

Chapter 12

Liquid–Liquid and Solid–Liquid Extraction

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INTRODUCTION

Extraction is a term that is used for any operation in which a constituent of a liquid or a solid is transferred to another liquid (the *solvent*). The term *liquid–liquid extraction* describes the processes in which both phases in the mass transfer process are liquids. The term *solid–liquid extraction* is restricted to those situations in which a solid phase is present and includes those operations frequently referred to as *leaching*, *lixiviation*, and *washing*. These terms are used interchangeably below.

Extraction involves the following two steps: contact of the *solvent* with the liquid or solid to be treated so as to transfer the soluble component (*solute*) to the solvent, and separation or washing of the resulting solution. The complete process may also include a separate recovery procedure involving the solute and solvent; this is normally accomplished by another operation such as evaporation, distillation, or stripping. Thus, the streams leaving the extraction system usually undergo a series of further operations before the finished product is obtained; either one or both solutions may contain the desired material. In addition to the recovery of the desired product or products, recovery of the solvent for recycling is also often an important consideration.

In practice, the manner and the equipment in which these operations are carried out is based on the difference in physical states. Because solids are more difficult to handle and do not readily lend themselves to continuous processing, leaching is commonly accomplished in a batch-wise fashion by agitating the crude mixture with the leaching agent and then separating the residual insolubles from the resultant solution. Liquid–liquid extraction may also be carried out in a batch operation. The ease of moving liquids, however, makes liquid extraction more amenable to continuous flow in various types of columns and/or stages.

For design calculations or analysis of operations, one can apply either data on the equilibrium attained between the phases or the rate of mass transfer between

phases described in earlier chapters. The usual design approach is often through the theoretical-stage concept, as discussed in the absorption and distillation chapters, and also discussed below.

Two sections follow. The first is concerned with liquid–liquid extraction and the second with solid–liquid extraction. Equilibrium considerations, equipment and simple design procedures/predicative methods, although different for both processes, are included for both topics. The notation employed is that typically employed in industry.

LIQUID–LIQUID EXTRACTION

Liquid–liquid extraction is used for the removal and recovery of primarily organic solutes from aqueous and nonaqueous streams. Concentrations of solute in these streams range from either a few hundred parts per million to several mole/mass percent. Most organic solutes may be removed by this process. Extraction has been specifically used in removal and recovery of phenols, oils, and acetic acid from aqueous streams, and in removing and recovering freons and chlorinated hydrocarbons from organic streams.

The Extraction Process

Treybal⁽¹⁾ has described the liquid–liquid extraction process in the following manner. If an aqueous solution of acetic acid is agitated with a liquid such as ethyl acetate, some of the acid but relatively little water will enter the ester phase. Since the densities of the aqueous and ester layers are different at equilibrium, they will settle on cessation of agitation and may be decanted from each other. Since the ratio of acid to water in the ester layer is now different from that in the original solution and also different from that in the residual water solution, a certain degree of separation has occurred. This is an example of stage-wise contact and it may be carried out either in a batch or continuous fashion. The residual water may be repeatedly extracted with more ester to additionally reduce the acid content. As will be discussed shortly, one may arrange a countercurrent cascade of stages to accomplish the separation. Another possibility is to use some sort of countercurrent or crosscurrent continuous-contact device where discrete stages are not involved.

More complicated processes may use two solvents to separate the components of a feed. For example, a mixture of para- and ortho-nitrobenzoic acids may be separated by distributing them between the insoluble liquids chloroform and water. The chloroform preferentially dissolves the para isomer and the water the ortho isomer. This is called *double-solvent* or *fractional extraction*.⁽¹⁾

The liquid–liquid extraction described above is a process for separating a solute from a solution based on the combination of the concentration and solubility driving force between two immiscible liquid phases. Thus, liquid extraction effectively involves the transfer of solute from one liquid phase into a second immiscible

liquid phase. The simplest example involves the transfer of one component from a binary mixture into a second immiscible phase such as is the case for the extraction of an impurity from wastewater into an organic solvent. Liquid extraction is usually selected when distillation or stripping is impractical or too costly (e.g., the relative volatility for the two components falls between 1.0 and 1.2).

Recovery of the solute and solvent from the product stream is often carried out by stripping or distillation. The recovered solute may be either treated, reused, resold, or disposed of. Capital investment in this type of process primarily depends on the particular feed stream to be processed.

The solution whose components are to be separated is the *feed* to the process. The feed is composed of a *diluent* and *solute*. The liquid contacting the feed for purposes of extraction is referred to as the *solvent*. If the solvent consists primarily of one substance (aside from small amounts of residual feed material that may be present in a recycled or recovered solvent), it is called a *single solvent*. A solvent consisting of a solution of one or more substances chosen to provide special properties is a *mixed solvent*. The solvent-lean, residual feed solution, with one or more constituents removed by extraction, is referred to as the *raffinate*. The solvent-rich solution containing the extracted solute(s) is the *extract*.

The degree of separation that arises because of the aforementioned solubility difference of the solute in the two phases may be obtained by providing multiple-stage countercurrent contacting and subsequent separation of the phases, similar to a distillation operation. In distillation, large density differences between the gas–liquid phases are sufficient to permit adequate dispersion of one fluid in the other as each phase moves through the column. However, in liquid extraction, the density differences are significantly smaller and mechanical agitation of the liquids is frequently employed at each stage to increase contact and to increase the mass transfer rates.

The minimum requirement of a liquid extraction unit is to provide intimate contact between two relatively immiscible liquids for the purposes of mass transfer of constituents from one liquid phase to the other, followed by the aforementioned physical separation of the two immiscible liquids. Any device or combination of devices that accomplishes this is defined in this text as a *stage*. If the effluent liquids are in equilibrium, so that no further change in concentration would have occurred within them after longer contact time, the stage is considered a *theoretical* or *ideal stage*. The approach to equilibrium attained is a measure of the *stage efficiency*. Thus, a theoretical or equilibrium stage provides a mechanism by which two immiscible phases intimately mix until equilibrium concentrations are reached and then physically separated into clear layers. A multi-stage cascade is a group of stages usually arranged in a countercurrent flow between stages for the purpose of enhancing the extent of separation.

Equipment

There are two major categories of equipment for liquid extraction. The first is *single-stage* units, which provide one stage of contact in a single device or combination of

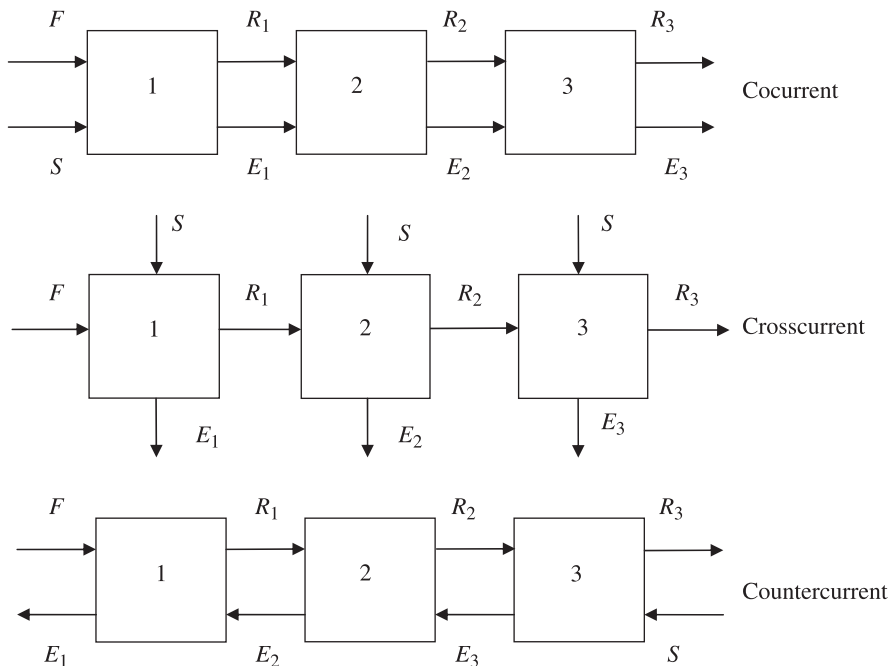


Figure 12.1 Multistage extractors.

devices. In such equipment, the liquids are mixed, extraction occurs, and the insoluble liquids are allowed to separate as a result of their density differences. Several separate stages may be used in an application. Second, there are *multistage* devices, where many stages may be incorporated into a single unit. This type is normally employed in practice.

There are also two categories of operation: batch or continuous. In addition to *cocurrent* flow (rarely employed) provided in Figure 12.1 for a three-stage system, *crosscurrent* extraction is a series of stages in which the raffinate from one extraction stage is contacted with additional fresh solvent in a subsequent stage. *Crosscurrent* extraction is usually not economically appealing for large commercial processes because of the high solvent usage and low solute concentration in the extract. Figure 12.1 also illustrates *countercurrent* extraction in which the extraction solvent enters a stage at the opposite end from where the feed enters and the two phases pass each other countercurrently. A photograph of a bench scale version of this unit (Unit Operations Laboratory—Manhattan College) is provided in Figure 12.2.

It can be shown that multistage *cocurrent* operation only increases the residence time and therefore will not increase the separation above that obtained in a single stage, provided equilibrium is established in a single stage. *Crosscurrent* contact, in which fresh solvent is added at each stage, will increase the separation beyond that obtainable in a single stage. However, it can also be shown that the degree of

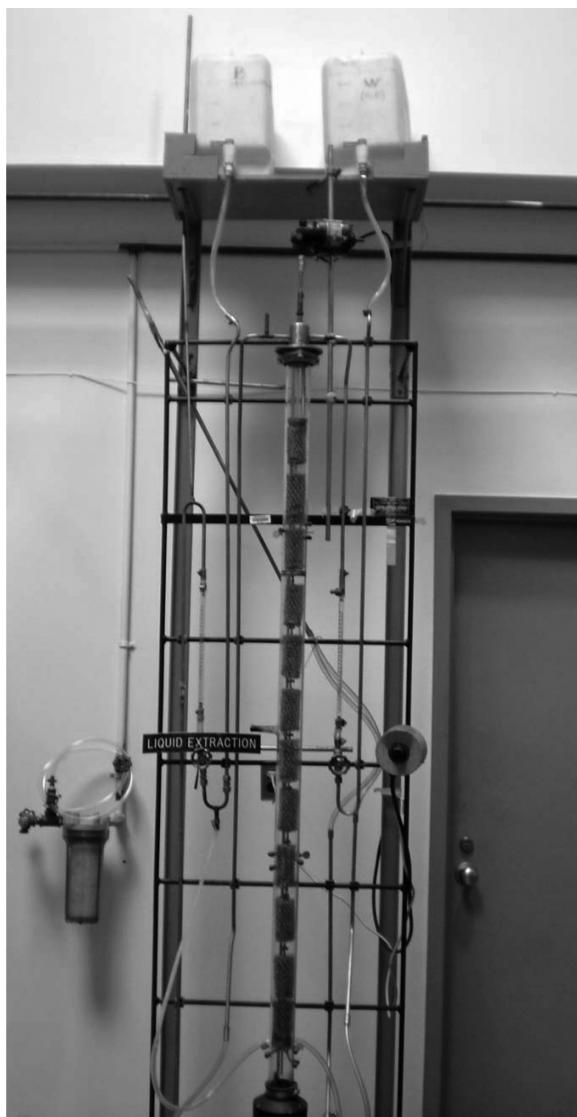


Figure 12.2 Liquid extraction experiment (Manhattan College).

separation enhancement is not as great as can be obtained by *countercurrent* operation with a given amount of solvent (see Chapter 8).

The maximum separation that can be achieved between two solutes in a single equilibrium stage of the two phases is governed by equilibrium factors and the relative amounts of the two phases used, i.e., the *phase ratio*. A combination of the overall and component mass balances with the equilibrium data allows the compositions of

the phases at equilibrium to be computed. If the separation achieved is inadequate, it can be increased by either changing the phase ratio or by the addition of more contacting stages.

Solvent Selection

There are several principles that can be used as a guide when choosing a solvent for a liquid extraction process. These are typically conflicting and certainly no single substance would ordinarily possess every desirable characteristic for a process. Compromises are inevitable, and in what follows, an attempt will be made to indicate the relative importance of the various factors that must be considered. Selectivity receives preferential treatment but 10 other factors are also reviewed.

Selectivity is the first and most important property ordinarily considered in deciding on the applicability of a solvent; selectivity refers to the ability of a solvent to extract one component of a solution in preference to another. The most desirable solvent from a solubility aspect would be one that would dissolve a maximum of one component and a minimum of the other. As in the case of vapor–liquid equilibrium, numerical data that quantify selectivity can be measured or determined. The numerical values of the selectivity, normally designated as β , are available in literature.⁽¹⁾

Note that there are numerous possible selectivities for a three component system. For example, it could be defined as $[(x_{CB}/x_{AB})/(x_{CA}/x_{AA})]$ where x_{CB} is the concentration of solute C in the B rich solution, x_{AB} is the concentration of the third component in B , x_{CA} is the concentration of C in the A rich solution, while x_{AA} is the concentration of A in the A rich solution. Like relative volatility, β has been shown to be approximately constant for a few systems. However, in most cases, β varies widely with concentrations.

The importance of “good” selectivity for extraction processes parallels that of relative volatility for distillation. Practical processes require that β exceeds unity and the more so the better. Selectivities close to unity will result in a large extraction unit, a large number of extraction stages, and in general, a more costly investment and operation. As one might suppose, if $\beta = 1$, the separation is impossible.

Furthermore, in all liquid–liquid extraction processes, it is necessary to remove the extracting solvent from the two products resulting from the separation. This is important not only to avoid contamination of the products with the solvent but also to permit reuse of the solvent in order to reduce the cost of operation. In practically every instance, the recovery process is ultimately carried out with fractional distillation, and the relative volatility of the solvent and substance to be separated must be high in order to ensure that distillation (see Chapter 9 for more details) may be carried out inexpensively. In most extraction processes, the quantity of solvent used is greater than that of the desired products. If in the recovery by distillation, the solvent is the more volatile component, large quantities will need to be vaporized and the process will be costly. Therefore, it is preferable in such cases that the solvent be the less volatile component; distillation will involve vaporization of the desired products that are

present in smaller amounts. If the solute in the solution is nonvolatile, then distillation will become difficult and it may be necessary to recover the solvent by evaporation.

A difference in densities of the contacted phases is also essential and should be as great as possible. Not only is the rate of disengaging of the immiscible layers thereby enhanced but also the capacity of the contacting equipment is increased. It is insufficient to examine merely the relative density of the solution to be extracted and the pure extracting solvent since after mixing the mutual solubility of the two will alter the densities. For continuous contacting equipment, it is important to be certain that a satisfactory density difference for the contacted phases exists throughout the process.

The interfacial tension between immiscible phases, which must be settled or disengaged, should preferably be high for continuous processes. However, too high an interfacial tension may lead to difficulties in achieving adequate dispersion of one liquid into the other, while too low a value may lead to the formation of stable emulsions.

Chemical reactions between the solvent and components of the solution yielding products extraneous to the process are naturally undesirable. Polymerization, condensation, or decomposition of the solvent at any temperature achieved during the process, including the solvent recovery stage, is not desirable.

The extracting solvent and solution to be extracted should be highly immiscible. Solvent recovery in highly insoluble systems is simpler and, for a given distribution coefficient, the selectivity will be greater.

In order to reduce the cost of equipment, the solvent should cause no severe corrosion difficulties with common materials of equipment construction. Expensive alloys and other unusual materials should not be required.

Low power requirements for pumping, high heat-transfer rates, high rates of extraction, and general ease of handling are all corollaries of low viscosity. Hence, this is a desirable property of solvents employed in extraction processes.

The vapor pressure of the solvent should be sufficiently low so that storage and extraction operations are possible at atmospheric or only moderately high pressures. This may conflict with the requirement of high relative volatility with the solution being extracted and a compromise may be necessary. Low flammability is, of course, desirable for safety reasons (see Part III, Chapter 22).

Regarding toxicity, highly poisonous materials are difficult to handle industrially. Unless elaborate plant safety devices are planned with frequent medical inspection of personnel, the more toxic substances must be avoided (once again, see Part III, Chapter 22).

Low cost and ready availability in adequate quantities usually parallel each other and are of course desirable solvent attributes. While it is true that solvents are recovered from product solutions, make-up solvent to replace inevitable process losses must be expected.

Of all the desirable properties described, favorable selectivity, recoverability, interfacial tension, density and chemical reactivity are essential for the process to be carried out. The remaining properties, while not always important from a technical standpoint, must be given consideration in good engineering work and in cost estimation of a process.

Equilibrium

Liquid–liquid extraction processes can involve three components (ternary system). In order to better understand the equilibria associated with a three component system, it is first necessary to become acquainted with the standard method of representing such systems. Two-dimensional equilibrium diagrams for ternary systems can best be plotted on an equilateral triangle, each of whose apexes represents 100% concentration of each component (see Fig. 12.3). A series of grid lines representing fractional concentrations of a particular component is drawn parallel to the base opposite that apex which represents the component. Thus, every point on the diagram corresponds to a certain percentage composition of each of the three components. It is important to note that an apex signifies a single component; any point on one of the sides describes a binary system. There are various types/classifications of these three component systems. Only one that exhibits a single lion's share with extraction of pure components will be reviewed in the presentation to follow.

Consider the case where acetic acid is the solute in water and *n*-butanol is used as an “extractant” to extract the acetic acid out of the water phase. This three-component system consists of three liquid components that exhibit partial miscibility. For this system, acetic acid and *n*-butanol form one pair of partially miscible liquids. Their partial miscibility may be interpreted by means of a ternary diagram seen in Figure 12.4. For simplicity, each of the components is denoted by a letter corresponding to its name as shown.⁽²⁾

At a given temperature and pressure, water and *n*-butanol are partially soluble in each other. But, if the mutual solubility limits are exceeded, two layers are formed: one consists of a solution of *n*-butanol in water, the other of water in *n*-butanol. Suppose acetic acid, which is completely miscible with both *n*-butanol and water, is now added to the system. Obviously, acetic acid will distribute itself between the two liquid phases. The two layers will disappear to form a solution if sufficient acetic acid is introduced. Points *a* and *b* designate the compositions of two liquid layers resulting from mixing water and *n*-butanol in some arbitrary overall proportion such as *c*. The addition of acetic acid to the solution will change the compositions of the two layers from *a* and *b* to *a*₁ to *b*₁, respectively. The line *a*₁*b*₁ that passes through *c*₁ connects the compositions of the two layers in equilibrium and is called a *tie line*. Different tie lines can be constructed through the continuous addition of *C* until a single solution is obtained. Complete miscibility occurs at the *plait point*,

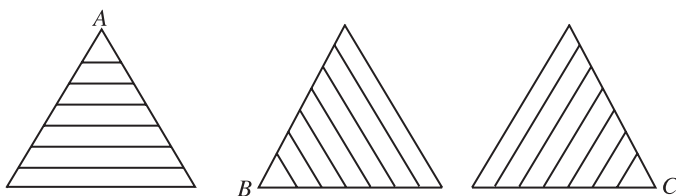


Figure 12.3 Triangular concentration diagrams for a ternary system (*A*, *B*, *C*).

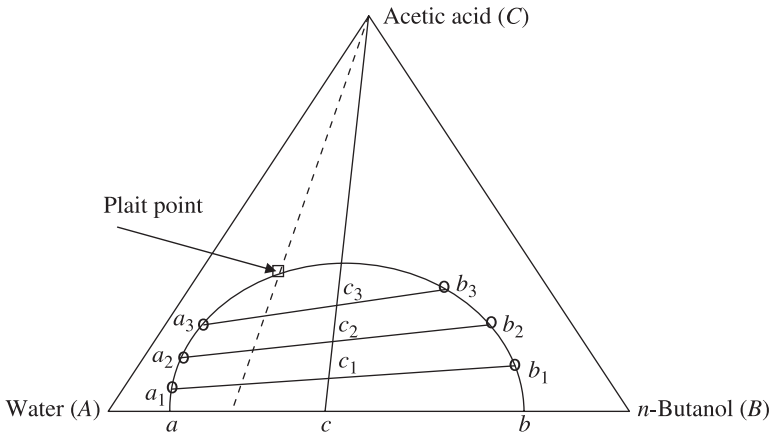


Figure 12.4 Ternary equilibrium diagram with tie lines.

at which condition the two solutions coalesce into a single liquid phase of constant composition, i.e., the tie lines converge on the *plait point*.⁽²⁾

In the equilateral triangle shown in Figure 12.4, the sum of the perpendicular distances from any point to the three sides of the triangle is equal to the altitude of the triangle; this makes the plot particularly useful for correlating ternary data. As described above, solutions that are *A*-rich yield the left-hand portion of the bimodal curve up to the plait point and those that are *B*-rich are found in the right-hand portion. And, as noted, the tie lines are straight lines that connect the concentrations of phases in equilibrium, and the two solutions or phases become identical at the plait point when the tie lines converge to a single point. Once again, there is obviously an infinite number of tie lines within the bimodal curve. A similar graph can be drawn on right triangle coordinates.

ILLUSTRATIVE EXAMPLE 12.1

Using the equilibrium data provided in Tables 12.1 and 12.2, plot the equilibrium curve for the *n*-butanol–acetic acid–water ternary system at 30°C.

SOLUTION: The plotting of the data is left as an exercise for the reader, but the bottom portion of the curve for an equilateral triangle plot is provided in Figure 12.5. Note that the plait point is usually represented in the literature by “+” in a circle and the (equilibrium) tie line points by “○”. Plotting the tie lines is left as an exercise for the reader as well. ■

Graphical Procedures

The calculation of the number of equilibrium stages required to achieve a given degree of separation by countercurrent contact requires simultaneous solution of the mass balance equations with equilibrium data from stage to stage. For purposes of calculation,

Table 12.1 Equilibrium Data for *n*-Butanol–Acetic Acid–Water System at 30°C

<i>n</i> -Butanol (wt%)	Acetic acid (wt%)	Water (wt%)
7.30	0.00	92.70
7.13	3.15	90.00
8.04	5.46	86.50
14.25	12.75	73.00
15.20	13.10	71.70
30.90	15.10	54.00
49.35	14.45	36.50
56.46	12.14	31.70
69.82	6.02	24.46
79.50	0.00	20.50
Estimated plait point		
27.50	14.90	57.50

Table 12.2 Tie Line Data for *n*-Butanol–Acetic Acid–Water System at 30°C

Acetic acid in <i>n</i> -butanol layer (wt%)	Acetic acid in water layer (wt%)
1.42	0.88
2.50	1.82
3.68	2.63
4.90	3.64
6.04	4.37
8.49	6.35
10.70	8.20
15.00	12.00

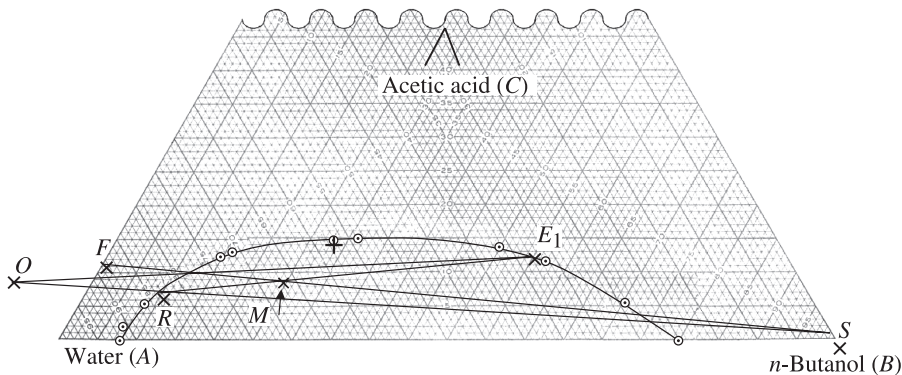


Figure 12.5 Ternary equilibrium curve for *n*-butanol, acetic acid, and water.

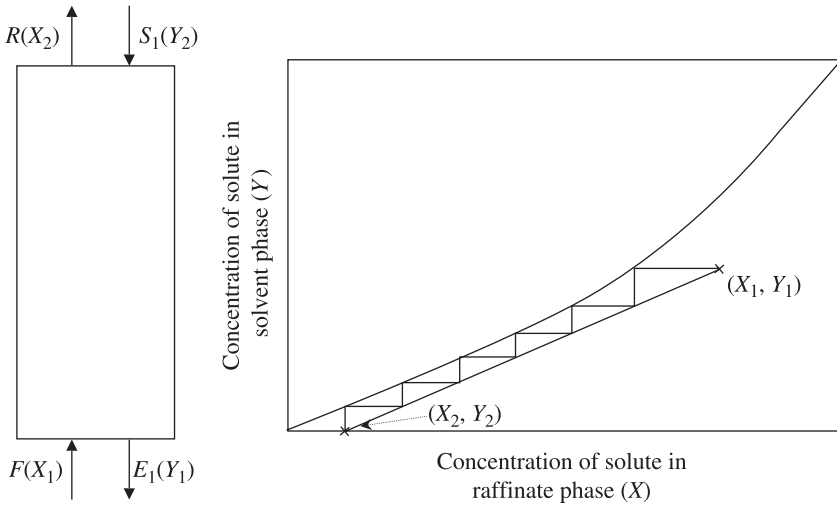


Figure 12.6 Graphical construction for calculating the number of theoretical stages (immiscible phases).

it is important to distinguish two classes of system: those in which the two phases are completely immiscible or in which the relative miscibility of the two phases is constant and independent of the solute concentration, and those in which the relative miscibility of the two phases varies with the solute concentrations.

In the former case above, the solute-free flow rates of the two phases may be assumed constant throughout a multistage countercurrent extractor (the actual phase flow rates will vary as a result of solute transfer, but not the flow rate of the solvent). The number of equilibrium stages required to effect a given separation can then be obtained conveniently from an X – Y (solute free basis) plot by stepping off stages between the operating and equilibrium lines, just as in a gas absorption or distillation problem. The constant flow rates result in a straight operating line. The technique is illustrated in Figure 12.6 for a simple system.

The situation for partially miscible systems is different. Consider the acetic acid, n -butanol, water system discussed above. The acidic nature and polarity of the acetic acid makes it soluble in water while its hydrophobic part makes it soluble in n -butanol. Thus, the two phases have different solubility traits and this leads to a separation of substances according to the solubility of each chemical in other substances. It is for this reason that liquid–liquid extraction is used as a substitute for distillation and evaporation, particularly when the substances to be separated are chemically different. Extraction utilizes differences in the solubilities of the components rather than differences in their volatilities. Since solubility depends on chemical properties, extraction exploits chemical differences instead of vapor–pressure differences.

ILLUSTRATIVE EXAMPLE 12.2

Outline how to determine the number of theoretical stages for a given separation.

SOLUTION: The determination of the number of theoretical stages required for a given separation can be performed graphically as illustrated by the equilateral triangle coordinate plot in Figure 12.5. The known ternary data are plotted on these coordinates and the bimodal curve defined. Points F , S , E_1 , and R_N represent the acid feed solution, solvent feed (n -butanol), final extract and final raffinate, respectively (see X points). Points M and O are arrived at by construction. By using lines extended from point O through the bimodal curve as well as existing and interpolated tie line data, the construction lines drawn will yield the number of theoretical stages required. Treybal provides a more detailed presentation.⁽¹⁾ ■

ILLUSTRATIVE EXAMPLE 12.3

Outline how to calculate the overall stage efficiency for a process.

SOLUTION: The overall stage efficiency, E , is calculated from

$$E = \frac{N_{\text{theo}}}{N_{\text{act}}} \times 100 \quad (12.1)$$

ILLUSTRATIVE EXAMPLE 12.4

The actual number of stages in the extraction unit at Manhattan College is 12. If the ideal stages are determined to be 6.2, calculate the overall stage efficiency.

SOLUTION: Apply Equation (12.1), incorporating the given values for the actual and theoretical number of stages. This yields,

$$\begin{aligned} E &= \frac{6.2}{12} \times 100 \\ &= 51.7\% \end{aligned}$$

Analytical Procedures

Fortunately, simple analytical procedures are available to perform many of the key extraction calculations. These remove the need for any graphical solutions (as outlined in Illustrative Example 12.2), while providing fairly accurate results. This development follows.

Earlier, the equilibrium constant, K , was defined as the ratio of the mole fraction of a solute in the gas to the mole fraction of the solute in the liquid phase. A distribution coefficient, k , can also be defined as the ratio of the weight fraction of solute in the extract phase, y , to the weight fraction of solute in the raffinate phase, x , i.e.,

$$k = \frac{y}{x} \quad (12.2)$$

For shortcut methods, a distribution coefficient k' (or m) is represented as the ratio of the weight ratio of solute to the extracting solvent in the extract phase, Y , to the

weight ratio of solute to feed solvent in the raffinate phase, X . In effect, Y and X are weight fractions on a *solute-free basis*.

$$k' = m = \frac{Y}{X} \quad (12.3)$$

Consider first the crosscurrent extraction process in Figure 12.7. This may be viewed as a laboratory unit since the extract and raffinate phases can be analyzed after each stage to generate equilibrium data as well as to achieve solute removal. If the distribution coefficient, as well as the ratio of extraction solvent to feed solvent (S'/F') are constant, and the fresh extraction solvent is pure, then the number of crosscurrent stages (N) required to achieve a specified raffinate composition can be estimated from:

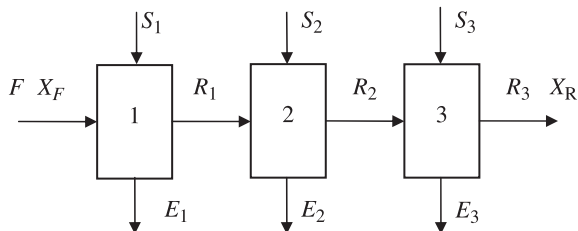
$$N = \frac{\log(X_F/X_R)}{\log\left(\frac{k'S'}{F'} + 1\right)} \quad (12.4)$$

Here, X_F is the weight fraction of solute in feed, X_R is the weight fraction of solute in raffinate, S' is the mass flow rate of solute free extraction solvent to each stage, and F' is the mass flow rate of the solute free feed solvent. Once again, X_F and X_R are weight fractions on a solute-free basis. The term $k'(S'/F')$ will later be defined as the extraction factor, ε —analogous to the absorption factor A discussed in Chapter 10.

As noted earlier, most liquid-liquid extraction systems can be treated as having either:

- 1 immiscible (mutually non-dissolving) solvents,
- 2 partially miscible solvents with a low solute concentration in the extract, or
- 3 partially miscible solvents with a high solute concentration in the extract.

Only the first case is addressed below. The reader is referred to the literature for further information on the second and third cases.⁽¹⁾



S = mass flow rate of extracting solvent
 F = mass flow rate of solvent feed

Figure 12.7 Three-stage crosscurrent extraction.

For the first case where the solvents are immiscible, the rate of solvent in the feed stream (F') is the same as the rate of feed solvent in the raffinate stream (R'). Also, the rate of extraction solvent (S') entering the unit is the same as the extraction solvent leaving the unit in the extract phase (E'). However, the total flow rates entering and leaving the unit will be different since the extraction solvent is removing solute from the feed. Thus, the ratio of extraction-solvent to feed-solvent flow rates (S'/F') is equivalent to (E'/R').

ILLUSTRATIVE EXAMPLE 12.5

With reference to Figure 12.7, derive an expression for the feed concentration leaving a single ideal (equilibrium) stage. Assume the extraction solvent is pure.

SOLUTION: Assume both the solvent feed and extraction solvent S to be constant, i.e.,

$$\begin{aligned}F' &= R_1 = \text{constant} \\S' &= E_1 = S_1 = \text{constant}\end{aligned}$$

A material balance around stage 1 gives

$$F'X_F + S'(0) = F'X_1 + S'Y_1$$

Assume this is an equilibrium stage so that

$$m = \frac{Y_1}{X_1}$$

Substitution into the above equation gives

$$X_1 = \left(\frac{F'}{F' + S'm} \right) X_F \quad \blacksquare$$

ILLUSTRATIVE EXAMPLE 12.6

Refer to the three theoretical stage crosscurrent flow systems pictured in Figure 12.7. If the same amount of fresh solvent S' is fed to each stage of the three equilibrium batch extraction stages, verify that Equation 12.4 is correct.

SOLUTION: For equilibrium stage 1

$$X_1 = \left(\frac{F'}{F' + S'm} \right) X_F$$

For equilibrium stage 2

$$\begin{aligned}X_2 &= \left(\frac{F'}{F' + S'm} \right) X_1 \\ &= \left(\frac{F'}{F' + S'm} \right)^2 X_F\end{aligned}$$

For equilibrium stage 3

$$\begin{aligned} X_3 &= \left(\frac{F'}{F' + S'm} \right) X_2 \\ &= \left(\frac{F'}{F' + S'm} \right)^2 X_1 \\ &= \left(\frac{F'}{F' + S'm} \right)^3 X_F \end{aligned}$$

For N equilibrium stages

$$X_R = X_N = \left(\frac{F'}{F' + S'm} \right)^N X_F$$

Rearranging the above equation gives

$$\frac{X_F}{X_N} = \left(\frac{F' + S'm}{F'} \right)^N$$

or

$$\frac{X_F}{X_N} = \left(\frac{F'}{F' + S'm} \right)^{-N}$$

Taking the log of both sides gives

$$\log \left(\frac{X_F}{X_N} \right) = N \log \left(1 + \frac{S'm}{F'} \right)$$

or

$$N = \frac{\log(X_F/X_R)}{\log \left(\frac{mS'}{F'} + 1 \right)} \quad (12.4) \quad \blacksquare$$

ILLUSTRATIVE EXAMPLE 12.7

Calculate the number of theoretical stages required for a crossflow system employing the same quantity of fresh solvent for each stage. Pertinent data include:

$$S' = 10 \text{ lb/min}$$

$$F' = 10 \text{ lb/min}$$

$$X_F = 0.51$$

$$X_R = 0.01 \text{ (design requirement)}$$

$$m = 0.72$$

SOLUTION: Employ Equation (12.4).

$$N = \frac{\log(X_F/X_R)}{\log \left(\frac{mS'}{F'} + 1 \right)}$$

Substitution gives

$$\begin{aligned} N &= \frac{\log(0.51/0.10)}{\log\left(\frac{(0.72)(10)}{(10)} + 1\right)} \\ &= 0.7076/0.2355 \\ &= 3.01 \end{aligned}$$

The reader is left the exercise of calculating the discharge solvent concentration from the first stage. ■

ILLUSTRATIVE EXAMPLE 12.8

Calculate the discharge solution concentration X_R for a crossflow system with nine *actual* stages. Employ the same quantity of fresh solvent for each stage. Assume the information provided in the previous example applies. In addition, the overall stage efficiency is 67%.

SOLUTION: Since the overall efficiency is 67%, the number of *theoretical* stages N_{theo} is

$$N_{\text{theo}} = (0.67)(9) = 6$$

Equation (12.4) may be rearranged to solve for X_R .

$$\begin{aligned} X_R &= \left(\frac{1}{1.72}\right)^6 0.51 \\ &= (0.0386)(0.51) \\ &= 0.0199 \\ &\approx 2\% \end{aligned}$$

By writing an overall material balance around the countercurrent unit illustrated in Figure 12.8 (a similar unit in the Unit Operations Laboratory at Manhattan College is provided in Fig. 12.2), the describing material balance equation can be rearranged into a McCabe–Thiele type of operating line with a slope F'/S' ($F' = F = R$; $S' = S = E$)

$$\begin{aligned} FX_F + SY_S &= R_S X_R + E_1 Y_E \\ Y_E &= \frac{F}{S}(X_F - X_R) + Y_S \end{aligned} \quad (12.5)$$

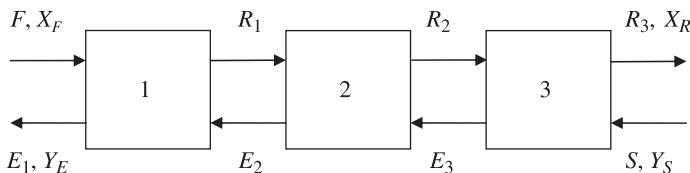


Figure 12.8 Countercurrent extraction.

where Y_E is the weight ratio of solute removed to the extraction solvent and Y_S is the weight ratio of solute to be removed to the extraction solvent.

If the equilibrium line is straight, its intercept is zero, and if the operating line is straight, the number of theoretical stages can be calculated with one of the following equations, which are forms of the Kremser equation. When the intercept of the equilibrium line is greater than zero, Y_S/k'_S should be used instead of Y_S/m , where k'_S is the distribution coefficient at Y_S . Also, these equations contain an extraction factor (ε), which is calculated by dividing the slope of the equilibrium line, m , by the slope of the operating line, F'/S' , i.e.,⁽³⁾

$$\varepsilon = \frac{m \cdot S'}{F'} \quad (12.6)$$

If the equilibrium line is not straight, a geometric mean value of m should be used. This quantity is determined by the following equation,⁽⁴⁾

$$m = \sqrt{m_1 \cdot m_2} \quad (12.7)$$

where subscripts 1 and 2 denote the feed stage and the raffinate stage, respectively. When $\varepsilon \neq 1.0$,

$$N = \frac{\ln \left[\frac{\left\{ \frac{X_F - (Y_S/m)}{(X_R - Y_S)/m} \right\} \left(1 - \frac{1}{\varepsilon} \right) + \frac{1}{\varepsilon}}{\ln \varepsilon} \right]}{\ln \varepsilon} \quad (12.8)$$

When $\varepsilon = 1.0$,

$$N = \left[\frac{X_F - (Y_S/m)}{X_R - (Y_S/m)} \right] - 1 \quad (12.9)$$

ILLUSTRATIVE EXAMPLE 12.9

Referring to Figure 12.8, use the following data to determine the degree to which an overall material balance is satisfied:

$$F = 0.13 \text{ lb/min}$$

$$S = 0.433 \text{ lb/min}$$

$$R = 0.0945 \text{ lb/min}$$

$$E = 0.0878 \text{ lb/min}$$

SOLUTION: Apply an overall material balance to the unit:

$$F + S = R + E \quad (12.10)$$

Substitute the data provided into the above equation:

$$0.13 \text{ lb/min} + 0.0433 \text{ lb/min} \stackrel{?}{=} 0.0945 \text{ lb/min} + 0.0878 \text{ lb/min}$$

$$0.1733 \text{ lb/min} \stackrel{?}{=} 0.1823 \text{ lb/min}$$

The percent deviation (based on the inlet stream) is:

$$\text{Error} = \left(\frac{0.1823 - 0.1733}{0.1733} \right) \times 100$$

$$= 4.9\% \quad \blacksquare$$

ILLUSTRATIVE EXAMPLE 12.10

Referring to the previous example, if the solute free basis mass fraction of the solute (e.g., acetic acid) in the feed, solvent, extract, and raffinate are 0.1339, 0.0, 0.1058, and 0.00183, respectively (lb/lb), determine the degree to which a solute (e.g., acetic acid) balance is satisfied.

SOLUTION: Apply a component balance to the unit:

$$(F)(X_F) + (S)(Y_S) = (E)(Y_E) + (R)(X_R) \quad (12.11)$$

Substitute the data provided along with data from the previous example into the above equation

$$(0.13 \text{ lb/min})(0.1369) + (0.0433 \text{ lb/min})(0.0) \stackrel{?}{=} (0.0945 \text{ lb/min})(0.01058)$$

$$+ (0.0878 \text{ lb/min})(0.00183)$$

$$0.01742 \text{ lb/min} \stackrel{?}{=} 0.009998 \text{ lb/min} + 0.00016 \text{ lb/min}$$

$$0.01742 \text{ lb/min} \stackrel{?}{=} 0.01015 \text{ lb/min}$$

The percent deviation (based on the inlet stream) is,

$$\text{Error} = \frac{0.01742 \text{ lb/min} - 0.01015 \text{ lb/min}}{0.01742 \text{ lb/min}} \times 100$$

$$= 41.7\%$$

The deviation here is much larger than the previous example, suggesting some inconsistency in the data. ■

ILLUSTRATIVE EXAMPLE 12.11

A 200 lb/h process stream containing 20 wt% acetic acid (A) in water (W) is to be extracted down to 1 wt% with 400 lb/h of a methyl isobutyl ketone (MIBK) ternary mixture containing 0.05 wt% acetic acid and 0.005 wt% water. Determine F' , S' , X_F , X_R , Y_S , and Y_E .

SOLUTION: Calculate the feed solvent flow rate (F') and the extraction solvent flow rate (S') in lb/h. Note that the weight percents are *not* on a solute free basis.

$$F' = F \cdot (1 - x_A) = 200 \text{ lb/h}(1 - 0.2) = 160 \text{ lb/h}$$

$$S' = S \cdot (1 - y_A - y_W)$$

$$= 400 \cdot (1 - 0.00005 - 0.0005) = 400 \cdot (1 - 0.00055) = 399.8 \text{ lb/h}$$

Calculate the solute-free weight ratios of A in the feed (X_F), raffinate (X_R), and extraction solvent (Y_S):

$$X_F = \frac{0.2 \cdot 200 \text{ lb/h}}{160 \text{ lb/h}} = 0.25$$

$$X_R = \frac{1}{100 - 1} = 0.0101$$

$$Y_S = \frac{0.0005}{1 - 0.0005} = 0.0005$$

Calculate the weight ratio of A in the extract (Y_E) using a modified form of Equation (12.5):

$$Y_E = \frac{F'X_F + S'Y_S - R'X_F}{E'}$$

Substituting gives,

$$Y_E = \frac{(0.25 \cdot 160) + (0.0005 \cdot 399.8) - (0.0101 \cdot 160)}{399.8} = 0.0965 = 9.65\% \quad \blacksquare$$

ILLUSTRATIVE EXAMPLE 12.12

Using the values from Illustrative Example 12.11, determine the number of theoretical stages required to achieve the desired acetic acid removal. The equilibrium data for the MIBK and acetic acid system can be represented by $Y = 1.23(X)^{1.1}$ for acetic acid weight ratios between 0.01 and 0.25.

SOLUTION: Determine the weight ratio of the liquid leaving the first stage (X_1), which is in equilibrium with the liquid leaving the same stage (Y_E):

$$X_1 = \frac{Y_E}{1.23 \cdot X_1^{1.1}} = \left(\frac{0.0965}{1.23} \right)^{1/1.1} = 0.0988$$

Next, obtain an expression for the slope of the equilibrium line, noting that the slope of a line is the first derivative of the function for the line

$$Y = 1.23 \cdot X^{1.1}$$

$$\frac{dY}{dX} = 1.1 \cdot (1.23 \cdot X^{0.1}) = 1.353 \cdot X^{0.1}$$

Calculate the slope of the equilibrium line at the feed stage (m_1), i.e., for $X_1 = 0.0988$,

$$m_1 = \frac{dY}{dX} = 1.353(X)^{0.1} = 1.353 \cdot (0.0988)^{0.1} = 1.073$$

Calculate the slope of the equilibrium line at the feed stage (m_R), i.e., for $X_R = 0.0101$,

$$m_R = \frac{dY}{dX} = 1.353(X_R)^{0.1} = 1.353 \cdot (0.0101)^{0.1} = 0.8545$$

Determine the geometric mean equilibrium slope (m) from Equation (12.7):

$$m = \sqrt{1.073 \cdot 0.8545} = 0.958$$

Also calculate the extraction factor (ε) from Equation (12.6):

$$\varepsilon = 0.958 \left(\frac{399.8 \text{ lb/h}}{160 \text{ lb/h}} \right) = 2.39$$

Finally, calculate the number of theoretical stages from Equation (12.8):

$$N = \frac{\ln \left[\frac{\left\{ \frac{X_F - (Y_S/m)}{(X_R - Y_S)/m} \right\} \left(1 - \frac{1}{\varepsilon} \right) + \frac{1}{\varepsilon}}{\ln \varepsilon} \right]}{\ln \varepsilon}$$

Substituting,

$$\begin{aligned} N &= \frac{\ln \left[\frac{\left\{ \frac{0.25 - (0.0005/1.074)}{(0.0101 - 0.0005)/1.074} \right\} \left(1 - \frac{1}{2.39} \right) + \frac{1}{2.39} \right]}{\ln 2.39} \\ &= 3.23 \end{aligned}$$

Since integer values of actual stages are generally employed, four theoretical stages may be required for the desired separation. ■

SOLID–LIQUID EXTRACTION (LEACHING)⁽⁴⁾

There are three key unit operations that involve the “mass transfer” between solids and liquids:

- 1 Crystallization
- 2 Solid–liquid phase separation
- 3 Solid–liquid extraction

Crystallization receives treatment in Chapter 14 while the physical separation of solids and liquids (2) appears as a section in Chapter 16. This last section in this chapter addresses the important topic of (3) solid–liquid extraction.⁽⁴⁾

Solid–liquid extraction involves the preferential removal of one or more components from a solid by contact with a liquid solvent. The soluble constituent may be solid or liquid, and it may be chemically or mechanically held in the pore structure of the insoluble solid material. The insoluble solid material is often particulate in nature, porous, cellular with selectively permeable cell walls, or surface-activated. In engineering practice, solid–liquid extraction is also referred to by several other names such as *chemical extraction*, *washing extraction*, *diffusional extraction*, *lixiviation*, *percolation*, *infusion*, and *decantation-settling*. The simplest example of a

leaching process is in the preparation of a cup of tea. Water is the solvent used to *extract* or *leach*, tannins and other substances from the tea leaf. A brief description/definition of terms adopted by some is provided below.⁽⁵⁾

The entire field of liquid–solid extraction may be subdivided in a number of ways. The authors have chosen to subdivide the field in the following fashion:

- 1 Leaching—The contacting of a liquid and a solid, e.g., with the potential of imposing a chemical reaction upon one or more substances in the solid matrix so as to render them soluble.
- 2 Chemical extraction—This is similar to leaching but it applies to removing substances from solids other than ores. The recovery of gelatin from animal bones in the presence of alkali is typical.
- 3 Washing extraction—The solid is crushed to break the cell walls, permitting the valuable soluble product to be washed from the solid matrix. Sugar recovery from cane is a prime example.
- 4 Diffusional extraction—The soluble product diffuses across the denatured cell walls (no crushing involved) and is washed out of the solid. The recovery of beet sugar is an excellent case in point.

Process Variables

In the design of solid–liquid systems, the rate of extraction is affected by a number of independent variables. These are:

- 1 Temperature
- 2 Concentration of solvent
- 3 Particle size
- 4 Porosity and pore-size distribution
- 5 Agitation
- 6 Solvent selection
- 7 Terminal stream composition and quantities
- 8 Materials of construction

Details on each of the above design/system variables are provided below:

- 1 As with most rate phenomena (e.g., chemical reaction), extraction is enhanced by an increase in temperature. The maximum temperature that can be used for a particular system is determined by either the boiling point of the solvent, degradation of the product or solvent, economics, or all of the above. Processes that depend on a chemical reaction are significantly enhanced by a rise in temperature. However, many solid–liquid extraction systems are controlled by diffusional processes and the improvement is less dramatic in these systems. The process temperature for leaching also varies, depending on the raw material

and desired final product. For instance, in tea production, the feed water temperature enters the extraction unit between 130–190°F, whereas in coffee production, the extract water temperature enters the unit at 360°F. Temperature affects the solute solubility, solvent vapor pressure, and selectivity, as well as the quality of the final product.

- 2 The concentration of solvent is also an important factor, particularly in the case of aqueous solutions in which a chemical reaction plays a part. In oil seed extraction, the concentration of the solvent is of minor consequence because the rate of extraction is limited by the diffusion of the oil from the seed.
- 3 Particle size is significant in most cases since it is a direct function of the total surface area that will be available for either reaction or diffusion. It is probably of greatest importance in extracting cellular materials because a reduction in particle size also results in an increase in the number of cells ruptured. Particle size is of lesser importance in ores since porosity and pore-size distribution often take on greater significance.
- 4 In ores, porosity and pore-size distribution can affect the rate of extraction because the leaching solution must flow or diffuse in and out of the pores and, in many instances, the movement of the solute through the pores to the surface of the particle is by diffusion. A reduction in particle size usually results in a decrease in the average time of passage of a solute molecule from the interior of the ore particle to the surface of the particle.
- 5 In nonagitated systems, the solute molecules must not only diffuse to the surface of the particle but must also diffuse to the main stream in order to be carried to a collection point. Agitation tends to reduce resistance to mass transfer and to cancel the effects that restrict efficiency.
- 6 A solvent needs to provide for a high selectivity of the solute to be extracted from a solid, as well as the capability to produce a high quality extract (see previous section for additional details). Other items to be considered include chemical stability at process conditions, low viscosity, low vapor pressure to reduce losses, low toxicity and flammability, low density, low surface tension, ease and economy of solute recovery from the extract stream, and cost. Solvent cost and potential losses (fugitive or otherwise) must also be taken into consideration.
- 7 The terminal stream quantity and composition are the primary variables that control the economics of any extraction process. In order for a plant to be profitable, it must be able to meet certain production goals within the constraints of a plant's capabilities. The plant engineer is responsible for stretching those capabilities to their fullest extent to meet production quotas.
- 8 The corrosive properties of the solvent and its solutions are definite factors in setting equipment costs, particularly where metal construction is required. Selection of the proper materials of construction can insure a long life of the equipment. It can avoid loss of not only product quality but also value as a result of contamination.

The choices for the above variables are made based on the specific process under evaluation with typical needs often determined through experimentation.

Equipment and Operation

The methods of operation of a leaching system can be specified by four categories: operating cycle (batch, continuous, or multibatch intermittent), direction of streams (cocurrent, countercurrent, or hybrid flow), staging (single-stage, multistage, or differential-stage), and method of contacting. The following is a list of typical leaching systems:

- 1 Horizontal-basket design
- 2 Endless-belt percolator
- 3 Kennedy extractor
- 4 Dispersed solids leaching
- 5 Batch stirred tanks
- 6 Continuous dispersed solids leaching
- 7 Screw conveyor extraction

As one might suppose, details on leaching equipment and operation is similar to that for liquid–liquid extraction systems. The simplest method of operation for a solid–liquid extraction or washing of a solid is to bring all the material to be treated and all the solvent to be used into intimate contact once and then to separate the resulting solution from the undissolved solids. The *single-contact* or single-stage batch operation is encountered in the laboratory and in small-scale operations but rarely in industrial operations because of the low recovery efficiency of soluble material and the relatively dilute solutions produced.

If the total quantities of solvent to be used is divided into portions and the solid extracted successively with each portion of fresh solvent after draining the solids between each addition of solvent, the operation is called *multiple-contact* or *multi-stage*. Although recovery of the soluble constituents is improved by this method, it has the disadvantage that the solutions obtained are still relatively dilute. This procedure may be used in small-scale operations where the soluble constituent need not be recovered.

If the solid and solvent are mixed continuously and the mixture fed continuously to a separating device, a *continuous single-contact operation* is obtained.

High recovery of solute with a highly concentrated product solution can be obtained only by using *countercurrent operation* with a number of stages. In countercurrent operation, the product solution is last in contact with fresh solid feed and the extracted solids are last in contact with fresh solvent. Details on the above three methods of operation are provided below.⁽⁶⁾

The single stage operation is shown in Figure 12.9 and represents both the complete operation of contacting the solids feed and fresh solvent and the subsequent mechanical (or equivalent) separation.

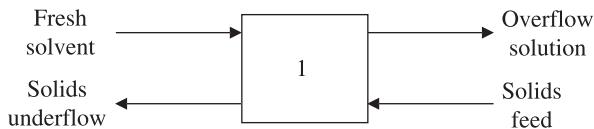


Figure 12.9 Single-stage leaching unit.

The second type is the *multistage* system shown in Figure 12.10 with the flow direction termed cross-flow. Fresh solvent and solid feeds are mixed and separated in the first stage. *Underflow* from the first stage is sent to the second stage where more fresh solvent is added. This is repeated in all the subsequent stages.

The third type of flow is the *multistage countercurrent* system shown in Figure 12.11. The underflow and *overflow* streams flow countercurrent to each other.⁽³⁾

Figure 12.12 shows a material balance for a continuous countercurrent process.⁽³⁾ The stages are numbered in the direction of flow of the solid (e.g., sand). The light phase is the liquid that overflows from stage to stage in a direction opposite to that of the flow of the solid, dissolving solute as it moves from stage N to stage 1. The heavy phase is the solid flowing from stage 1 to stage N . Exhausted solids leave stage N , while concentrated solution overflows leave from stage 1. For purposes of analysis, it is customary to assume that the solute free solid is insoluble in the solvent so that the flow rate of this solid is constant throughout the process unit.

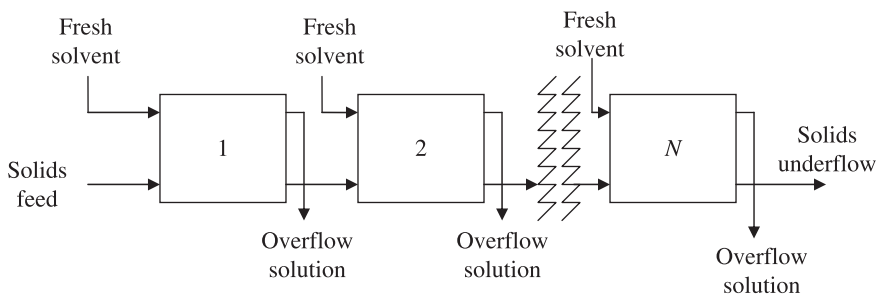


Figure 12.10 Multistage cross-flow leaching unit.

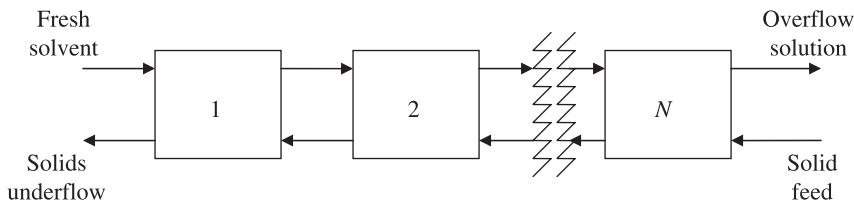


Figure 12.11 Multistage countercurrent leaching unit.

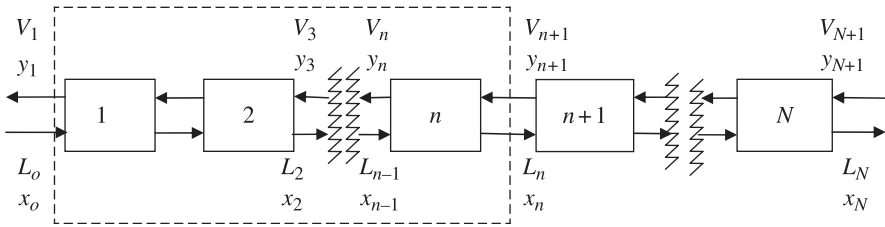


Figure 12.12 Material balance-countercurrent process.

Design and Predictive Equations

Design and predictive equations for leaching operations can be more involved than those for liquid extraction. As before, the solute/solvent equilibrium and process throughput determine the cross-sectional area and the number of theoretical and/or actual stages required to achieve the desired separation. And, as with many of the previous unit operations discussed so far, the number of equilibrium stages and stage efficiencies can be determined under somewhat similar conditions for the countercurrent units discussed earlier.

As in distillation (see Chapter 9) and absorption (see Chapter 10), the quantitative performance of a countercurrent system can be analyzed by utilizing an equilibrium line and an operating line, and, as before, the method to be employed depends on whether these lines are straight or curved.

Provided sufficient solvent is present to dissolve all the solute in the entering solid and there is no adsorption of solvent by the solid, equilibrium is attained when the solid is completely “saturated” and the concentration of the solution (as formed) is uniform. Assuming these requirements are met, the concentration of the liquid retained by the solid leaving any stage is the same as that of the liquid overflow from the same stage. Therefore, an equilibrium relationship exists for this (theoretical) stage in question.

The equation for the operating line is obtained by writing a material balance. From Figure 12.12,

$$V_{N+1} + L_o = V_1 + L_N \quad (\text{total solution, including solute}) \quad (12.12)$$

$$V_{N+1}y_{N+1} + L_o x_o = V_1 y_1 + L_N x_N \quad (\text{solute}) \quad (12.13)$$

Eliminating V_{N+1} , and solving for y_{N+1} , gives

$$y_{N+1} = \left[\frac{1}{1 + \left(\frac{V_1 - L_o}{L_N} \right)} \right] x_N + \frac{V_1 y_1 - L_o x_o}{L_N + V_1 - L_o} \quad (12.14)$$

If the density and viscosity of the solution change considerably with solute concentration, the solids from the lower stages might retain more liquid than those in the higher stages. The slope of the operating line then varies from stage to stage.

If, however, the mass of the solution retained by the solid is independent of concentration, L_N is constant, and the operating line is straight. The two above mentioned conditions describe *variable* and *constant overflow*, respectively.

It is usually assumed that the inerts are constant from stage to stage and insoluble in the solvent. Since no inerts are usually present in the extract (overflow) solution and the solution retained by the inerts is approximately constant, both the underflow L_N and overflow V_N are constant, and the equation for the operating line approaches a straight line. Since the equilibrium line is also straight, the number of stages can be shown to be (with reference to Fig. 12.12)

$$N = \frac{\log\left(\frac{y_{N+1} - x_N}{y_1 - x_1}\right)}{\log\left(\frac{y_{N+1} - y_1}{x_N - x_1}\right)} \quad (12.15)$$

The above equation should not be used for the entire extraction cascade if L_o differs from L_1, L_2, \dots, L_N (i.e., the underflows vary within the system). For this case, the compositions of all the streams entering and leaving the first stage should first be calculated before applying this equation to the remaining cascade.^(3,7)

ILLUSTRATIVE EXAMPLE 12.13

Calculate the grams of water that need to be added to 40 g of sand containing 9.1 g salt to obtain a 17% salt solution.

SOLUTION: Set V to be the grams of water required. The describing equation is

$$\frac{9.1}{9.1 + V} = 0.17$$

Solving for V ,

$$V = 44.4 \text{ g}$$

ILLUSTRATIVE EXAMPLE 12.14

Refer to the previous example. If the salt solution is to be reduced to 0.015, calculate the amount of salt that must be removed (“leached”) from the solution.

SOLUTION: Let Z be equal to the final amount of salt in the sand–water–salt solution. The describing equation is

$$\frac{Z}{40 + Z} = 0.15$$

Solving for Z ,

$$Z = 0.61 \text{ g salt}$$

The amount of salt removed is therefore $9.1 - 0.61 = 8.49 \text{ g}$.

ILLUSTRATIVE EXAMPLE 12.15

A sand-salt mixture containing 20.4% salt enters a solid-liquid extraction at a rate of 2500 lb/h. Calculate the hourly rate of fresh water that must be added for 99% of the salt to be “leached” from the sand-salt mixture if the discharge salt-water solution contains 0.153 (mass) fraction salt.

SOLUTION: Let W equal to the hourly rate of water. The describing equation from a mass balance is

$$\frac{(0.204)(2500)}{(0.204)(2500) + W} = 0.153$$

Solving for W ,

$$W = 2820 \text{ lb/h}$$

Also note that the feed consists of 510 lb salt and 1990 lb sand. On discharge, the sand contains only 5.1 lb salt. The discharge water solution consists of the 2820 lb water plus 504.9 lb salt. ■

ILLUSTRATIVE EXAMPLE 12.16

A countercurrent leaching system is to treat 100 kg/h of crushed sugar stalks with impurity-free water as the solvent. Analysis of the stalks is as follows:

Water = 38% (by mass)

Sugar = 10%

Pulp = 52%

If 95% sugar is to be recovered and the extract phase leaving the system is to contain 12% sugar, determine the number of theoretical stages required if each kilogram of dry pulp retains 2.5 kg of solution.

SOLUTION: For a basis of 100 kg (one hour of operation) of sugar stalks,

Water = 38 kg

Sugar = 10 kg

Pulp = 52 kg

For 95% sugar recovery, the extracted solution contains

$$0.95(10) = 9.5 \text{ kg sugar}$$

and

$$\left(\frac{1 - 0.12}{0.12}\right)(9.5) = 69.7 \text{ kg water}$$

The total extract solution is then

$$V_1 = 9.5 + 69.7 = 79.2 \text{ kg}$$

The underflow solution is

$$L_1 = L_2 = \dots = L_N = (2.5)(52) = 130 \text{ kg}$$

Since $L_0 = 10 + 38 = 48 \text{ kg}$, a material balance on the initial stage must be performed:

$$L_0 + V_2 = L_1 + V_1 = 48 + V_2 = 79.2 + 130$$

$$V_2 = 161.2 \text{ kg}$$

Applying a componential solute (sugar) balance across the first stage,

$$161.2y_2 + 10 = 9.5 + 130(0.12)$$

$$y_2 = 0.0937$$

As indicated above, the remaining $(N-1)$ stages operate with the underflow and overflow solutions relatively constant. For this part of the system, and subject to this assumption,

$$N - 1 = \frac{\log\left(\frac{y_{N+1} - x_N}{y_1 - x_1}\right)}{\log\left(\frac{y_{N+1} - y_1}{x_N - x_1}\right)} \quad (12.16)$$

For this equation,

$$y_{N+1} = 0.0$$

and

$$x_N = \frac{0.05(10)}{130} = 0.00385$$

Substitution of the values into the above equation gives

$$N - 1 = \frac{\log\left(\frac{0 - 0.00385}{0.0973 - 0.12}\right)}{\log\left(\frac{0 - 0.0937}{0.00385 - 0.12}\right)} = 8.26$$

$$N = 9.26 \text{ stages}$$

■

ILLUSTRATIVE EXAMPLE 12.17

Refer to Illustrative Example 12.16. Calculate the actual stages required if the overall stage efficiency is 85%.

SOLUTION: The 9.26 stages represent the theoretical number of stages. The actual number of stages, N_{act} , is

$$N_{\text{act}} = \frac{9.26}{0.85} = 10.89 \text{ stages}$$

Eleven stages are suggested. ■

ILLUSTRATIVE EXAMPLE 12.18

Assume that salt (NaCl) is to be recovered by leaching a salt mixture containing insoluble impurities. The salt content of the mixture is 20 wt% and is to be reduced to 1.0 wt%. Pure water at 80°F is the leaching agent. Determine how much water is required per 100 lb of solids for a single-stage operation. Each pound of insoluble matter leached in a stage retains 1.5 lb of solution under the operating conditions.

SOLUTION: Assume 100 lb of feed (L_o) as a basis. The feed contains 80 lb of insolubles and 20 lb of NaCl. The solid phase leaving the stage contains the 80 lb of insolubles that represents 99% of the dry solid phase. Therefore, the solids are

$$\frac{80 \text{ lb}}{0.99} = 80.8 \text{ lb (total)}$$

This represents 80 lb of the insoluble matter plus 0.8 lb of salt. The solution retained by insoluble matter is 1.5 (80 lb) or 120 lb, and includes the 0.8 lb of NaCl. The solution concentration in the insoluble matter is therefore

$$\frac{0.8 \text{ lb}}{120 \text{ lb}} = 0.00667$$

Leaching liquor leaving the stage contains (20 - 0.8) lb, or 19.2 lb of salt. For an *equilibrium stage*, this is at the same solution concentration as that in the solid phase. Therefore, the mass of this phase is

$$\frac{19.2 \text{ lb}}{0.00667} = 2880 \text{ lb}$$

The solvent (salt-water solution) required can be determined by an overall material balance.

$$\begin{aligned} V_2 + L_o &= V_1 + L_1 \\ V_2 &= 2880 + 120 - 20 \\ V_2 &= 2980 \text{ lb} \end{aligned}$$

■

ILLUSTRATIVE EXAMPLE 12.19

Refer to the previous example. Perform the calculation for a three-staged continuous counter-current system.

SOLUTION: This requires a trial-and-error solution. Stream V_4 , rather than V_2 , is the unknown. For a three-stage countercurrent operation, assume 450 lb for V_4 . The solution retained by the solids leaving stage 3 now contains 0.8 lb salt (s). Therefore,

$$x_3 = \frac{0.8}{120} = 0.00667$$

A material balance on the third stage shows 450 lb leaching agent entering (V_4), plus 120 lb solution L_2 (L is constant) from the preceding stage. Stream V_3 must still be 450 lb and the salt content of stream V_3 is $(450)(0.00667) = 3.0015$ lb salt. The salt content in L_2 is $(23.0015 - 0.8) = 2.2015$.

Considering the second stage in the same manner, one finds that x_2 must be

$$x_2 = \frac{2.2015}{120} = 0.0183$$

The salt content of stream V_2 is $(450)(0.0183) = 8.2556$ lb and of stream L_1 is 6.054. For the first stage to supply the 6.054 lb in stream L_1 , x_1 must be

$$x_1 = \frac{6.054}{120} = 0.05045$$

The salt content in stream V_1 is,

$$V_1 = (0.05045)(450) = 22.70 \text{ lb}$$

The salt content in stream L_o will therefore be $(22.70 - 0.8) = 21.90$ lb as compared to its “actual” value of 20 lb. The assumed value for V is reasonable. Another trial yields a value for V_4 of approximately 440 lb. ■

The Baker equation⁽⁸⁾ is useful for calculating concentrations when the number of ideal stages is known, or vice versa. If the fresh solvent contains no solute, Baker provided the following equation:

$$\frac{1}{f} = 1 + a_n \sum_1^n a^{n-1} \quad (12.17)$$

where f = ratio of solute in the underflow from first stage to solute in the underflow fed to the last stage

a = ratio of overflow solution leaving stage $N-1$ to solution in the underflow leaving the first stage

a_n = ratio of overflow solute leaving the last stage to the solution in the underflow leaving the last stage

a' = ratio of solvent in overflow leaving stage $N-1$ to solvent in underflow leaving first stage

a'_n = ratio of solvent in overflow leaving the last stage to solvent in the underflow leaving the last stage

In the case of constant solvent-to-inerts ratio, the quantity a' replaces a and a'_n replaces a_n .

ILLUSTRATIVE EXAMPLE 12.20

One hundred tons/day of ore containing 15% solubles and 5% moisture by mass is to be leached with 100 tons/day of water in a continuous countercurrent system consisting of three ideal stages. The underflow from each stage contains approximately 0.3 lb solution/lb inerts. Determine the percentage of solubles recovered.

SOLUTION: Take 1 day of operation as a basis. The underflow from each stage contains $100 - 15 - 5 = 80$ tons of inerts and $(0.3)(80) = 24$ tons of solution. Therefore, the total underflow (assumed constant) from each stage is equal to $(80 + 24) = 104$ tons. Applying an overall material balance, the weight of solution leaving the third stage, V_{N+1} , is $100 + 100 - 104$ or 96 tons. Material balances around stages 1 and 2 dictates overflows of 100 tons of solution from each of these stages. See also Figure 12.12. Since the fresh solvent contains no solute, Equation (12.17) applies. Therefore,

$$a = \frac{V_1}{L_1} = \frac{100}{24} = 4.167$$

$$a_n = \frac{V_{N+1}}{L_N} = \frac{96}{24} = 4.00$$

For the case where $N = 3$, applying Equation (12.17) gives

$$\frac{1}{f} = 1 + a_n + a_n a + a_n a^2$$

Substituting,

$$\frac{1}{f} = 1 + 4.0 + 4.0(4.167) + 4.0(4.167)^2 = 91.1$$

$$f = \frac{1}{91.1} = 0.0110$$

Percent solubles recovered = $100(1 - 0.0110) = 98.9\%$. ■

ILLUSTRATIVE EXAMPLE 12.21

Refer to Illustrative Example 12.20. Calculate the composition of the overflow discharge stream.

SOLUTION: The solubles in overflow discharge = $(0.989)(15) = 14.84$ tons. The percent solubles in overflow discharge = $(14.84/96) = 15.4\%$. By difference, the percent water in the overflow discharge is 84.6%. ■

For the case of constant underflow, another equation is available for calculating the number of theoretical stages, N , in a continuous multistage countercurrent leaching operation. It is valid for both constant solution-to-inerts or solvent-to-inerts ratios. The

equation, developed by Chen,⁽⁹⁾ is:

$$N = \frac{\log \left[1 + (r - 1) \left(\frac{x_o - y_1}{x_N - y_1} \right) \right]}{\log(r)} \quad (12.18)$$

where $r = s/IF$

x = weight fraction of solute in underflow solution

y = weight fraction of solute in overflow solution

s = flow rate of fresh solvent or clear liquid overflow from each stage

I = flow rate of inert solids

F = liquid retained in solid inerts

ILLUSTRATIVE EXAMPLE 12.22

One hundred tons of underflow feed containing 20 tons of solute, 2 tons of water and 78 tons of inert material, I , is to be leached with water to give an overflow effluent concentration of 15% solute and a 95% recovery of solute. The underflow from each stage carries 0.5 lb of solution per lb of inerts. Calculate the number of ideal stages required.⁽¹⁰⁾

SOLUTION: For a 95% recovery of solute,

$$\text{Recovered solute} = (0.95)(20 \text{ tons}) = 19 \text{ tons}$$

For a 15% solute weight fraction in the effluent

$$\frac{19}{s + 19} = 0.15$$

where s = tons of water.

Solving for s ,

$$s = 107.67 \text{ tons}$$

Based on the problem statement:

$$y_1 = 0$$

$$x_o = 0.20$$

$$I = 78 \text{ tons}$$

$$F = 0.5 \text{ lb solution/lb inerts}$$

In addition,

$$x_N = \frac{1.0}{(0.5)(78)} = \frac{1}{39}$$

$$x_N = 0.0256$$

To employ Equation (12.18), first calculate r :

$$r = \frac{s}{IF} = \frac{107.67}{(78)(0.5)} = 2.736$$

Substituting into Equation (12.18),

$$N = \frac{\log \left[1 + (r - 1) \left(\frac{x_o - y_1}{x_N - y_1} \right) \right]}{\log(r)}$$

$$N = \frac{\log \left[1 + (2.736 - 1) \left(\frac{0.2}{0.0256} \right) \right]}{\log(2.736)}$$

$$N = \frac{1.163}{0.437} = 2.66$$

■

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