_2$ can equally well be read off the graphs or tables of pressure drop given by manufacturers, as shown in Table 13.3-1.

13.3-3 Flow Through Fluidized Beds of Resin

Upward flow of sufficient velocity causes a bed of resin to expand and fluidize unless it is restrained at the upper surface. The resin particles move freely relative to one another during fluidization since they are no longer in contact, and the upper level expands as the liquid velocity increases. Fine particles are carried upward out of the bed. The pressure drop over the fluidized resin is marginally larger than the static head of liquid since the density of resin is only slightly greater than water.

Even flow distribution across the complete cross-section of the bed is the most important aspect of design. This can be achieved by flow distribution using pipe manifolds with carefully sized orifices. A plate with perforations or bubble caps to distribute flow can also be used to support a bed.

The expansion of a fluidized bed of resin is an important variable in determining how much resin will be held in a vessel. This property of a resin is measured very readily in a simple laboratory experiment. For uniform bead size, correlation of data can be done with the Richardson-Zaki equation expressed in the form

$$\frac{U}{U_t} = \varepsilon^n$$

(13.3-3)

where $U_t$ is the terminal settling velocity of typical resin beads and $n$ is a constant with values between 2.8 and 3.5 for resin beads. The same data can be expressed more conveniently in the form of the ratio of bed depth at one velocity to that at another velocity. The effect of viscosity is very significant since a change of 1°C will change the viscosity by about 3% and noticeably affect the resin inventory of a stage.

Resin manufacturers often express the fluidization properties of their resins in terms of the percentage expansion of the bed related to its packed depth. This expansion cannot be calculated directly from the above equation since a range of bead sizes is present. Typical data are shown in Fig. 13.3-1, taken from a Rohm and Haas pamphlet. These curves can be correlated by an equation giving the expansion as a function of the 1.5 power of the flow rate. An equation of almost identical form can be derived from the Richardson-Zaki equation by expressing the expansion in terms of the void fraction and using appropriate values for $n$. 
13.3-4 Flow of Resin Slurries

The flow of resin slurries is an extremely important aspect of the design of ion-exchange plants since all movement of resin both in continuous and batch plants is done using some form of hydraulic transport. Resin beads are also comparatively fragile and attrition during transfer operations must be avoided. Resin is crushed by being trapped in closing valves, by passing through positive displacement pumps, by passing through regions of high shear such as the impellers of centrifugal pumps or high-speed agitators, and by water hammer from valves opening or closing too rapidly.

The two common methods of moving resin are by using airlifts between open tanks and by displacing resin hydraulically in dense-phase flow between closed vessels. In both cases the pipeline velocities are relatively low and resin is not broken. An early type of continuous ion-exchange plant, the Dorr Hydrosoftener, used liquid jet ejectors to move resin slurries but no data are available on the effect of this operation on resin life. The Wemco recessed impeller pump is used on a very large ion-exchange plant recovering uranium to the satisfaction of the operators. Resin particles do not pass through the impeller.

The variables in the use of hydraulic displacement systems for resin transfer are shown in Fig. 13.3-2. It is obvious that the pump handles only clear liquid which is forced into the top of a pressurized tank to move the settled resin bed as a dense slurry out of a pipe near the base of the tank. Systematic studies done on this phenomenon showed that the slurry moved along the pipe as closely packed as in the settled bed itself. The voidage of the delivered slurry was proved to be constant. This technique can be used for accurate control of resin flow rates since the flow rate of slurry is a constant fraction of the flow rate of displacing liquid.

Hydraulic displacement is used in the Higgins technique, which includes flow through vessels up to 1 m in diameter. Typical line velocities are of the order of 1 m/s. The pressure drop for clean resin and clear water is marginally greater than that for water at the same flow rate but accumulation of tramp rubbish such as wood chips or fine sediment can form blockages at low points in pipelines. Plant practice is to install centrifugal pumps with twice the static head requirements of the delivery line to drive the displacement liquid. Pipelines of lengths up to several hundred meters have been used to carry resins. The installation of pipe tees with valves at low points in the line facilitates clearing out blockages. An important aspect of the flowsheet shown in Fig. 13.3-2 is that resin slurry passes through a number of valves that
open to allow passage. However, control interlocks must prevent these valves from closing until the line has been flushed clear of resin slurry.

Airlifts are simple devices for pumping liquids or slurries through low heads and have been used in hydraulics for many generations. Their throughput is sensitive to the submergence and to the flow rate of air. The output pulsates and cannot be controlled accurately. The air injection pipe must end downward-facing to avoid settlement and must always have a small bleed of air to keep the end open. The formation of bubbles around the air injection point causes severe local abrasion of the pipe in slurry systems which must be reinforced with abrasion-resistant lining.

The performance of an airlift can be derived from hydrostatic principles in terms of the submergence of the air injector below the liquid level in the feed tank \( h_a \), the delivery height above this level \( h_r \), and the pressure and density of air at ambient atmospheric pressure \( P_a \) and \( \rho_a \). The atmospheric pressure is expressed as an equivalent height \( h_a \) of a liquid of density \( \rho \). The following equation gives an estimate of the mass of air required per unit mass of liquid (or slurry) ignoring frictional losses in the system:

\[
\frac{\text{kg air}}{\text{kg liq}} = \frac{p\rho_g}{P_a \ln \left( \frac{h_r + h_a}{h_a} \right)}
\]  

(13.3-4)

13.3-5 Fixed-Bed Equipment

The simplest type of fixed bed is shown in Fig. 13.3-3 which is illustrative of a modern large plant for water purification. The vessel is of a conventional dished-end pressure construction with supports and an access manhole. Construction materials for the vessel are usually mild steel with a lining of rubber or plastic. Stainless steel is sometimes used and smaller vessels are made of reinforced plastic. The depth of settled resin bed is seldom more than about 1 m but the vessel must allow freeboard of about another meter above the upper surface of resin for expansion during fluidization to clean rubbish out of the bed.

The normal direction of flow in such a bed is downward so that the resin acts as a packed bed without any relative movement of particles. The bed of resin can be supported by various means. The simplest is to fill the vessel to cover the lower dished end with coarse sand in which distributor manifold pipes are buried. This can create problems because the volume of liquid trapped in the voids of the sand can cause cross-contamination between cycles of operation. An internal false floor with distributor cups of plastic screwed into place on a grid pattern overcomes this problem. Such construction is more expensive and has to be supported structurally to take the entire pressure thrust on the bed during flow. Some plants use an elaborate manifold of distributor pipes laid against the lower dished end which is itself filled with resin.

Regeneration of resin takes place in the same vessel and can be done downward using the same distributors. However, it is more efficient to regenerate the resin using flow countercurrent to that in normal service. This involves feeding eluant upward through the bed while avoiding fluidizing the resin. Various methods of preventing fluidization include the use of collector pipe manifolds just below the upper surface and placing rubber bellows either above the bed or submerged in the resin to prevent movement during the upward flow of liquid.

The upper surface of the resin bed acts as an efficient filter for any fine particles present in the feed during normal service. It is therefore necessary to backwash or fluidize the resin with clear water to remove these solids to waste at the end of a service cycle. The flow distributor at the base and a collecting manifold at the top of the vessel are used in this operation.

A common type of process in water purification involves the use of a mixed bed of cation- and anion-exchange resins to deionize water, often following separate cation- and anion-exchange beds. The use of such mixed-bed columns enables very low levels of impurities to be attained. Regeneration of such columns
can be done by making use of the different densities of anion- and cation-exchange resins. After fluidizing the bed for some time with water, the anion-exchange resin forms a distinct layer on top of the cation-exchange resin. The two layers are allowed to settle and are regenerated in sequence. First, alkaline solution is fed downward from a distributor just above the top of the bed and removed by a distributor near the interface of the two layers. Second, a short rinse removes most of the alkaline solution; this is followed by acidic regenerant being fed at the interface and taken off below the bed. Third, the bed is remixed with air agitation after the residual acid has been rinsed out.

At least two fixed beds are required to give continuous service of purified water but three are normally used for recovery processes. This ensures that barren effluent is always below the limit and that each bed is fully loaded with product before regeneration takes place. Automatic control of a fixed-bed plant regulates the times of the various cycles and controls feed rates at predetermined values. For fully automatic control of cycles, up to six automatic shut-off valves per vessel are required.

13.3-6 Moving-Bed Equipment

One class of semicontinuous ion-exchange plant is based on moving a packed bed in counterflow to the normal service flow of solution. It is always necessary to shut off normal flow to achieve bed movement. Hydraulic displacement is used to move the bed with either a piston or pump driving the displacement water. A number of different designs have been suggested in the literature but only two have achieved commercial success, that is, the Higgins technique and a design suggested by Porter and developed and marketed by Asahi Chemical Company of Japan.
The Higgins loop, developed by I. R. Higgins and Roberts at Oak Ridge in 1954, is illustrated in Fig. 13.3-4 which shows a vertical sketch of a typical plant incorporating an extraction or treating section through which the main liquid feed passes in downflow. This section is connected with a large-diameter pipework as a continuous loop around which resin circulates in increments during resin transfer operations. There is therefore a net flow of resin from extraction to backwash to regeneration to rinse and again to extraction. During normal service resin flow exists as a packed bed in the extraction and regeneration sections which are isolated from one another by valves A, B, C, and D. During resin transfer, external flows of liquid are valved off and the main loop valves A, C, and D are opened to allow resin to be moved around incrementally by the action of displaced water. Valves A, C, and D are closed and the slug of resin is backwashed before opening valve B to let it settle into the pulse section.

The basic idea behind the Asahi design was suggested by R. Porter in 1956. Since then the concept has been developed by the Asahi Chemical Company in Japan to handle rayon processing effluent by recovering copper and the system has also been installed worldwide for standard water treatment operations.

The extraction or treating section is comprised of a packed bed with upward flow which pins the bed to the top of the vessel during normal operation, as shown in Fig. 13.3-5. At the end of the service cycle, the feed flow is valved off and the bed falls to the bottom of the vessel, drawing a supply of regenerated resin through a nonreturn valve into the top of the vessel. When normal feed flow is resumed, that part of the bed above the feed distributor is pinned again to the top of the vessel while that below is displaced downward and out of the vessel to the top of a backwash column where it is fluidized to remove fines. Resin settling to the base of the backwash column is fed to a regeneration vessel which operates in a manner similar to the extraction column.

Normal service flow in both these designs takes place through a packed bed of resin which is shallower than conventional fixed beds. Very high flow rates are therefore possible, allowing use of vessels smaller than conventional designs.

### 13.3.7 Fluidized-Bed Equipment

Fluidized beds of resin have always been used for backwashing in ion-exchange practice. The use of fluidized beds as a means of contacting fluids with particles has been applied since the 1940s and 1950s.
Fluidization of particles with density only slightly greater than the liquid does not create the large bubbles characteristic of fluidization with gases; however, other fluidization phenomena such as movement of particles and expansion of the bed take place.

A number of designs using fluidization to promote effective contact between liquid and resin particles have appeared in the literature and have been applied on laboratory or pilot-plant scale. The main problem common to all such ideas is that of transferring resin countercurrent to liquid flow in a manner such that both resin flow rate and resin inventory in each stage are controlled. The advantage of fluidization lies in the fact that the bed does not filter out fine particles but allows them to flow out with the liquid product. Also, evolved gas does not accumulate in a fluidized bed. The other advantage of fluidized over packed beds is negligible pressure drop, but this can be negated by the need to use much lower liquid velocities leading to a larger plant.

The first design based on fluidized beds to contact resin with solution was suggested by the Dorr Company as the Dorrco softener. This used a column comprising a series of trays on which fluidized beds of resin were supported. Liquid flowed continuously upward through the beds while resin was drawn from each bed and fed to the one below using a liquid ejector driven by product water. Transfers of resin from extraction to regeneration columns were also carried out with liquid ejectors.

Another principle of operation has been described by Cloete and Streat and George et al. of the U.S. Bureau of Mines working independently. This technique relies on periodic cutoff of liquid flow through a series of fluidized beds which allows the beds to settle onto trays. The entire content of the column then flows by gravity or is pumped in a reverse direction for a distance of a few hundred millimeters: this operation causes a part of each bed to be transferred simultaneously to the bed below. Upward normal service flow is then resumed and the series of fluidized beds is re-established. Various related ideas have been published: for example, the suggestion by McNeill et al. of using slow pulsations to cause resin flow, and the idea of stopping liquid flow to allow reverse resin flow by sedimentation as suggested by Levin in a confidential report in 1955 at the National Institute for Metallurgy in Johannesburg, South Africa. The Cloete-Streat principle is illustrated in Fig. 13.3-6 which gives the basic flowsheet for a plant recovering uranium from a dilute leach solution. Liquid feed containing about 200 ppm uranium flows upward through
The 4.85 m diameter column at a flow rate of 332 m$^3$/h for a forward flow period of 4.5 h. At the end of this period the feed is shut off for a settling period of 5 min and then reversed for 5 min, during which time the top level falls by 400 mm and about 6.3 m$^3$ of resin is transferred downward between each of the 12 stages. Forward flow is then re-established and the slug of 6.3 m$^3$ of resin in the conical base of the column is displaced out to the regeneration column by the transfer pump. Thus, the average flow rates are 320 m$^3$/h of leach solution and 1.35 m$^3$/h of resin. Each tray contains a fluidized bed of 9.25 m$^3$ resin expanded to twice its settled level by the flow rate of feed at a superficial velocity of 18 m/h. Flow is distributed by 1945 holes of 12 mm diameter in the tray, giving an open area of 1.2% of the tray area.

The first commercial plant of this type was constructed in Germiston, South Africa for separating zinc and iron from spent hydrochloric acid pickle liquor. Subsequently, much larger units have been built in South Africa for recovering uranium at the following mines: Randfontein Estates, Blyvooruitzicht, Chemwes, Harmony, and Vaal Reefs. The same type of equipment based on a 3 m diameter column has been recovering traces of gold from 528 m$^3$/h of effluent mine water at Welkom gold mine in South Africa using activated charcoal instead of ion-exchange resin. The feed contains 30 ppb gold and about 5 kg of gold per month is recovered.

The studies on the basic principles of engineering and process design were done at Imperial College in England; subsequent demonstration on pilot plants was done by industrial companies in England, by the U.S. Bureau of Mines at Salt Lake City, and by the National Institute for Metallurgy (now MINTEK) in South Africa.

A further variation on the use of fluidized beds to contact resin with solution is that adopted by Himsley. This is illustrated in Fig. 13.3-7 showing an elevation sketch of a typical plant. Liquid feed flows continuously upward through a series of stages in a column. All except one of the stages contain fluidized beds of resin. Batches of resin are transferred sequentially downward by selectively reversing the flow from stage to stage. The bed selected for transfer is effectively collapsed by causing liquid flow reversal, which then displaces the resin downward into the vacant stage below. The batch of resin in the base of the column is transferred out to the top of the regeneration section by the same method. The design of the trays is unusual since there is only one distributor with the shape indicated in Fig. 13.3-7. The successive stage-by-stage flow reversals require a manifold of valves around the transfer pump whose throughput must be larger than that of the feed pump. Screens or cups at the top of each stage prevent resin being sucked through the transfer pump.

A design was developed by Porter specifically for very large flow rates and outdoor construction based on a cascade of open-topped tanks. Solution was pumped from stage to stage in an early design which was based on rectangular concrete tanks. Modern plants use circular rubber-lined steel tanks and elevate each tank slightly so that gravity flow can take place. Liquid flow is continuous, entering the tanks at a low level through pipe distributor manifolds and overflowing into weirs at the top and finally passing over
screens to collect traces of entrained resin. Resin is transferred in batches from one stage to the next one upstream, which is vacant, by the use of airlifts which draw from near the base of a stage and recycle a slurry of resin and solution into the stage upstream. Fully loaded resin is taken in a batch from the feed stage. A typical stage is illustrated in Fig. 13.3-8.

The largest version of this design was installed at the Rossing Uranium plant in South West Africa (Namibia). The stages are open rectangular tanks made of rubber-lined concrete 3.8 m high with a plan size of 6.2 m. There are four parallel streams handling a total of 3600 m$^3$/h through a cascade of five stages giving a superficial velocity of 23 m/h. Resin inventory per stage is 26 m$^3$, and the total resin inventory in use in the process is about 914 m$^3$. This is the largest uranium plant in the world and probably one of the largest ion-exchange operations of any type. 2

13.3-8 Stirred-Tank Equipment

The idea of agitating a batch of resin with solution in a beaker to cause reaction is well known for ion-exchange laboratory experiments and is used to study the kinetics of ion-exchange reactions. The use of this concept as a plant technique is limited by the following factors:

1. Agitation must be mild to avoid attrition of resin.
2. A number of tanks in series must be used to effect high conversions.
3. The concentration of resin in suspension is low.

The main application for this technique is in a system where the liquid feed contains fine solids that would block a fixed bed or tend to float resin out of a fluidized bed owing to the high density or viscosity of the feed. The process is used for the recovery of uranium from ore deposits containing a high proportion of clay minerals. Such ores produce a slimy pulp that is expensive to filter and thus there is an incentive to extract dissolved metal directly from the leach pulp. A number of plants were constructed in the 1950s in the United States on this principle—known as resin-in-pulp (RIP) operations. The simplest possible method of agitation, namely, to inject air into the base of the mixing tanks, was used in the early plants. 20

One of the examples of such a plant is illustrated in Fig. 13.3-9. Air lifts take a slurry of the contents of the mixer to a vibrating screen above the next stage upstream and the airlifts are operated continuously to provide a flow of resin that is countercurrent to the flow of pulp. Very similar equipment is used for the recovery of gold from leached pulps using activated-charcoal granules in the size range 2–4 mm. This is now the preferred technology for gold recovery in new plants in the United States, Canada, Australia, and South Africa. 21

The flowsheet for gold plants consists of equipment very similar to that used in RIP operations but the equipment differs mainly in the process used for elution of gold under pressure and regeneration of charcoal in a kiln at 600–700°C.

The main problems in design and operation of RIP plants are associated with the screens which are necessary to separate resin (or activated-carbon granules) from the pulp overflowing from each tank and finally to the effluent. These not only block readily with tramp rubbish but they are broken by careless operators and abrade resin if vibrated. Extensive pilot-plant work has been done by Carman 22 and Read 23 to develop a plant with resin floating in the pulp in efforts to develop a screenless RIP recovery process for both uranium and gold.

![Figure 13.3-8 Porter fluidized bed.](image)

![Figure 13.3-9 Stirred-tank resin-in-pulp process: similar technology is used for adsorption with activated carbon.](image)
This far-sighted work was further extended with the concept of an inverted fluidized bed of floating resin in the leach reactors themselves, the resin-in-leach or RELIX process. These ideas have not yet proved successful enough for full-scale plant deployment, so development has concentrated on obtaining high throughput with minimal attrition through screens.

One screen design that has been widely applied in South African ion-exchange plants is the DSM (Dutch State Mines) design based on triangular-sectioned wire mesh. These units require low head, are static, and are strongly built. An alternative screen concept has been suggested by Laxen et al. with somewhat similar proposals from Shoemaker. In both these designs the overflow screen is submerged below the surface of the pulp and pulp is caused to flow tangentially across the screen cloth. Laxen and coworkers achieve this effect by bubbling air across the screen, with a weir behind the screen so that a pulsating flow is caused by the curtain of air bubbles; in Shoemaker’s design the surges of pulp resulting from the agitation of the tank cause the same effects. Pulp flow velocities through the screen at a superficial rate of 120 m/h can be achieved in practice with the design of Laxen and coworkers. The use of slow pulsing to clear screens in an RIP plant is described by Arden et al.

The use of air for agitation in pulp systems is very well known in the mineral processing industry. The energy used for mixing can be reduced by the use of mechanical agitation, which is generally more efficient, but at the cost of increased capital. An illustration of the type of plant used in the recovery of gold from leach pulp is given in Fig. 13.3-10 taken from Oldshue. This plant uses draft tube agitators with provision for restarting from shutdown. The slots cut into the draft tube follow a suggestion from Australia. The agitator impeller itself is mounted in the top part of the tube so that it remains above the level of settled pulp.

The design of mechanical agitators is based on predicting the energy required just to suspend all solids off the bottom of the tank. Correlations for predicting this value exist for most types of agitator but cannot be relied on since they often give contradictory results, as pointed out in a recent book by Oldshue. Successful plants have therefore been based on extensive pilot-scale testwork. The effect of the agitator on the attrition rate of resin or carbon must also be considered.

### 13.4 Recent Developments in Ion Exchange

#### 13.4.1 Selective Ion-Exchange Materials

Conventional ion-exchange resins have been discussed in detail in Section 13.1-1 and these materials must represent in excess of 90% of all ion-exchange resin used in traditional applications such as water treatment, sugar processing, and purification of pharmaceuticals. However, there is a growing interest in the development of selective polymers for application in a wide range of specialty operations ranging from the recovery of trace uranium in seawater to the separation and purification of the platinum group metals in hydrometallurgy. Research and development is most exhaustive in hydrometallurgy, especially in the field of precious metals recovery, platinum group metals separation, and base metal recovery. It is interesting to note that separations in the first-row transition metals have been achieved with selective liquid extractants consisting of nitrogen- and oxygen-containing ligands, for example, hydroxyoximes. However, these ele-
mments will form weak anionic complexes, especially in chloride media, and this is also true of the second- and third-row transition metals; such characteristics make it possible to carry out separations among the precious metals, that is, gold, and silver, and the platinum group metals. There is a considerable economic incentive to develop solid-phase ion-exchange processes for the recovery of precious or alternatively toxic metals, such as mercury, from low-grade dilute solutions. Therefore, the literature concerning the development of selective ion-exchange polymers is expansive and cannot be fully discussed here. Recently, Warshawsky\(^1\) presented a comprehensive review article that discusses the trends in the synthesis of selective chelating polymers containing oxygen, nitrogen, phosphorus, and sulfur ligands.

**CHELATING RESINS WITH NITROGEN-CONTAINING PENDANT GROUPS**

Tertiary and quaternary polymeric amines are produced in large quantities and are effective for some specialty separation processes. The most notable is the recovery of uranyl sulfate or uranyl carbonate from acid or alkali leach solutions. Some selectivity is also found among the first-row transition-metal chloride complexes. The incorporation of a chelating ethylenediamine group—\((\text{NH}-\text{CH}_2-\text{C}=\text{NH})_n\)—increases markedly the stability of the polymeric ligand-metal complex. For example, crosslinked chloromethylated styrene divinylbenzene copolymers containing di-, tri-, or tetrathylene imine groups show high affinity for Au(III), Hg(II), and Cu(II). Jones and Grinstead\(^2\) have prepared more complex ethylenediamine derivatives and suggested their use for Fe(II) and Cu(II) separation.

**CHELATING RESINS WITH NITROGEN- AND OXYGEN-CONTAINING PENDANT GROUPS**

Amino-diacetic acid ion-exchange resins have been available for commercial use since the early 1960s. Resins of this type are useful for the separation of the first-row transition metals, although the selectivity is very dependent on pH. More recently, attempts have been made to synthesize more elegant polymer supports and ligands. Many workers have proposed chelating ligands based on poly(vinylimidazole) or poly(vinylimidazole) dicarboxylate groups.\(^3\) It has been suggested that the loading rates for base metals, Cu(II), Ni(II), and Co(II) are enhanced with this type of structural modification.

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Hydroxylamine polymers have also been explored extensively. Vernon and Eccles\(^4\) have prepared several hydroxoxime-type polymers and recommended their use for copper separation from iron at low pH value. Amidoxime-type functional groups are found to chelate uranium at low concentrations in seawater and to offer a potential solution to the problem of separating heavy metals from acidic solutions.

**CHELATING RESINS WITH SULFUR-CONTAINING PENDANT GROUPS**

Sulfur ligands are known to complex or precipitate most of the heavy transition metals. Early developments in this field arose out of pollution control and analytical applications. Typical polymer derivatives are based on macroreticular polymethacrylate beads containing pendant mercapto groups. Such resins are reactive for Ag(I), Hg(II), and Au(III). Thioglycolate resins have been developed and used for the laboratory separation of Ag(I), Bi(III), Sn(IV), Sb(III), Hg(II), Cd(II), Pb(II), and U(VI). Similar resins are dithiocarbamates and their derivatives. Recently, the platinum group metals (PGMs) have been separated in chloride media using a combined ion-exchange and liquid-liquid extraction process.\(^5\) The adsorption step involves a weak base isothiouronium group capable of extracting the chlorocomplexes of the PGMs. Industrial exploitation of this technique has occurred already.

**CHELATING RESINS WITH PHOSPHORUS-CONTAINING PENDANT GROUPS**

Phosphoric acid, esters, and phosphine oxides are very effective extractants for uranium, gold, and the first-row transition metals. One commercially available chelating resin contains aminophosphonic groups attached to a crosslinked polystyrene matrix. Although developed for the decalcification of brines, this resin shows high selectivity for the separation of trace amounts of uranium in wet process phosphoric acid.\(^6\) A general review of phosphorus containing polymers is given by Efendiev.\(^7\)

**CHELATING RESINS WITH OXYGEN-CONTAINING PENDANT GROUPS AND MACROCYCLIC STRUCTURES**

Phenolic ion exchangers derived from a phenol–formaldehyde condensation reaction appeared in the first generation of ion-exchange polymers. More recently, styrene–divinylbenzene copolymers incorporating azo-substituted cresol and salicylic acid, catechol, hydroquinone, and benzoquinone have been described. The quinone-type polymers selectively sorb Hg(III) and the catechol resins sorb Cr(VI).

The complexion of metal salts by neutral macrocyclic ligands is well known.\(^8\) Polymeric crown ethers are an expanding group of functional ion exchangers capable of selective sorption of alkaline metals such as K, Cs, Na, and Li. The crown ether may be derived from a conventional chloromethylated hydrocarbon backbone which is converted to a polybenzylated catechol. Crown ethers are highly reversible and possess rapid reaction kinetics, thus allowing for an interesting thermal elution procedure whereby a species is sorbed at 20°C and eluted at 60°C.

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\(^1\) Warshawsky, \(^2\) Jones and Grinstead, \(^3\) Many workers have proposed chelating ligands based on poly(vinylimidazole) or poly(vinylimidazole) dicarboxylate groups, \(^4\) Vernon and Eccles, \(^5\) Hydroxylamine polymers have also been explored extensively, \(^6\) Vernon and Eccles, \(^7\) Efendiev, \(^8\) Hydroxylamine polymers have also been explored extensively.
SOLVENT-IMPREGNATED ION-EXCHANGE RESINS

The idea of developing solvent impregnated ion-exchange resins was to combine the selectivity and specificity of conventional liquid extractants with the advantages of a discrete polymer support material, thus tailoring adsorbents for a specific separation process, usually in the field of hydrometallurgy. Although it is now possible to functionalize polymers as outlined above, it is still difficult to overcome some steric problems and thus it is interesting to consider the potential use of liquid extractants immobilized within a polymer matrix. This can be achieved by physical impregnation of the reagent onto a polymeric or other porous support without chemical binding of any sort. Alternatively, copolymerization of a monomer (e.g., styrene) crosslinking agent (divinylbenzene) in the presence of a reagent (e.g., tri-n-butyl phosphate) will produce a polymer “encapsulated” product. Typical of these products are the Levextrel resins developed by Bayer AG.9 An exhaustive review of extraction with solvent-impregnated resins has been published by Warshawsky.10 Selective ion-exchange resins have been prepared by either route and applied to the recovery of uranium from radioactive waste, treatment of aqueous wastes containing nonferrous metals, and certain specialty applications. The principal difficulty in the use of these materials is the slow diffusion of the reagent out of the polymer matrix. Although this can be overcome by reimpregnation, the possible environmental implications and cost would make large-scale commercial use unlikely.

13.4-2 New Types of Ion-Exchange Materials

Ion-exchange materials are normally synthesized in granular form and in most cases spherical particles of a precise size distribution are supplied. This facilitates their use in packed columns or in sophisticated continuous countercurrent contactors. For most applications, the particle surface area and therefore the reaction rate are quite adequate and most processes can be performed efficiently and economically. In some applications, for example, the treatment of unclarified liquors, the sorption of slow-diffusing species, and the use of fluidized ion-exchange particles—it is desirable to modify the properties of the ion-exchange materials. Increasing particle size or the relative density will improve the hydraulics in a fluidized bed, whereas a reduction in particle size might improve kinetics for a very slow-diffusing species. Alternatively, ion-exchange fibers and woven fabrics have been prepared for these and similar applications. Sorption of a solute onto fibers is inherently rapid due to the large surface area of reactive sites that can be exposed at any one instant in time. However, supporting the fibers or fabric and contacting the ion exchanger with the liquid phase calls for novel engineering design. The usual idea involves the use of an endless belt and this has been tried for the recovery of copper from a dilute aqueous solution using phosphorylated cotton toweling.11 A similar idea involved the polymerization of a quaternary ammonium resin onto cotton cloth and this was used to remove chromate ions from a dilute aqueous solution.12 Separately, Vernon and Shah13 have synthesized a poly(amidoxime)-poly(hydroxamic acid) fiber and shown that this will sorb significant amounts of uranium from seawater. It is suggested that this fiber could be produced as an endless belt and thus sustain continuous retrieval of uranium by continuous countercurrent operation.

Electrodialysis requires selective ion-exchange membranes. In the simplest form these are synthetic ion exchangers in the form of sheet or film. Heterogeneous membranes are produced from finely milled ion-exchange particles and formed into sheets with an inert binder. Interpolymeric membranes are made from a homogeneous mixture of two polymer solutions, one forming the polyelectrolyte and the other a film-forming material, for example, polystyrene sulfonic acid and polyacrylonitrile. Homogeneous membranes can be produced which contain ionic groups in the film-forming matrix, for example, methacrylic acid. Ion-exchange membranes can carry either cationic or anionic functional groups and can exclude mobile ions of similar charge by the high concentration of fixed groups in the membrane. Thus, for example, a flow of electric current through a cation membrane is carried entirely by the flux of mobile cations. Ion-exchange membranes are capable of selective ion transport. More information on electrodialysis can be found in Chapter 21.

Specialist ion-exchange resins have been developed in recent years in an attempt to overcome typical problems encountered in ion-exchange process technology. Blesing et al.14 have described the synthesis of novel magnetic microresins suitable for application in desalination, water treatment, and hydrometallurgy. These resins are usually manufactured in the form of beads, typically in the size range of 100-500 µm and containing about 10-15% by volume of a magnetic material such as iron oxide as an inert core. Reactive sites are produced by shell graft polymerization of organic monomers onto the inert core. Since the discrete particles are small, they react faster than conventional ion-exchange resins, but they can be used successfully in fluidized-bed systems at economic flow rates because the microbeads agglomerate magnetically into large flocs when agitation ceases. These flocs have hydraulic properties similar to conventional ion exchangers. The recent status of continuous ion exchange using magnetic microresins has been presented by Swintont al.15

A slightly different approach to the preparation of composite materials has been tried in an attempt to synthesize high-density ion-exchange materials possessing rapid kinetics and thus suitable for fluidized-bed application in hydrometallurgy, especially for uranium recovery from unclarified solutions. Usually, an inert porous core material such as alumina or silica gel is impregnated with a reactive monomer, for example, a substituted vinyl pyridine, and crosslinking agent such as divinylbenzene. The resultant im-
pregnate is reacted to polymerize the organic reagent within the pores of the inorganic matrix. Very-high-density sorbents have been synthesized using a stannic oxide core, although the ion-exchange capacity is relatively low and the material only moderately stable over the entire pH range. An interesting idea is the impregnation of liquid extractants such as Alamine 336 (a long-chain tertiary amine) into an inert porous support such as crushed fireclay or firebrick. It was claimed that materials of this kind were selective for uranium sorption but suffered from instability to the leaching of the reagents and poor hydraulic behavior. None of these or similar ideas have yet proved to be commercially viable.

NOTATION

\( a \)  
stoichiometric coefficient

\( a_i \)  
ionic activity of species \( i \)

\( C \)  
concentration of ions in solution phase

\( \bar{C} \)  
resin-phase concentration of ions

\( C_i \)  
solution-phase concentration of species \( i \)

\( \bar{C}_i \)  
resin-phase concentration of species \( i \)

\( d_p \)  
diameter of resin beads

\( D \)  
diffusion coefficient in solution phase

\( \bar{D} \)  
diffusion coefficient in resin phase

\( \bar{D}_e \)  
effective diffusivity coefficient

\( F \)  
Faraday constant

\( g \)  
gravitational acceleration

\( h \)  
height of liquid vessel

\( J_i \)  
flux of species \( i \) in solution

\( k_2 \)  
second-order reaction rate constant

\( k_s \)  
rate constant based on surface area

\( k_{mi} \)  
mass transfer coefficient of species \( i \) in the liquid film

\( K_a \)  
thermodynamic equilibrium constant [Eq. (13.1-3)]

\( K \)  
selectivity coefficient [Eq. (13.1-3)]

\( L \)  
depth of bed

\( m_i \)  
distribution coefficient

\( \Delta P \)  
pressure drop across bed

\( P_a \)  
 atmospheric pressure

\( R \)  
gas constant

\( r_0 \)  
radius of ion-exchange bead

\( S \)  
surface area of resin beads per unit volume of beads

\( T \)  
temperature

\( U \)  
superficial velocity of liquid through empty bed

\( U_t \)  
terminal settling velocity of particle through liquid

\( t \)  
time

\( V \)  
solution volume

\( \bar{V} \)  
resin volume

\( X \)  
extent of resin conversion

\( x \)  
equivalent ionic fraction in solution

\( y \)  
equivalent ionic fraction in resin phase

\( z_i \)  
valency of species \( i \)

Greek Letters

\( \alpha \)  
separation factor

\( \phi \)  
electrical potential gradient

\( \delta \)  
liquid film thickness

\( \gamma_i \)  
activity coefficient of species \( i \)

\( \epsilon \)  
fraction of voids in bed
\( \mu \)  dynamic viscosity of liquid
\( \rho \)  density of liquid
\( \rho_s \)  absolute density of resin beads

Subscripts

A  ionic component or species
B  ionic component or species
\( i \)  refers to either species A or B in a binary ion-exchange system

Note: Overbars refer to species in resin phase.

REFERENCES

Section 13.1


Section 13.2


**Section 13.3**


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**Section 13.4**


