SEPARATION PROCESS PRINCIPLES

Second Edition

J. D. SEADER / ERNEST J. HENLEY

Part 4

Separations That Involve a Solid Phase

Chapters 16, 17, and 18 cover separation operations in which one or more components in a solid phase undergo mass transfer to or from a fluid phase. Chapter 16 covers selective leaching of material from a solid to a liquid solvent. This operation is widely used in the food industry. Crystallization from a liquid and desublimation from a vapor are discussed in Chapter 17, where evaporation, which often precedes crystallization, is included. Both solution crystallization to produce inorganic crystals and melt crystallization to produce organic crystals are considered. Chapter 18 is concerned with the drying of solids and the myriad types of equipment used industrially. A section on psychrometry is included.

Chapter 16

Leaching and Washing

Leaching, sometimes called solid–liquid (or liquid–solid) extraction, involves the removal of a soluble fraction (the solute or *leachant*) of a solid material by a liquid solvent. The solute diffuses from the solid into the surrounding solvent. Either the extracted solid fraction or the insoluble solids, or both may be the valuable product. Leaching is widely used in the metallurgical, natural product, and food industries. In the former, leaching may involve oxidation or reduction reactions of the solid with the solvent. Equipment is available to conduct leaching under batch, semicontinuous, or continuous operating conditions. Effluents from a leaching stage are essentially solids-free liquid, called the *overflow,* and wet solids, called the *underflow.* To reduce the concentration of solute in the liquid portion of the underflow, leaching is often accompanied by two or more countercurrent-flow washing stages. The combined process produces a final overflow, called the *extract,* which contains some of the solvent and most of the solute; and a final underflow, called the *extracted* or *leached solids,* which are wet with almost-pure, remaining solvent. Ideally, the soluble solids are perfectly separated from the insoluble solids, but solvent is distributed to both products. Additional processing of the extract and the leached solids is necessary to recover the solvent for recycle.

Some industrial applications of leaching include: (1) removal of copper from ore with sulfuric acid, (2) recovery of gold from ore with sodium-cyanide solution, (3) extraction of sugar from sugar beets with hot water, (4) extraction of tannin from tree bark with water, and (5) the removal of caffeine from green coffee beans with supercritical CO_2.

16.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to:

- Describe equipment used for batch and continuous leaching.
- Explain differences between leaching and washing.
- List assumptions for an ideal, equilibrium leaching or washing stage.
- Calculate recovery of a solute for a continuous, countercurrent leaching and washing system for a constant ratio of liquid to solids in the underflow or for a variable-underflow ratio.
- Apply rate-based leaching to food-processing applications.
- Develop and apply the rate-based, shrinking-core model to reactive mineral processing.

Industrial Example

As an example of leaching, consider the extraction of vegetable oil from soybeans with a commercial hexane solvent in a pilot-plant size countercurrent-flow, multistage leaching unit, as described by Othmer and Agarwal [1]. Although edible oils can be extracted from a number of different field and tree crops, including coconuts, cottonseeds, palm, peanuts, grapeseed, soybeans, and sunflower seeds, the highest percentage of edible oil is from soybeans. In 1979–1980, world production of soybean oil was 14 million metric tons. Oil from soybeans is high in polyunsaturated fats and, thus, is less threatening from a cholesterol standpoint. When the oil content of seeds and beans is high, some of the oil can be removed by compressing the solids in a process known as *expression,* as discussed in Perry and Green [2]. For soybeans, whose oil content is typically less than 0.30 lb per lb of dry and oil-free solids, leaching is a more desirable technique than expression because a higher yield of oil can be achieved by leaching.

The soybeans are dehulled, cleaned, cracked, and flaked before being fed to the extractor. Typically, the cleaned soybeans contain 8 wt% moisture and 20 wt% oil. The dry and oil-free soybeans have a particle specific gravity of about 1.425 and the oil has a specific gravity of 0.907 with a viscosity at 25°C of 50 cP. Approximately 50% of the flake volume is taken up by oil, moisture, and air. It might be expected that whole soybeans, rather than flakes, might be fed to the extractor, with leaching taking place by molecular diffusion of the

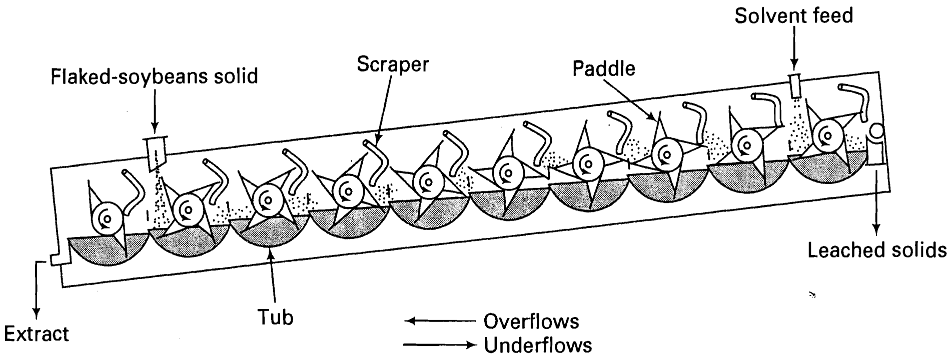


Figure 16.1 Kennedy extractor for leaching of oil from soybeans.

solvent uniformly into the seed, followed by diffusion of the oil through the solvent and out of the seed. If so, the mass-transfer process within the seed could be modeled with Fick's second law. However, experiments by King, Katz, and Brier [3] found that although extraction of oil with solvent in uniformly porous inorganic solids, like porous clay plates, obeyed Fick's law of molecular diffusion, extraction of oil from soybeans did not, presumably because of the complex internal structure of soybeans. Furthermore, Othmer and Agarwal [1], using whole and carefully cut half soybeans, found that diffusion was extremely slow. After 168 hours in contact with hexane, less than 0.08% of the original oil in the whole beans and less than 0.19% of the oil in the half beans was extracted. Such a slow diffusion rate for particles that are approximately 5 mm in diameter is probably due to the location of the oil within the insoluble cell walls, requiring that the oil pass through the walls by slow osmotic pressure differences.

The extent and rate of extraction of the oil is greatly enhanced by flaking the soybeans to thicknesses in the 0.005–0.02-in. range. The flaking process ruptures the cell walls, greatly facilitating contacting of the oil with the solvent. Using trichloroethylene [3] or *n*-hexane [1] as the solvent, with flakes of diameters ranging from 0.04 to 0.24 in., approximately 90% of the oil can be extracted in 100 minutes. The ideal solvent for commercial applications of the leaching of soybeans should have a high solubility of the oil to minimize the amount of solvent needed, a high volatility to facilitate the recovery of solvent from the oil by evaporation or distillation, nonflammability to eliminate the chance of fire and explosion, low cost, ready availability, chemical stability, low toxicity, and compatibility with inexpensive materials of construction to minimize or eliminate corrosion. Although in a number of respects, especially nonflammability, trichloroethylene is an ideal solvent, it is now considered to be a very hazardous chemical because of its high toxicity. The favored solvent is commercial hexane (mostly *n*-hexane), which presents a fire hazard but has a low toxicity.

The pilot-plant leaching unit used by Othmer and Agarwal, and known as the Kennedy extractor, is shown in Figure 16.1. The soybeans enter continuously at the low end and are leached in a countercurrent cascade of tubs by hexane solvent, which enters at the upper end. The flakes and solvent are agitated and the underflows are pushed uphill from one tub to the next by slowly rotating paddles and scrapers, while the overflows move downhill from tub to tub. The paddles are perforated to drain the solids when they are lifted above the liquid level in the tub by the paddle. The cascade can contain as many tubs as required; Othmer and Agarwal used 15.

Soybean flakes of 0.012 in. average thickness and containing, on the average, 10.67 wt% moisture and 0.2675 g oil/g dry oil-free flakes were fed to the Kennedy extractor at a continuous flow rate of 6.375 lb/h. The solvent flow rate was 10.844 lb/h. Leaching took place at ambient conditions. After 11 hours of operation, a steady state was achieved that delivered an extract, called a *miscella,* of 7.313 lb/hr, containing 15.35 wt% oil. The leached solids contained 0.0151 g oil/g dry oil-free flakes. Thus, 94.4% of the oil was extracted. The residence time in each tub was 3 minutes, giving a total residence time of 45 minutes. From these data, a mass-balance check can be made for oil and solvent, and the liquid-to-solids ratio in the leached solids can be estimated. These calculations are left as an exercise.

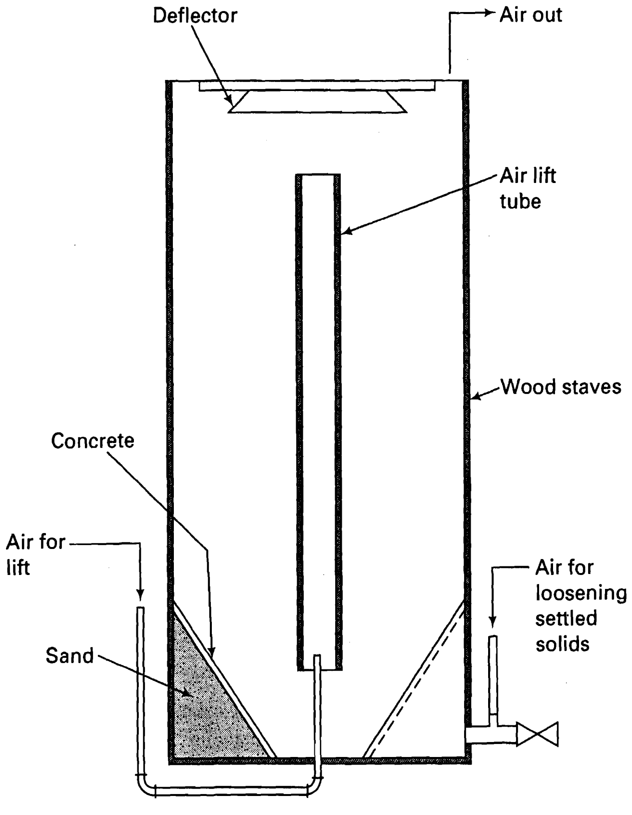
16.1 EQUIPMENT FOR LEACHING

Often, the solids to be leached must undergo pretreatment before being fed to the extraction equipment, in order to obtain reasonable leaching times. For example, seeds and beans are dehulled, cracked, and flaked, as described above for soybeans. When vegetable and animal material cannot be flaked, it may be possible to cut it into thin slices, as is done with sugar beets prior to the leaching of the sugar with water. In this case, the cell walls are left largely intact to minimize the leaching of undesirable material, such as colloids and albumens. Metallurgical ores are crushed and ground to small particles because the small regions of leachable material may be surrounded by relatively impermeable insoluble material. When the insoluble material is quartzite, leaching may be extremely slow. Van Arsdale [4] cites the very important effect of particle size on the time required for effective leaching by aqueous sulfuric acid of a copper ore. The times for particle diameters of 150 mm, 6 mm, and less than 0.25 mm are approximately 5 years, 5 days, and 5 hours, respectively. When the solid to be leached contains a high percentage of solute, pretreatment may not be necessary because disintegration of the remaining skeleton of insoluble material may take place at the surface of the particles as leaching takes place. When the entire solid is soluble, leaching may be rapid, such that only one stage of extraction, called *dissolution,* may be required.

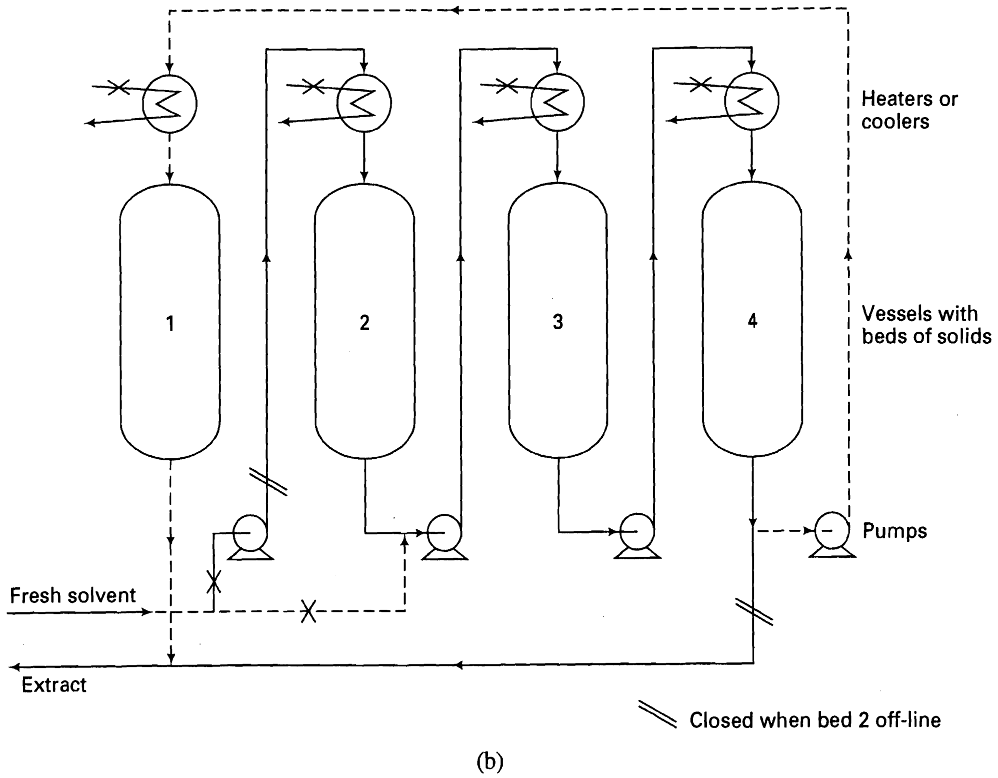
Industrial equipment for solid–liquid extraction is designed for either batchwise or continuous processing. The method of contacting of the solid with the solvent is either by *percolation* of the solvent through a bed of solids or by *immersion* of the solid in the solvent with agitation of the solid–liquid mixture. When immersion is used, countercurrent, multistage operation is common. With percolation, either a stagewise or differential contacting device can be used. An extractor must be efficient for its particular application so as to minimize the need for solvent because of the high cost of solvent recovery.

Batch Extractors

When the solids to be leached are in the form of fine particles, perhaps smaller than 0.1 mm in diameter, batch leaching is conveniently conducted in an agitated vessel. A simple configuration is the Pachuca tank [5], shown in Figure 16.2a and used extensively in the metallurgical industry. The tank is a tall, cylindrical vessel constructed of wood, concrete, or a metal-like steel, which can be lined with an inert,



(a)



(b)

Figure 16.2 (a) Pachuca tank for batch leaching of small particles.

[From *Handbook of Separation Techniques for Chemical Engineers,* 2nd edition, P.A. Schweitzer, Editor-in-chief, McGraw-Hill, New York (1988) with permission.]

(b) Shanks countercurrent multibatch battery system for leaching of large particles by percolation.

[From C.J. King, *Separation Processes,* 2nd edition, McGraw-Hill, New York (1980) with permission.]

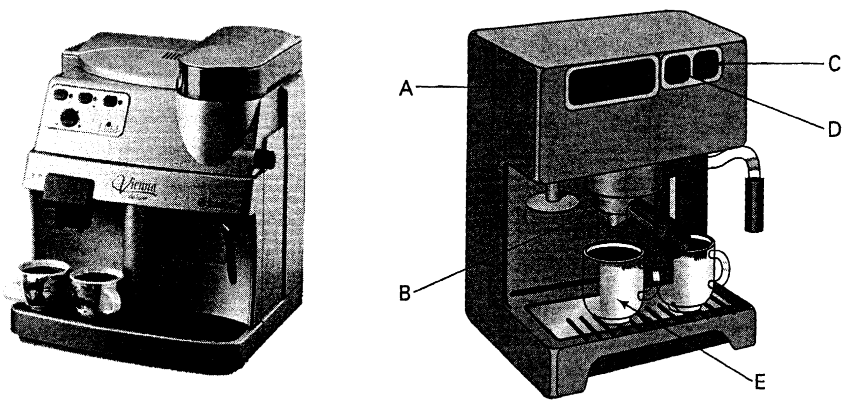
noncorrosive material such as lead. The solvent and solids are placed in the tank and agitation is achieved by an air lift, whereby air bubbles entering at the bottom of a circular tube, concentric with the tank, cause upward flow and subsequent circulation of the solid–liquid suspension. During agitation, air continuously enters and leaves the vessel. When the desired degree of leaching has been accomplished, agitation is stopped and the solids are allowed to settle into a sludge at the bottom, from where the sludge is removed with the assistance of air. The supernatant extract is removed by siphoning from the top of the tank. Agitation can also be achieved by a paddle stirrer or by the use of a propeller mounted in a draft tube in a manner to provide upward flow and subsequent circulation of the solid–liquid suspension, much like that in the Pachuca tank.

When the solids are too coarse to be easily suspended by immersion in the solvent with agitation, the percolation technique can be used. Again a tall, cylindrical vessel is employed. The solids to be leached are dumped into the vessel, followed by percolation of the solvent down through the bed of solids, much like fixed-bed adsorption. To achieve a high concentration of the solute in the solvent, a series of vessels is arranged in a multibatch, countercurrent-leaching technique developed in 1841 by James Shanks and often called an extraction battery using the Shanks system. This technique can be used for such applications as the batch removal of tannin from wood or bark, sugar from sugar beets, and water-soluble substances from coffee, tea, and spices. A typical arrangement of vessels is shown in Figure 16.2b, where Vessel 1 is shown off-line for emptying and refilling of solids. The solvent enters and percolates down through the solids in Vessel 2, and then percolates through Vessels 3 and 4, leaving as final extract from Vessel 4. The extraction of solids in Vessel 2 is completed first. When that occurs, Vessel 2 is taken off-line for emptying and refilling of solids and Vessel 1 is placed on-line. Now the fresh solvent first enters Vessel 3, followed by Vessels 4 and 1. In this manner, fresh solvent always contacts the solids that have been leached for the longest time, thus realizing the benefits of countercurrent contacting. Heat exchangers are provided between vessels to adjust the temperature of the liquid phase, and pumps can be used to move the liquid from vessel to vessel. Any number of vessels can be included in the battery. Although the Shanks system is batchwise with respect to the solids, the system is continuous with respect to the solvent and extract.

Espresso Machine

A widely used batch-leaching machine is the espresso coffee maker. Although a beverage from coffee beans was first made about 1100 BC on the Arabian peninsula, it was not until many centuries later that a method and a machine was devised to produce a high-quality coffee, called espresso (a term that connotes a cup of coffee expressly for you, made quickly and individually, and intended to be drunk right away). The prototype of the espresso machine was created in France in 1822, and the first commercial espresso machine was manufactured in Italy in 1905. By the 1990s, espresso machines were in common use in many countries of the world, producing billions of cups annually. Today, coffee, and, particularly, espresso, is a world commodity that is second only to oil.

A photograph of a typical consumer espresso machine is shown in Figure 16.3a, while a simpler diagram to help understand its operation is presented in Figure 16.3b. In the machine, 7 to 9 grams of coffee beans are ground to a powder of particle size ranging from 250 to 750 microns by a special burr grinder that minimizes the temperature increase of the grounds. The bed of powder, contained as a thin layer in a filter housing, is tamped to increase its uniformity. Water is pumped to a pressure of 9–15 atmospheres and heated rapidly to from 88 to 92°C. The high pressure is required for pressure infusion of hot water into the particles so that extraction can proceed rapidly. During a period of from 20 to 30 sec, the hot water is percolated through the bed of coffee powder to produce a 45-ml shot. The shot has a viscosity of warm honey, and is topped by a thick, dark, golden-cream foam ("crema"). A typical machine produces two shots, which can be added to water, milk, or other liquids or blends to produce various beverages, including



(a) (b)

Figure 16.3 (a) Consumer espresso machine. (b) Operation: (A) pressure vessel, (B) portafilter holding ground coffee, (C) on/off switch, with built-in pressure indicator, (D) solenoid valve for espresso coffee, (E) shot cup holding leached, espresso coffee.

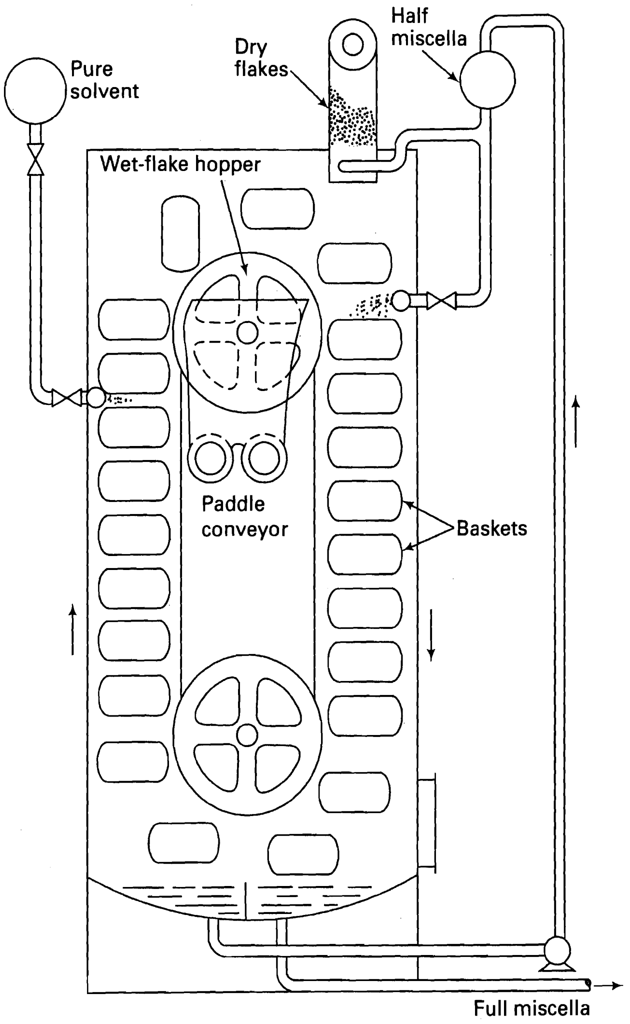
Americano, Breve, Cappuccino, Latte, Lungo, Macchiato, Mocha, or Ristretto.

The short-time interval between grinding and leaching, the short residence time of the leaching process, the very small particle size of the coffee powder, and the controlled temperature and pressure of the water during leaching combine to maximize the extraction of the favorable flavor-and-aroma chemicals and minimize the extraction of chemicals associated with bitterness, such as quinine and caffeine. Furthermore, the creama traps the aroma, preventing its escape into the surrounding air. At the pull of a lever or the push of a button, espresso coffee is produced that is concentrated, full in body, and rich in flavor and aroma. A number of experimental studies of espresso production are reported in the literature, e.g., Andueza et al. [16, 17, 18].

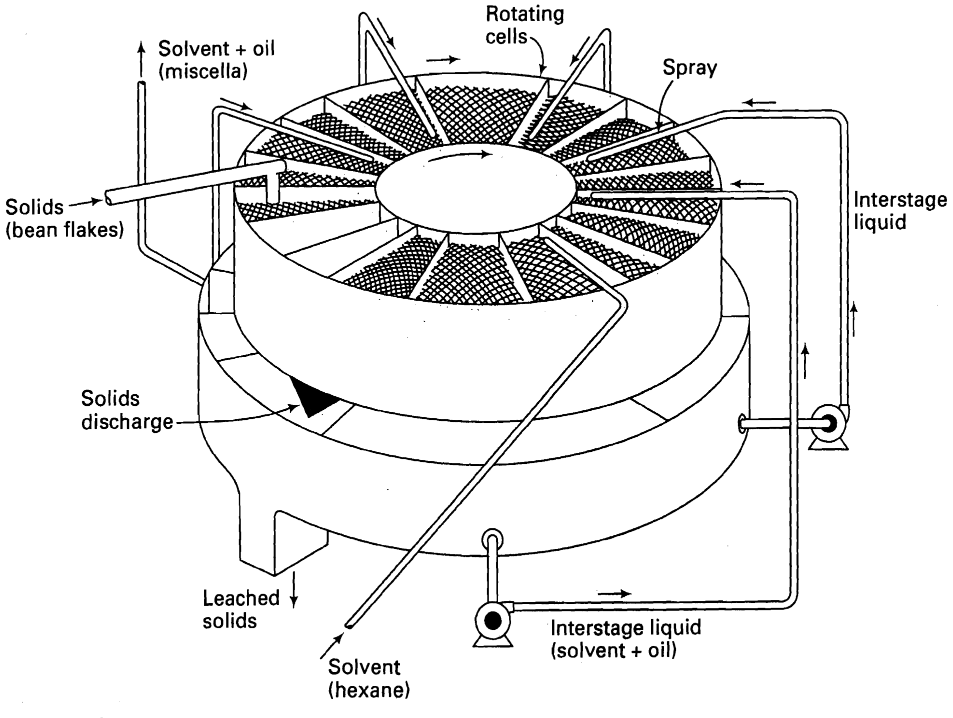
Continuous Extractors

When leaching is to be carried out on a large scale, it is preferable to use an extraction device that can be operated with continuous flow of both solids and liquid. Many such patented devices are commercially available, especially for applications in the food industry, as discussed by Schwartzberg [6]. Some of the more widely discussed extractors are shown schematically in Figure 16.4. These devices differ mainly with respect to the manner in which the solids are transported through and the degree to which agitation of the solid–liquid mixture is provided in the equipment.

According to Schwartzberg, several extractors that have been described in the literature are now either obsolete or infrequently used, because of various limitations, including ineffective contacting of solid and liquid phases, bypassing,



(a) Bollman vertical, moving-basket, conveyor extractor



(b) Rotocel extractor

Figure 16.4 Equipment for continuous leaching.

[From *Handbook of Separation Techniques for Chemical Engineers,* 2nd edition, P.A. Schweitzer, Editor-in-chief, McGraw-Hill, New York (1988) with permission.]

[From R.E. Treybal, *Mass-Transfer Operations,* 3rd edition, McGraw-Hill, New York (1980) with permission.]

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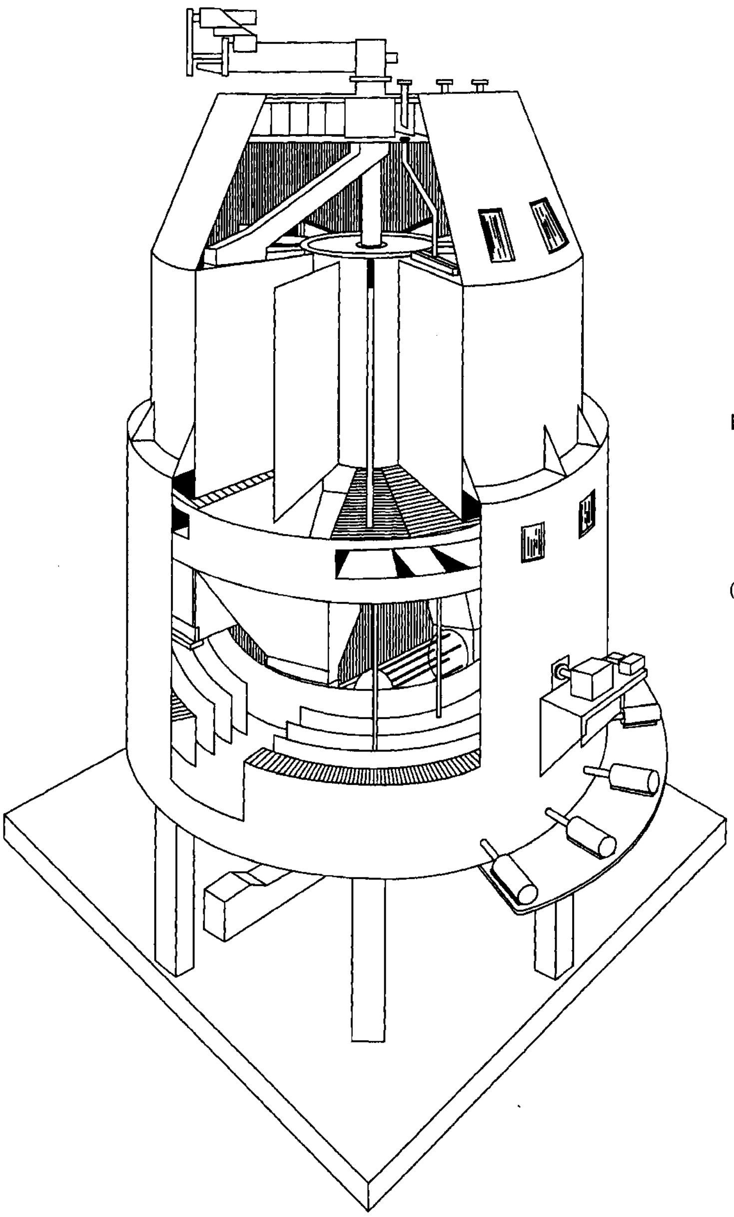
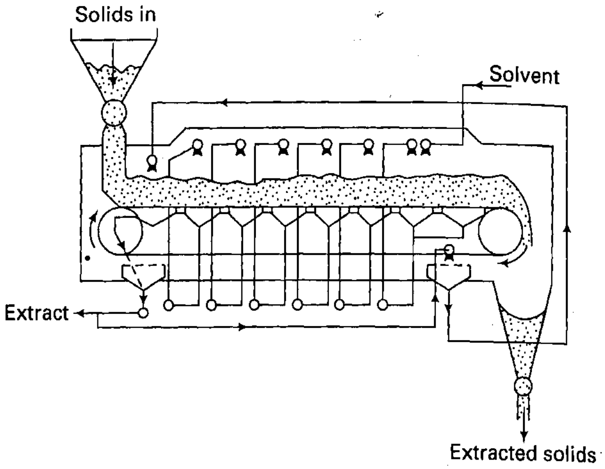
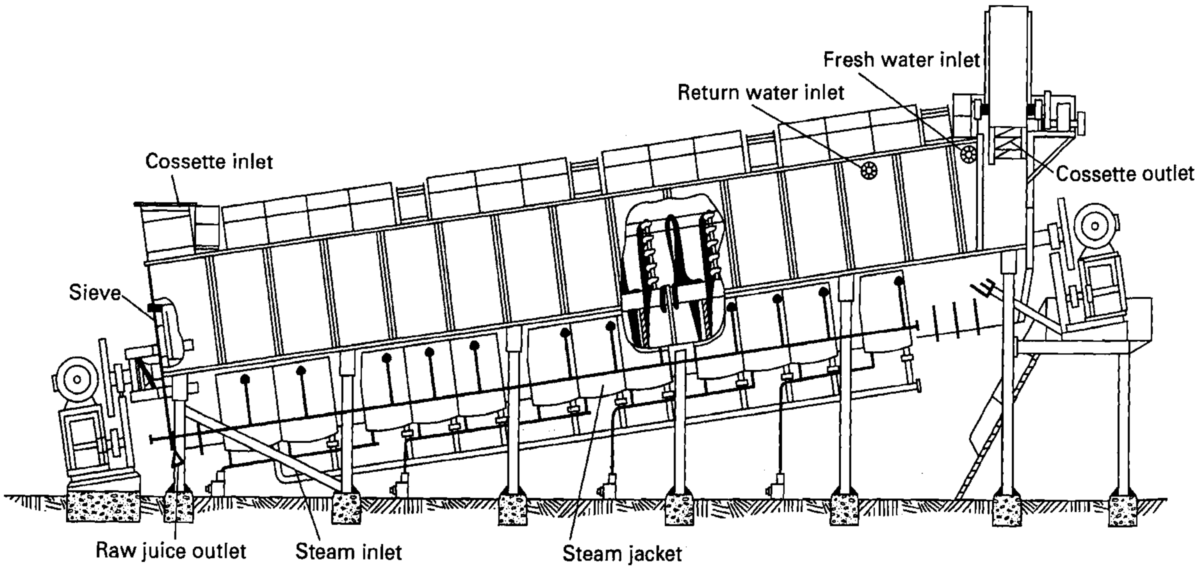


(c) French stationary-basket extractor



(d) Continuous, perforated-belt extractor



(e) D.D.S. double-screw, slope extractor

Figure 16.4 (*Continued*).

and fines entrainment. These include the Hildebrand, Detrex, Anderson, Allis Chalmers, and Bonotto extractors. The Kennedy extractor described above for application to oil extraction from soybeans may also have a low efficiency in some applications, but is still used and still available.

The Bollman vertical moving-basket conveyor extractor, shown in Figure 16.4a, has been widely used to extract oil from flaked seeds and beans. Baskets with perforated bottoms are moved around a vertical loop by a motor-driven chain drive. The solvent percolates down, from basket to basket, through the solids. When a basket reaches the top of the extractor, the basket is inverted to dump the extracted solids and then filled with fresh solids. The flow of liquid is countercurrent to the solids contained in ascending baskets and cocurrent in descending baskets. Fresh solvent enters near the top of the ascending leg and collects as "half miscella" in the left-hand part of the sump at the bottom. From there, the half miscella is pumped to the top of the descending leg, from which it flows down to the right-hand part of the sump and is withdrawn as final extract, called "full miscella." A typical Bollman extractor is 14 m high, with each basket filled with solids to a depth of about 0.5 m. According to Coulson et al. [7], the baskets are rotated very slowly at about one revolution per hour so as to give solids residence times of about 60 minutes. Each basket contains about 350 kg of flaked solids. Thus, for the 23 baskets shown in Figure 16.4a, almost 200,000 kg of solids can be extracted per day. About equal mass flows of flaked solids and solvent are fed to the extractor, and the full miscella is essentially solids-free with about 25 wt% oil.

Another widely used continuous extractor for flaked seeds and beans is the Rotocel extractor, shown in Figure 16.4b. In this device, which resembles a carousel and conveniently simulates the Shanks system, walled, annular sectors, called cells, on a horizontal plane, are slowly rotated by a motor. The cells, which hold the solids and are perforated on the bottom for solvent drainage, successively pass a solids feed area, a series of solvent sprays, a final spray and drainage area, and a solids-discharge area. Fresh solvent is supplied to the cell located just below the final spray and drainage area, from where the drained liquid is collected and pumped to the preceding cell location. The drainage from that cell is collected and pumped to the cell preceding that cell and so on. In this manner, a countercurrent flow of solids and liquid is achieved. The extracted solids typically contain 25–30 wt% liquid. Rotocel extractors are typically 3.4–11.3 m in diameter, 6.4–7.3 m in height, with bed depths of 1.8–3.0 m. They have processed up to three-million kg/day of flaked soybeans. The number of cells can be varied and residence time can be varied by varying the rate of rotation. A widely used variation of the Rotocel extractor is the French stationary-basket extractor, which is shown in Figure 16.4c and has about the same size and capacity as the Rotocel extractor. The sectored cells do not move. Instead, the solids feed spout and solids discharge zone rotate, with periodic switching of the solvent feed and discharge connections. Thus, the weight of moving parts is reduced.

Continuous, perforated-belt extractors of the type shown in Figure 16.4d are widely used to process sugar cane, sugar beets, oilseeds, and apples (for apple juice). The feed solids are fed from a hopper to a slow-moving, continuous and non-partitioned, perforated belt driven by motorized sprockets at either end. The height of the solids on the belt can be controlled by a damper at the outlet of the feed hopper. The belt speed is automatically adjusted to maintain the desired depth of solids. Extracted solids are discharged into an outlet hopper at the end of the belt by a scraper. Side walls prevent the solids from falling off the sides of the belt. Below the belt are compartments for collecting solvent. Fresh solvent is sprayed over the solids and above the compartments in a countercurrent fashion, starting from the discharge-end of the belt, in as many as 17 passes. Bed depths may range from 0.8 to 2.6 m. Units from 7 to 37 m long and with belts from 0.5 to 9.5 m wide have processed as much as 7,000,000 kg/day of sugar cane or sugar beets.

The D.D.S. (De Danske Sukker–fabriker) double-screw, slope extractor, shown in Figure 16.4e, is a very versatile unit. Although used mainly for extraction of sugar beets, the device has been applied successfully to a very wide range of other feed materials, including sugar cane, flaked seeds and beans, apples, pears, grapes, cherries, ginger, licorice, red beets, carrots, fishmeal, coffee, and tea. The opposite-turning screws of the metal ribbons are pitched so that they both move the solids uphill in parallel, cylindrical troughs. Extract flows through the screw surface downhill to achieve a differential, countercurrent flow with the solids. A novel feature is the ability to turn one screw slightly faster and then slightly slower than the other screw, causing the solids to be periodically squeezed. Units range in size from 2 to 3.7 m in diameter and 21–27 m in length and have been used to process as much as 3,000,000 kg/day of sugar beets in the form of cossettes (long, thin strips).

Continuous, Countercurrent Washing

When leaching is very rapid, as with small particles containing very soluble solutes, or when leaching has already been completed, or when solids are formed by chemical reactions in a solution, it is common to countercurrently wash the solids to reduce the concentration of the solute in the liquid adhering to the solids. This can be accomplished in a series of *gravity thickeners* or centrifugal thickeners, called *hydroclones,* arranged for countercurrent flow of the underflows and overflows as shown in Figure 16.5, and sometimes called a continuous, countercurrent decantation system. A typical continuous gravity thickener is shown in detail in Figure 16.6a. The combined feed to the thickener consists of feed solids or underflow from an adjacent thickener, together with fresh solvent or overflow from an adjacent thickener. The thickener has a threefold function. First, it must thoroughly mix the liquid and solids to obtain a uniform concentration of solute in the liquid. The thickener must also produce an overflow free of solids and an underflow with as

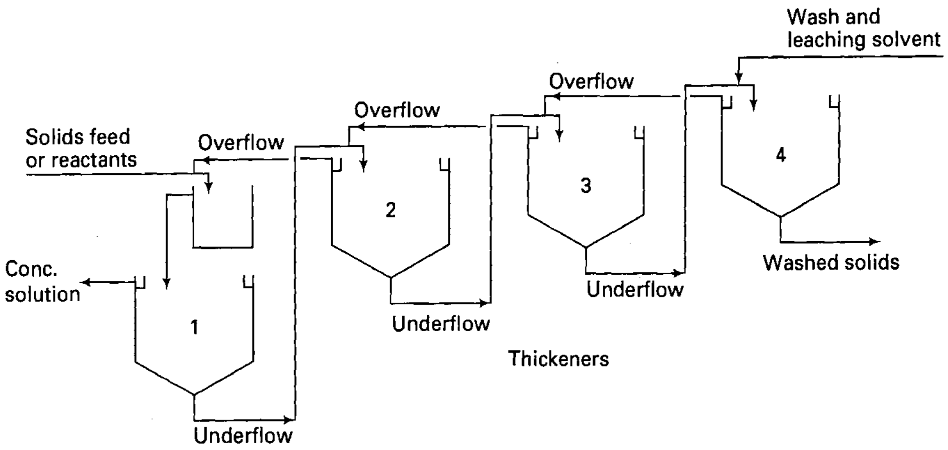
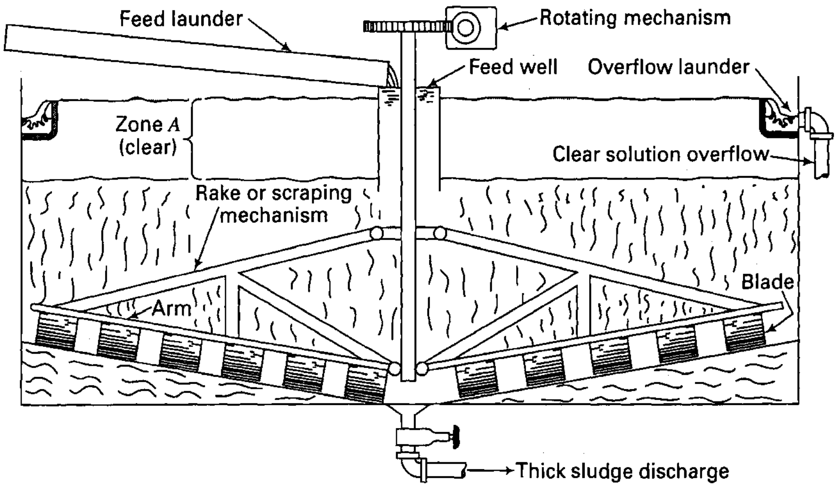
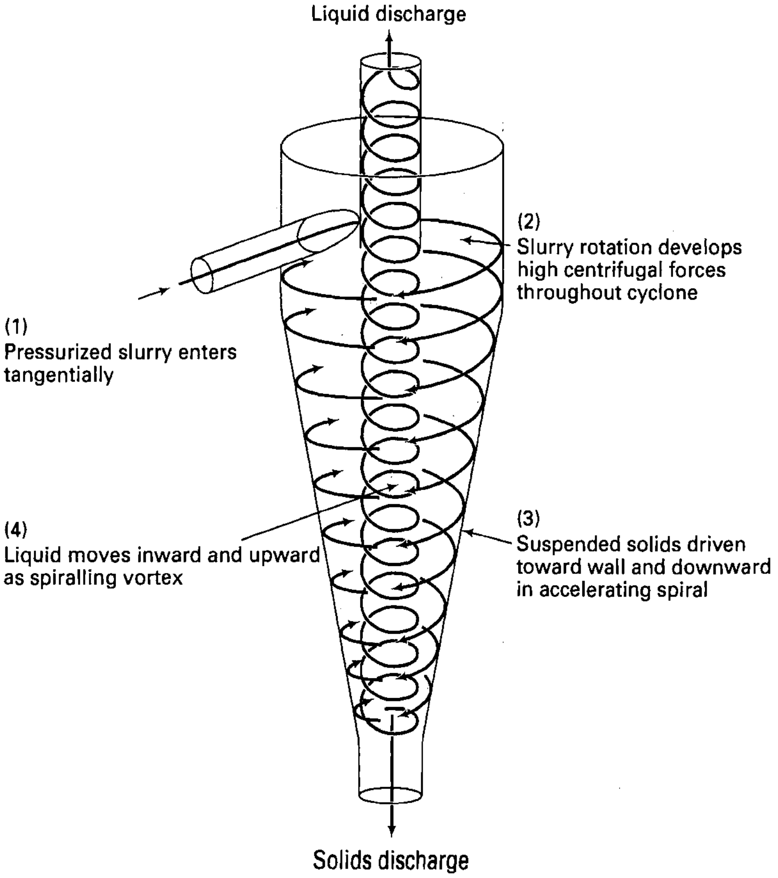


Figure 16.5 Continuous, countercurrent washing system using thickeners.



(a) Gravity thickener



(b) Hydroclone, centrifugal thickener

Figure 16.6 Thickeners.

[From *Handbook of Separation Techniques for Chemical Engineers*, 2nd edition, P.A. Schweitzer, Editor-in-chief, McGraw-Hill, New York (1988) with permission.]

high a fraction of solids as possible. The thickener consists of a large-diameter shallow tank with a flat or slightly conical bottom. The combined feed enters the tank near the center by a means of a feed launder that discharges into a feed well. Settling and sedimentation of the solid particles occur by gravity due to a solid particle density that is greater than the liquid density. In essence, solids flow downward and liquid flows upward. Around the upper, inner periphery of the tank is an overflow launder or weir for continuously removing clarified liquid. Solids settling to the bottom of the tank are moved inward toward a thick sludge discharge by a slowly rotating motor-driven rake. Thickeners as large as 100 m in diameter and 3.5 m high have been constructed. In large thickeners, the rake revolves at about 2 rpm.

The residence times of solids and liquids in a gravity thickener are often large (minutes or hours) and, as such, are sufficient to provide adequate residence time for mass transfer and mixing when small particles are involved. When long residence times are not needed and the overflow need not be perfectly clear of solids, the hydroclone, shown in Figure 16.6b, should be considered. The pressurized feed slurry enters the device tangentially to create, by centrifugal force, a downward spiraling motion. The higher-density, suspended solids are, by preference, driven to the wall, which becomes conical as it extends downward, and discharged as a thickened slurry at the bottom of the hydroclone. The liquid, which is forced to move inward and upward as a spiraling vortex, exits from a vortex-finder pipe that extends downward from the closed top of the hydroclone to a location just below the feed entry.

16.2 EQUILIBRIUM-STAGE MODEL FOR LEACHING AND WASHING

The simplest model for a continuous, countercurrent leaching and washing system, as shown in Figure 16.7, assumes that the solid feed consists of a solute, which is completely soluble in the solvent, and an inert substance or carrier that is not soluble in the solvent. Furthermore, the rate of leaching is rapid such that it is completed in a single leaching stage, which is followed by a series of one or more washing stages to reduce the concentration of solute in the liquid adhering to the solids in the underflow streams. All overflow streams are assumed to be free of solids. In Figure 16.7:

S = mass flow rate of inert solids, which is constant from stage to stage.

V = mass flow rate of entering solvent or overflow liquid (solvent plus solute), which varies from stage to stage.

L = mass flow rate of underflow liquid (solvent plus solute), which varies from stage to stage.

y = mass fraction of solute in the overflow liquid.

x = mass fraction of solute in the underflow liquid.

Alternatively, V and L can refer to mass flow rates of solvent on a solute-free basis and the symbols Y and X can be used to refer to mass ratios of solute to solvent in the overflow liquid and underflow liquid, respectively. Mole or volume flow rates can also be used.

An ideal leaching or washing stage is defined by Baker [8] as one where:

1. Any entering solid solute is completely dissolved into the liquid in the stage (assuming that the liquid contains sufficient solvent).
2. The composition of the liquid in the stage is uniform throughout, including any liquid within pores of the inert solid.
3. Solute is not adsorbed on the surfaces of the inert solid.
4. The inert solids leaving in the underflow from each stage are wet with liquid, such that mass ratio of solvent in that liquid (or the total liquid) to inert solids is constant from stage to stage.
5. Because of (2), the concentration of solute in the overflow is equal to that in the liquid portion of the underflow. This is equivalent to an equilibrium assumption.
6. Overflows contain no solids.
7. Solvent is not vaporized, adsorbed, or crystallized in a stage.

For the continuous, countercurrent system of ideal leaching stages in Figure 16.7, solute and total-liquid material balances can be used to solve various types of problems, including (1) the determination of the number of ideal stages required to achieve a specified degree of washing and (2) the

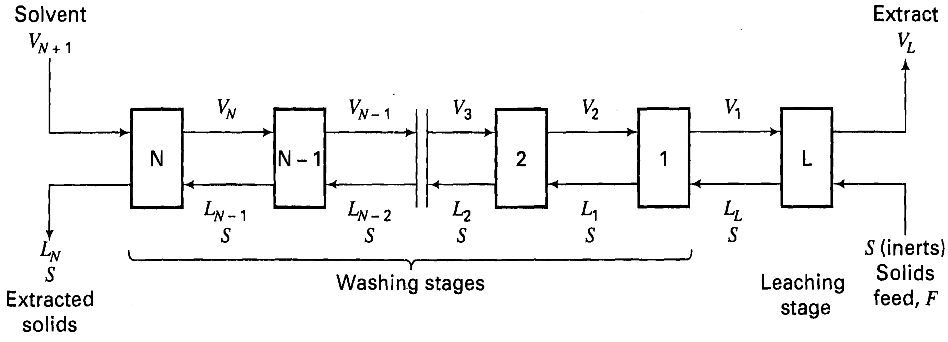


Figure 16.7 Continuous, countercurrent, ideal-stage leaching and washing system.

determination of the effect of washing for a specified degree of washing for a specified number of ideal stages. Depending on the nature of the problem, either an algebraic or a graphical method may be preferred. For most problems, it is usually best to consider the leaching stage separate from the washing stages, as illustrated in the following examples.

EXAMPLE 16.1

A finely divided solids feed, F, of 150 kg/h, containing 1/3 water-soluble Na_2CO_3 and 2/3 insoluble ash is to be leached and washed at 30°C in a two-stage, countercurrent system with 400 kg/h of water. The leaching stage consists of an agitated vessel that discharges the slurry into a thickener. The washing stage consists of a second thickener. Experiments show that the sludge underflow from each thickener will contain 2 kg of liquid (water and carbonate) per kg of insoluble ash. Assume ideal stages.

(a) Calculate the percent (%) recovery of carbonate in the final extract.

(b) If a third stage is added, calculate the amount of additional carbonate that will be recovered.

SOLUTION

At 30°C, the solubility of the carbonate in water is 38.8 kg/100 kg of water. Therefore, there is sufficient water to dissolve all the carbonate. Referring to Figure 16.7:

(a) $N = 1$ (L is the leaching stage)

$$S = \frac{2}{3}(150) = 100 \text{ kg/h of insoluble ash}$$

$$Na_2CO_3 \text{ in entering solids} = \frac{1}{3}(150) = 50 \text{ kg/h}$$

$$V_2 = \text{entering solvent} = 400 \text{ kg/h}$$

$$L_L = L_1 = 2S = 200 \text{ kg/h}$$

By total liquid material balances on Stage 1 and Stage L,

$$V_1 = V_2 + L_L - L_1 = 400 + 200 - 200 = 400 \text{ kg/h}$$
$$V_L = V_1 + 50 - L_L = 400 + 50 - 200 = 250 \text{ kg/h}$$

Na_2CO_3 material balance around washing Stage 1:

$$x_L L_L = y_1 V_1 + x_1 L_1 \tag{1}$$
$$200x_L = 400y_1 + 200x_1 \tag{2}$$

But, $y_1 = x_1$ from item (5) above for an ideal stage.

Combining (1) and (2),

$$x_L = 3x_1 \tag{3}$$

Na_2CO_3 material balance around leaching Stage L:

$$y_1 V_1 + 50 = x_L L_L + y_L V_L \tag{4}$$
$$400y_1 + 50 = 200x_L + 250y_L \tag{5}$$

But, again $\quad y_1 = x_1$ and $y_L = x_L \quad$ (6)

Combining (4), (5), and (6),

$$x_1 = 1.125x_L - 0.125 \tag{7}$$

Combining (3) and (7) and solving,

$$x_L = 0.158$$

Therefore, $y_L = 0.158$

From (7),

$$x_1 = 0.0526$$

$$\text{Recovery of } Na_2CO_3 = \frac{y_L V_L}{50} = \frac{(0.158)(250)}{50}$$
$$= 0.79 \text{ or } 79\%$$

(b) $N = 2$ washing stages

$$V_3 = 400 \text{ kg/h}$$
$$L_L = L_1 = L_2 = 2S = 200 \text{ kg/h}$$
$$V_2 = V_1 = 400 \text{ kg/h}$$
$$V_L = 250 \text{ kg/h}$$

Na_2CO_3 material balance around Stage 2:

$$\begin{aligned} x_1 L_1 &= y_2 V_2 + x_2 L_2 \\ 200x_1 &= 400y_2 + 200x_2 \end{aligned} \tag{8}$$

But, $\quad y_2 = x_2 \quad$ (9)

Combining (8) and (9),

$$x_1 = 3x_2 \tag{10}$$

Na_2CO_3 material balance around Stage 1:

$$\begin{aligned} y_2 V_2 + x_L L_L &= x_1 L_1 + y_1 V_1 \\ 400y_2 + 200x_L &= 200x_1 + 400y_1 \end{aligned} \tag{11}$$

But, $\quad y_2 = x_2 \quad$ (12)

$y_1 = x_1 \quad$ (13)

Combining (11), (12), and (13),

$$x_L = 3x_1 - 2x_2 \tag{14}$$

Na_2CO_3 material balance around Stage L:

This is the same as (7) in Part (a).

Solving (10), (14), and (7), which are all linear,

$$x_L = 0.1795$$
$$y_L = 0.1795$$
$$x_1 = 0.0769$$
$$x_2 = 0.0256$$

Recovery of $Na_2CO_3 = \frac{y_L V_L}{50} = \frac{(0.1795)(250)}{50} = 0.898$ or 89.8%

From Part (a), for two stages, recovery of Na_2CO_3 is $0.158(250) = 39.5$ kg/h

For three stages, recovery is $0.1795(250) = 44.9$ kg/h

Recover $44.9 - 39.5 = 5.4$ kg/h more Na_2CO_3 with three stages.

For this example, it is difficult to apply a graphical McCabe–Thiele-type method because only the slope of the operating line is known and not either end point.

EXAMPLE 16.2

Baker [8] presents the following problem, for which a McCabe–Thiele graphical method can be applied. Two tons (4,000 lb) per day of waxed paper containing 25 wt% soluble wax and 75 wt% insoluble pulp are to be dewaxed by leaching with kerosene in a continuous, countercurrent contacting system of the type shown in Figure 16.7. The wax will be completely dissolved by the kerosene in the leaching stage, L. Subsequent washing stages will be used to reduce the wax content in the liquid adhering to the pulp leaving the last stage, N, to 0.2 lb wax/100 lb pulp. The kerosene entering the system is recycled from a solvent-recovery system and contains 0.05 lb wax/100 lb kerosene. The final extract is to contain 5 lb wax/100 lb kerosene. Experiments show that the underflow from each stage will contain 2 lb kerosene/lb insoluble pulp. Determine the number of washing stages required, exclusive of the leaching stage.

SOLUTION

Referring to Figure 16.7 and using the nomenclature defined at the beginning of this section for the case of concentrations on a mass-ratio basis and flow rates on a solute-free basis, the following material balance equations apply:

Overall mass balance on solute (wax):

$$0.25(4{,}000) + \frac{0.05}{100}V_{N+1} = \frac{5}{100}V_L + \frac{0.2}{100}(0.75)(4{,}000)$$

or

$$0.05V_L - 0.0005V_{N+1} = 994 \qquad (1)$$

Overall mass balance on solvent (kerosene):

$$V_{N+1} = V_L + 2(0.75)(4{,}000)$$

or

$$V_{N+1} = V_L + 6{,}000 \qquad (2)$$

Solving (1) and (2)

$$V_{N+1} = \text{kerosene in entering solvent} = 26{,}140 \text{ lb/day}$$
$$V_L = \text{kerosene in exiting extract} = 20{,}140 \text{ lb/day}$$

Thus, the final underflow contains 26,140 − 20,140 = 6,000 lb/day of kerosene. Also,

$$X_N = \left[\frac{0.2}{100}(0.75)(4{,}000)\right]\Big/6{,}000$$
$$= 0.001 \text{ lb wax/lb kerosene in the final underflow.}$$

Material balances can now be made around the leaching stage.

Mass balance on kerosene:

$$V_1 = V_L + 2(0.75)(4{,}000)$$

Thus,

$$V_1 = 20{,}140 + 6{,}000 = 26{,}140 \text{ lb/day}$$

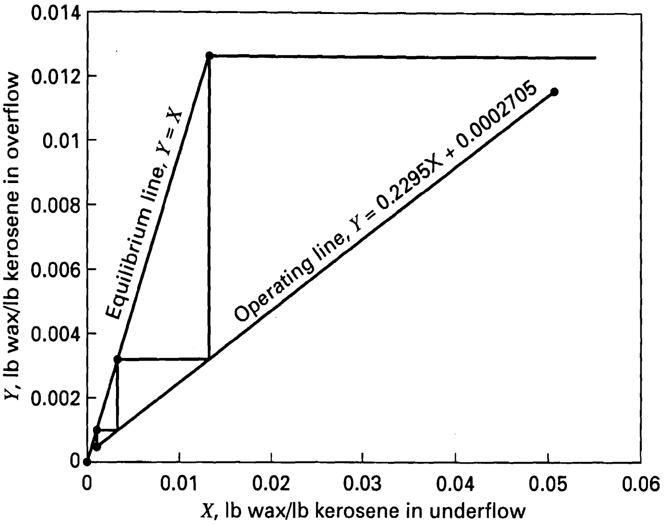


Figure 16.8 McCabe–Thiele diagram for Example 16.2.

Mass balance on wax:

$$\begin{aligned}26{,}140\,Y_1 + (0.25)(4{,}000) = \frac{5}{100}&(20{,}140)\\ &+ X_L(2)(0.75)(4{,}000)\end{aligned} \qquad (3)$$

But

$$X_L = Y_L = 0.05 \text{ lb wax/lb kerosene} \qquad (4)$$

Substituting (4) into (3) and solving,

$$Y_1 = 0.01174 \text{ lb wax/lb kerosene}$$

We now have the end points (solute compositions) at the two ends of the washing cascade. Referring to Figure 16.7,

$$Y_{N+1} = 0.0005 \quad \text{and} \quad X_N = 0.001 \text{ in lb wax/lb kerosene}$$
$$Y_1 = 0.01174 \quad \text{and} \quad X_L = 0.05 \text{ in lb wax/lb kerosene}$$

Furthermore, for the washing section, the mass ratio of kerosene in the underflow to kerosene in the overflow is constant at a value of

$$\frac{L_{n-1}}{V_n} = \frac{2(0.75)(4{,}000)}{26{,}140} = 0.2295$$

Therefore, the operating line on a McCabe–Thiele plot of Y versus X will be a straight line through the two end points, with a slope of 0.2295. This corresponds to a line given by the equation, $Y = 0.2295X + 0.0002705$. The equilibrium line is simply $Y = X$. The operating and equilibrium lines are plotted in Figure 16.8. The ideal washing stages, which can be stepped off starting from either end of the operating line, are stepped off here from stage N. It is seen that slightly less than three ideal washing stages are needed.

McCabe–Smith Algebraic Method

It is seen in Figure 16.8 that it can be difficult to accurately step off the number of washing stages. When the above ideal-stage model of Baker [8] applies, a more accurate algebraic method, developed by McCabe and Smith [9] from the Kremser equation of Chapter 5, can be applied. The method is developed here using solute concentrations in mass fractions, but the final equations can also be applied with mass ratios.

Combining (5-48), (5-50), (5-51), and (5-54),

$$y_{N+1} = y_1\left(\frac{1-A^{N+1}}{1-A}\right) - y_0^* A\left(\frac{1-A^N}{1-A}\right) \qquad (16\text{-}1)$$

where N = number of ideal washing stages and

$$y_0^* = Kx_0 = Kx_L = y_L \qquad (16\text{-}2)$$

For washing,

$$K = y/x = 1 \text{ and, therefore, } A = L/KV = L/V$$

Equation (16-1) can be written as follows by collecting terms in A^{N+1} and A:

$$A^{N+1}(y_1 - y_L) = A(y_{N+1} - y_L) + (y_1 - y_{N+1}) \qquad (16\text{-}3)$$

This equation can be simplified by writing an overall solute balance around all washing stages:

$$y_{N+1}V_{N+1} + x_L L_L = y_1 V_1 + x_N L_N \qquad (16\text{-}4)$$

But, for ideal washing stages, since

$$V_{N+1} = V_1, \quad L_L = L_N, \quad \text{and} \quad A = L/V,$$

(16-4) can be simplified to

$$y_{N+1} = y_1 + Ax_N - Ax_L \qquad (16\text{-}5)$$

But $y_L = x_L$. Therefore, (16-5) can be written:

$$(y_1 - y_{N+1}) = A(y_L - x_N) \qquad (16\text{-}6)$$

Combining (16-3) and (16-6) and rearranging gives

$$A^N = \left(\frac{y_{N+1} - x_N}{y_1 - y_L}\right) \qquad (16\text{-}7)$$

Solving (16-7) for N with $A = L/V$, gives

$$N = \frac{\log\left(\dfrac{x_N - y_{N+1}}{y_L - y_1}\right)}{\log(L/V)} \qquad (16\text{-}8)$$

The argument of the log term of the denominator can be written in terms of the end points to give

$$\frac{L}{V} = \left(\frac{y_1 - y_{N+1}}{x_L - x_N}\right) = \left(\frac{y_1 - y_{N+1}}{y_L - x_N}\right) \qquad (16\text{-}9)$$

Combining (16-8) and (16-9),

$$N = \frac{\log\left(\dfrac{x_N - y_{N+1}}{y_L - y_1}\right)}{\log\left(\dfrac{y_1 - y_{N+1}}{y_L - x_N}\right)} \qquad (16\text{-}10)$$

When the constant underflow liquid is given in terms of total (solvent plus solute) liquid, (16-8) or (16-9) is used directly, where L and V are total liquid flow rates. When the underflow liquid is given in terms of just the solvent, the y and x solute mass fractions in (16-8) and (16-9) are replaced by Y and X solute mass ratios, and V and L are liquid flow rates of solute-free solvent.

EXAMPLE 16.3

Solve for the number of ideal, continuous, countercurrent washing stages for the conditions of Example 16.2 using the McCabe–Smith equations.

SOLUTION

From the problem statement and the overall material balance and leaching stage calculations for Example 16.2,

$$Y_{N+1} = 0.0005$$
$$X_N = 0.001$$
$$Y_2 = 0.01174$$
$$Y_L = X_L = 0.05$$
$$L/V = 0.2295$$

From the mass ratio form of (16-8), the number of ideal leaching stages is:

$$N = \frac{\log\left(\dfrac{0.001 - 0.0005}{0.05 - 0.01174}\right)}{\log(0.2295)} = 2.95$$

The same result is obtained if (16-10) is used.

When the rate of leaching is slow, several countercurrent stages may be required, during which the effect of washing will be diminished. This is illustrated in the following example.

EXAMPLE 16.4

In Example 16.1, part (b), leaching was assumed to be completed in one stage, with two additional stages provided for washing. The recovery of the solute, Na_2CO_3, in the extract was 89.8%. Recalculate this example, assuming that 1/2 of the carbonate is leached in the first stage and the remaining 1/2 in the second stage, leaving only the last stage as a true washing stage. For convenience, number the stages as in Figure 16.9, which includes flow rates that are given or easily computed.

SOLUTION

Na_2CO_3 material balance around Stage 3:

$$x_2L_2 = y_3V_3 + x_3L_3$$
$$200x_2 = 400y_3 + 200x_3 \qquad (1)$$

But,

$$y_3 = x_3 \qquad (2)$$

Combining (1) and (2),

$$x_2 = 3x_3 \qquad (3)$$

Na_2CO_3 material balance around Stage 2:

$$y_3V_3 + x_1L_1 = x_2L_2 + y_2V_2$$
$$400y_3 + 200x_1 + 25 = 200x_2 + 425y_2 \qquad (4)$$

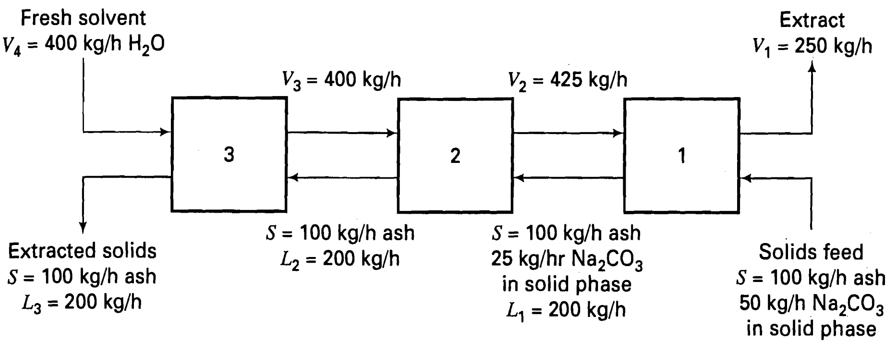


Figure 16.9 Leaching and washing system for Example 16.4.

But,

$$y_2 = x_2 \tag{5}$$

Combining (2), (4), and (5),

$$x_1 = 3.125x_2 - 2x_3 - 0.125 \tag{6}$$

Na_2CO_3 material balance around Stage 1:

$$\begin{aligned} y_2V_2 + 50 &= x_1L_1 + y_1V_1 + 25 \\ 425y_2 + 50 &= 200x_1 + 250y_1 + 25 \end{aligned} \tag{7}$$

But,

$$y_1 = x_1 \tag{8}$$

Combining (5), (7), and (8)

$$x_2 = 1.059x_1 - 0.0588 \tag{9}$$

Solving (3), (6), and (9),

$$x_1 = y_1 = 0.1681$$
$$x_2 = 0.1192$$
$$x_3 = 0.0397$$

Recovery of

$$\mathrm{Na_2CO_3} = \frac{y_1V_1}{50} = \frac{(0.1681)(250)}{50} = 0.841 \text{ or } 84.1\%$$

which is almost 6% less than in Part (b) of Example 16.1, where leaching was completed in one stage.

Variable Underflow

In previous Examples 16.1–16.4, the ratio of liquid to solids in the underflow from stage to stage was assumed to be constant. Experiments by Ravenscroft [10] on the extraction of oil from granulated halibut livers by diethylether showed that the ratio of liquid to solids in the underflow increased significantly with increasing concentration of oil in the liquid in the range of 0.04–0.64 gal oil/gal liquid. In the leaching experiments, equilibrium was achieved in 2–3 minutes of agitation, but 10 minutes was used. Thirty minutes was allowed for settling of the extracted livers, after which the free solution (overflow) was decanted, leaving the underflow. Ravenscroft ascribed the variable-underflow effect to an appreciable increase in viscosity and density of the liquid as the concentration of the oil was increased. When neither density nor viscosity vary significantly, experimental data of Othmer and Agarwal [1] show that the main variable affecting the liquid-to-solid ratio in the underflow is surface area-to-volume ratio of the solids. When the flow rate of underflow varies, the operating line on a McCabe–Thiele diagram will be curved instead of straight. The curvature can be established by computing two arbitrary, intermediate points, as illustrated in the following example.

EXAMPLE 16.5

Oil is to be extracted from 10,000 lb/h of granulated halibut livers, based on oil-free livers, which contain 0.043 gal of extractable oil per pound of oil-free livers. It is desired to extract 95% of the oil in a countercurrent extraction system using oil-free diethylether as the solvent. The final extract is to contain 0.65 gal oil per gal of extract. Assume that the volumes of oil and ether are additive, and that leaching will be completed in one stage. Although the experimental underflow data of Ravenscroft show some scatter, use the following smoothed data to predict underflow rates:

Gal oil per gal liquid	Gal liquid retained per lb oil-free livers
0.00	0.035
0.10	0.042
0.20	0.049
0.30	0.058
0.40	0.069
0.50	0.083
0.60	0.100
0.70	0.132

Determine the number of ideal stages required.

SOLUTION

First, determine the flow rate of solvent.

Oil in liver feed = 10,000(0.043) = 430 gal liquid/h

Oil in extract = 430(0.95) = 408.5 gal/h

Oil in underflow of extracted livers = 430 − 408.5 = 21.5 gal/h

By an iterative procedure, determine the gal/h of ether in the final underflow of extracted livers:

Assume 0.10 gal oil/gal liquid:

From the above data table, have 0.042 gal liquid/lb oil-free livers

Therefore, have 0.042(10,000) = 420 gal liquid/h and 0.10(420) = 42 gal/h oil, which is higher than the required value of 21.5 gal/h from above.

Assume 0.05 gal oil/gal liquid:

Linear interpolation of the above data table gives 0.0385 gal liquid/lb oil-free livers.

Therefore, have 0.0385(10,000) = 385 gal liquid/h

0.05(385) = 19.3 gal oil/h, which is too low

By interpolation, have 0.055 gal oil/gal liquid and 0.0389 gal liquid/lb oil-free livers

Therefore, final underflow contains 0.0389(10,000) − 21.5 = 367.5 gal ether/h

The final extract contains 408.5 gal oil/h, with given value of 65 vol % oil.

Therefore, final extract contains

$$\frac{0.35}{0.65}(408.5) = 220 \text{ gal ether/h}$$

Ether in solvent feed = 220 + 367.5 = 587.5 gal/h.

Overall material balance is

	Solvent feed	Livers feed	Final extract	Final underflow
Oil-free livers, lb/h	0	10,000	0	10,000
ether, gal/h	587.5	0	220	367.5
oil, gal/h	0	430	408.5	21.5

Ideal Leaching Stage:

Referring to Figure 16.7, the underflow leaving the leaching stage, L, will have the same concentration of oil as in the final extract. That concentration is the specification of 0.65 gal oil/gal liquid. From the above data table, by linear interpolation, gal liquid retained/lb oil-free livers = 0.116.

Therefore, letting x_j and y_j = volume fractions,

$$L_L = 0.116(10{,}000) = 1{,}160 \text{ gal liquid}$$

$$x_L = 0.65 \text{ gal oil/gal liquid}$$

Oil material balance around leaching stage:

$$y_1 V_1 + 430 = x_L L_L + 408.5$$

or

$$y_1 V_1 = 0.65(1{,}160) + 408.5 - 430 = 732.5 \text{ gal oil}$$

Ether material balance around leaching stage

$$(1 - y_1)V_1 = 0.35(1{,}160) + 220 = 626 \text{ gal ether/h}$$

$$y_1 = \frac{732.5}{732.5 + 626} = 0.539 \text{ gal oil/gal liquid}$$

We now have the end points of the operating line for the washing stages:

Stage N	Stage 1
$y_{N+1} = 0$	$y_1 = 0.539$
$x_N = 0.055$	$x_L = 0.65$

These two pairs of points together with the straight equilibrium line, $y = x$ are plotted on the McCabe–Thiele diagram of Figure 16.10. Because the underflow is variable, a straight line does not connect the end points of the operating line.

Calculation of Intermediate Points on the Operating Line

Determine by oil and total liquid material balances, values of y_{n+1} for $x_n = 0.30$ and 0.50. The material balance can be made from the solvent feed end to an arbitrary stage n.

For $x_n = 0.3$, with above data table giving 0.058 gal liquid/lb oil-free livers

Oil mass balance:

$$0.3(10{,}000)(0.058) = y_{n+1}V_{n+1} + 21.5 \tag{1}$$

Total liquid mass balance:

$$10{,}000(0.058) + 587.5 = V_{n+1} + (367.5 + 21.5) \tag{2}$$

Solving (1) and (2),

$$V_{n+1} = 778.5 \text{ gal/h}$$

$$y_{n+1} = 0.196 \text{ gal oil/gal liquid}$$

For $x_n = 0.50$, with 0.083 gal liquid/lb oil-free livers,

Oil mass balance:

$$0.5(10{,}000)(0.083) = y_{n+1}V_{n+1} + 21.5 \tag{3}$$

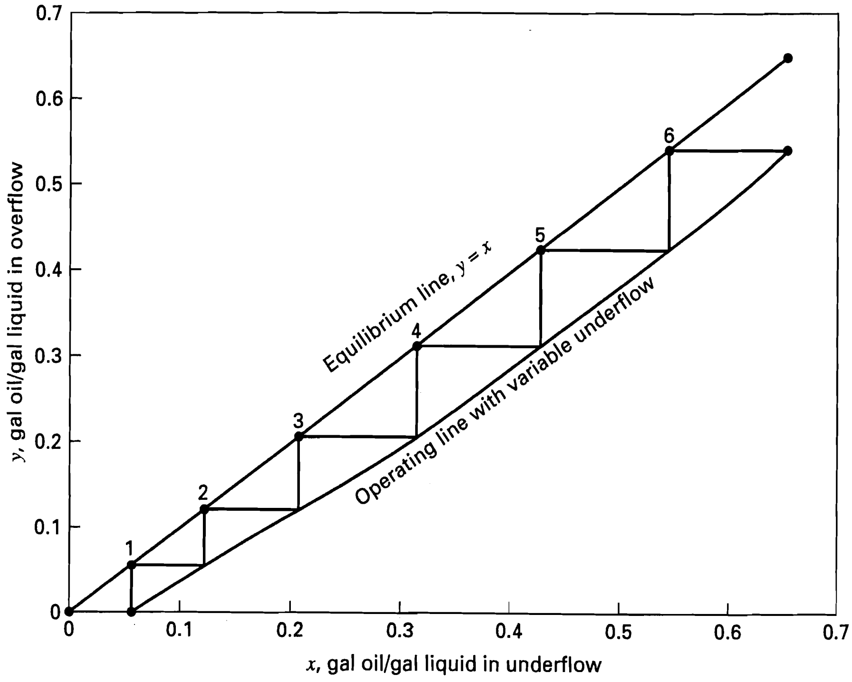


Figure 16.10 McCabe-Thiele diagram for Example 16.5.

Total liquid mass balance:

$$10{,}000(0.083) + 587.5 = V_{n+1} + (367.5 + 21.5) \qquad (4)$$

Solving (3) and (4),

$$V_{n+1} = 1{,}028.5 \text{ gal/h}$$

$$y_{n+1} = 0.383 \text{ gal oil/gal liquid}$$

When these two sets of x_n, y_{n+1} points are plotted, a curved operating line is obtained as shown in Figure 16.10. A total of almost exactly six washing stages can be stepped off. Adding the leaching stage to this gives a total of seven ideal stages.

16.3 RATE-BASED MODEL FOR LEACHING

Leaching involves the transfer of a solute from the interior of a solid into the bulk of a liquid solvent or extract. The process can be modeled by considering two steps (in series): (1) molecular diffusion of the solute through the solid, and (2) convection and eddy diffusion of the solute through the solvent or extract that is exterior to the solid. Practical rates of molecular diffusion through the solid are only achieved after the solvent penetrates the solid to become occluded liquid, unless the solvent is initially present in the solid. The solute then dissolves into that liquid and diffuses at a reasonable rate to the surface of the solid, leaving behind the insoluble solids and any sparingly soluble materials in the form of a framework. If relative motion exists between the solids and the exterior solvent solution, the resistance to mass transfer in the fluid phase may be negligible compared to that in the solid, and the entire leaching process can be modeled by diffusion through the solid.

Food Processing

Schwartzberg and Chao [11] present a summary of published experimental and theoretical studies of solute diffusion in the leaching of food materials in the form of slices, near-cylinders, and nearly spherical particles, including a compilation of effective diffusivities. As with diffusion of liquids and gases in porous-solid adsorbents, the diffusivity can be expressed as a true molecular diffusivity in the occluded fluid phase, or as an effective diffusivity through the entire solid, including the insoluble-solid framework, sometimes called the *marc,* and the occluded liquid. When an effective diffusivity, D_e, is used, and Fick's laws are applied, the concentration driving force is taken to be the concentration of solute, X_i in mass per unit volume of solid particle. Thus, if r is the direction of diffusion, Fick's first law for the solute, i, is

$$n_i = -D_e A\left(\frac{\partial X_i}{\partial r}\right) \qquad (16\text{-}11)$$

Fick's second law for constant effective diffusivity in the direction r is

$$\frac{\partial X_i}{\partial t} = \frac{D_e}{r^{\nu-1}}\frac{\partial}{\partial r}\left[r^{\nu-1}D_e\frac{\partial X_i}{\partial r}\right] \qquad (16\text{-}12)$$

where by comparison to (3-69), (3-70), and (3-71), $\nu = 1, 2,$ and 3 for rectangular, cylindrical, and spherical coordinates, respectively.

The rate of mass transfer through the solvent external to the solid can be written in terms of a mass-transfer coefficient and the concentration of the solute in the solvent or extract Y_i, as in (3-105), where subscripts s and b refer to the solid–liquid interface and the bulk liquid, respectively,

$$n_i = k_c A[(Y_i)_s - (Y_i)_b] \qquad (16\text{-}13)$$

At the solid–liquid interface at the exterior surface of the solid, (16-11) and (16-13) can be equated:

$$-D_e\left(\frac{\partial X_i}{\partial r}\right)_s = k_c[(Y_i)_s - (Y_i)_b] \qquad (16\text{-}14)$$

Let

$m = Y_i/X_i$

a = characteristic dimension of the solid, e.g., the radius of a cylinder or spherical particle, or the half-thickness of a slice. (16-15)

Combining (16-14) and (16-15) and expressing the result in the form of dimensionless groups,

$$-\left[\frac{\partial\left(\dfrac{Y_i}{(Y_i)_s - (Y)_b}\right)}{\partial(r/a)}\right]_s = \left(\frac{mk_c a}{D_e}\right) \qquad (16\text{-}16)$$

The dimensionless group on the right-hand side of (16-16) is called the Biot number for mass transfer:

$$(N_{\text{Bi}})_{\text{M}} = \frac{mk_c a}{D_e} \qquad (16\text{-}17)$$

which is analogous to the more common Biot number for heat transfer,

$$(N_{\text{Bi}}) = \frac{ha}{k} \qquad (16\text{-}18)$$

Biot numbers are quantitative measures of the ratio of internal (solid) resistance to external (fluid) resistance to transport. In Section 3.3, transient solutions are given to (16-12) for different geometries for the case of an initial uniform concentration, $X_o = c_o$, of the solute in the solid. At time $t = 0$, the solute concentration in the solid phase at the solid-fluid interface is suddenly brought to and then held at $X_s = c_s$. The solutions given are

Geometry	Concentration Profile	Rate of Mass Transfer at Interface	Average Concentration in Solid
Semi-infinite	(3-75)	(3-78)	—
Slab of finite thickness	(3-80), (3-81), and Figure 3.8	(3-82)	(3-85) and Figure 3.9
Infinite cylinder	Figure 3.10	—	Figure 3.9
Sphere	Figure 3.11	—	Figure 3.9

These solutions apply to the case in which the Biot number for mass transfer is infinite, such that the resistance in the fluid phase is negligible and $(Y_i)_b = (Y_i)_s$.

For an infinite Biot number, as indicated above, the solute concentration profile as a function of time is given in Figure 3.8 while the average solute concentration in the solid is given in Figure 3.9. In these plots of the solutions, a dimensionless time, the Fourier number for mass transfer, is used, where

$$(N_{\text{Fo}})_{\text{M}} = \frac{D_e t}{a^2} \qquad (16\text{-}19)$$

and a = flake or slice half thickness. When the internal resistance to mass transfer is negligible, which is almost never the case in the leaching of foods, the solution for the uniform concentration of solute in the solid is given by the following equation, whose derivation is left as an exercise:

$$\frac{X_i - \dfrac{(Y_i)_b}{m}}{(X_i)_o - \dfrac{(Y_i)_b}{m}} = \exp\left(\frac{-k_c t m}{a}\right) \qquad (16\text{-}20)$$

When $(N_{\text{Bi}})_{\text{M}} > 200$, the external (fluid) mass-transfer resistance is negligible and Figures 3.8 and 3.9 can be applied. When $(N_{\text{Bi}})_{\text{M}} < 0.001$, the internal (solid) mass-transfer resistance is negligible and (16-20) applies. When $(N_{\text{Bi}})_{\text{M}}$ lies between these two extremes, both resistances must be taken into account. Solutions for this general case are given by Schwartzberg and Chao [11].

Effective diffusivities for solutes in solids are complicated because they depend on the volume fraction of and concentration of solute in the occluded solvent, temperature, tortuosity of the diffusion path, and extent of adsorption of the solute by the marc. Values of solute effective diffusivities in a variety of foods, with water as the solvent, are tabulated by Schwartzberg and Chao [11]. Typical values for sucrose, when the cell walls are hard (e.g., sugar cane and coffee), range from 0.5 to 1.0×10^{-6} cm^2/s. When cells walls are soft (e.g., sugar beets, potatoes, apples, celery, and onions), values are higher, ranging from 1.5 to 4.5×10^{-6} cm^2/s. When the solute is a salt (e.g., NaCl and KCl), effective diffusivities are about four times higher. As mentioned above, the diffusion of oil from flaked oil seeds does not follow Fick's law. If, nevertheless, Fick's law is applied to determine the effective diffusivity, the values are found to decrease significantly with time. For example, data of Karnofsky [12], who leached oil from soybeans, cottonseeds, and flaxseeds, with hexane, give values of effective diffusivity that decrease over the course of extraction by about one order-of-magnitude. Other foods exhibit the same trend under certain conditions. Frequently, the diffusivity is not a constant, but varies with flake or slice thickness and solute concentration. Schwartzberg [11] discusses possible reasons for these effects.

A thin slice or flake of solid can be treated as a slab of finite thickness, with mass transfer from the thin edges ignored. For this case, (3-85) or Figure 3.9 can be used to determine the effective diffusivity from experimental leaching data or predict the rate of leaching. In (3-85), $E_{\text{avg}_{\text{slab}}}$ is the fractional unaccomplished approach to equilibrium for extraction, which decreases with time. As seen in Figure 3.9 and as can be demonstrated with (3-85), when $(N_{\text{Fo}})_{\text{M}} > 0.10$, the series solution is converged to less than a 2% error with only one term of the infinite series, given by

$$E_{\text{ave}_{\text{slab}}} = \frac{8}{\pi^2}\exp\left(-\frac{(N_{\text{Fo}})_{\text{M}}\pi^2}{4}\right)$$

or

$$\ln E_{\text{avg}_{\text{slab}}} = \ln(8/\pi^2) - \frac{\pi^2}{4}(N_{\text{Fo}})_{\text{M}} \qquad (16\text{-}21)$$

Thus, if Fick's law holds, and the diffusivity is constant, a plot of experimental data as log $E_{\text{avg}_{\text{slab}}}$ against time should yield a straight line with a negative slope from which the effective diffusivity can be determined, as illustrated in the following example.

EXAMPLE 16.6

In the commercial extraction of sugar (sucrose) from sugar beets with water, the process is controlled by diffusion through the sugar beet. Yang and Brier [13] conducted diffusion experiments with beets that were sliced into cossettes that were 0.0383 in. thick × 0.25 in. wide and 0.5–1.0 in. long. Typically, the cossettes contained 16 wt% sucrose, 74 wt% water, and 10 wt% insoluble fiber. Experiments were conducted at temperatures ranging from 65 to 80°C, with solvent water rates from 1.0 to 1.2 lb/lb fresh cossettes. For a temperature of 80°C and a solvent water rate of 1.2 lb/lb fresh cossettes, the following smoothed data were obtained:

E_{avg}	t, min.
1.0	0
0.39	10
0.19	20
0.10	30
0.050	40
0.025	50
0.0135	60

These data are plotted in Figure 16.11, where it is seen that a straight line can be passed through the data in the range of time from 10 to 60 minutes. From the slope of this line, using (16-19) and (16-21),

$$\frac{\pi^2}{4}\left(\frac{D_e}{a^2}\right) = 0.00113 \text{ sec}^{-1}$$

Since a = half thickness $= \dfrac{0.0383}{2}(2.54) = 4.86 \times 10^{-2}$ cm

Therefore,

$$D_e = \frac{0.00113(4.86 \times 10^{-2})^2(4)}{(3.14)^2} = 1.1 \times 10^{-6} \text{ cm}^2\text{/s}$$

For a continuous, countercurrent extractor, (16-21) can be used to determine the approximate time required for leaching the solids. The time is given in terms of $E = E_{\text{avg}}$ by

$$t = \int_{E_{\text{in}}}^{E_{\text{out}}} \frac{dE}{\left(\dfrac{dE}{dt}\right)} \qquad (16\text{-}22)$$

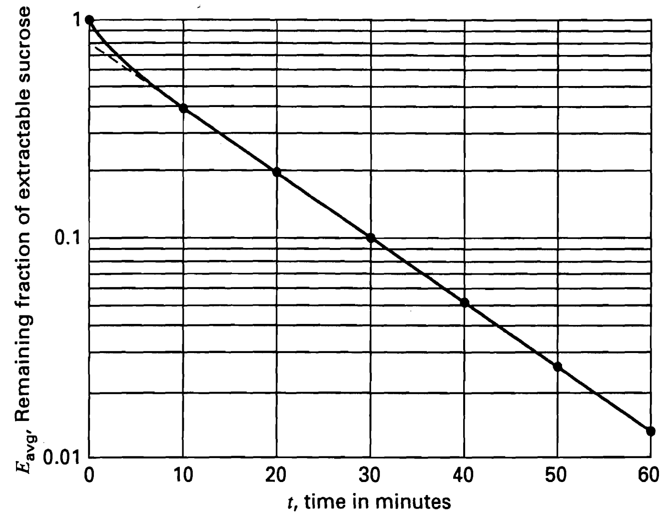


Figure 16.11 Experimental data for leaching of sucrose from sugar beets with water for Example 16.6.

If the solute diffusivity is constant, (dE/dt), except for small values of time, can be obtained by differentiating (16-21) and combining the result to eliminate time, t, to give

$$\frac{dE}{dt} = -\frac{\pi^2 D_e E}{4a^2} \tag{16-23}$$

Substitution of (16-23) into (16-22), followed by integration, gives

$$t = \frac{4a^2}{\pi^2 D_e} \ln\left(\frac{E_{\text{in}}}{E_{\text{out}}}\right) \tag{16-24}$$

When the solute diffusivity is not constant, which is more common, experimental plots of E as a function of time can be used directly to obtain values of (dE/dt) for use in (16-22), which can be graphically or numerically integrated, as shown by Yang and Brier [13].

EXAMPLE 16.7

The sucrose in 10,000 lb/h of sugar beets containing 16 wt% sucrose, 74 wt% water, and 10 wt% insoluble fiber is extracted in a continuous, countercurrent extractor at 80°C with 12,000 lb/h of water. If 98% of the sucrose is extracted and no net mass transfer of water occurs, determine the residence time in minutes for the beets. Assume the beets are sliced to 1 mm in thickness and that the effective sucrose diffusivity is that computed in Example 16.6.

SOLUTION

By material balance, the extracted beets contain

$$0.02(0.16)(10{,}000) = 32 \text{ lb/h sucrose}$$
$$0.74(10{,}000) = 7{,}400 \text{ lb/h water}$$
$$0.10(10{,}000) = 1{,}000 \text{ lb/h insoluble fiber}$$
$$\text{Total} = 8{,}432 \text{ lb/h}$$

Thus,

$$X_{\text{out}} = 32/8{,}432 = 0.0038 \text{ lb/lb}$$
$$X_{\text{in}} = 1{,}600/10{,}000 = 0.160 \text{ lb/lb}$$

where X is expressed on a weight fraction basis.

At the beet inlet end,

$$E_{\text{in}} = \frac{0.16 - (Y/m)_{\text{extract out}}}{0.16 - (Y/m)_{\text{extract out}}} = 1.0$$

At the beet outlet end, $(Y/m)_{\text{solvent in}} = 0$

Therefore,

$$E_{\text{out}} = \frac{0.0038}{1.0} = 0.0038$$

From (16-24),

$$t = \frac{4\left(\frac{0.1}{2}\right)^2}{(3.14)^2(1.1 \times 10^{-6})} \ln\left(\frac{1.0}{0.0038}\right) = 5{,}140 \text{ s} = 85.6 \text{ min}$$

Mineral Processing

Leaching can be used to recover valuable metals from low-grade ores. The leaching process is accomplished by reacting part of the ore with a constituent of the leach liquor, to produce ions of the metal, which are soluble in the liquid. In general, the reaction can be written as

$$\text{A}_{(l)} + b\text{B}_{(s)} \rightarrow \text{Products} \tag{16-25}$$

The removal of reactant B from the ore leaves pores in the solid particle for reactant A to diffuse through to reach reactant B in the interior of the particle.

Figure 16.12 shows a spherical mineral particle undergoing leaching. As the process proceeds, an outer porous leached shell develops, leaving an unleached core. The steps involved are:

1. Mass transfer of reactant A from the bulk liquid to the outer surface of the particle.
2. Pore diffusion of reactant A through the leached shell.
3. Chemical reaction at the interface between the leached shell and the unleached core.
4. Pore diffusion of the reaction products back through the leached shell.
5. Mass transfer of the reaction products back into the bulk liquid surrounding the particle.

Because the diameter of the unleached core shrinks with time, a mathematical model for the process, first conceived for application to gas–solid combustion reactions by Yagi and Kunii [14] in 1955 and extended to liquid–solid leaching by Roman, Benner, and Becker [15] in 1974 is referred to as the *shrinking-core model*. Although any one or more of the above five steps can control the process, the rate of leaching is often controlled by Step 2. Therefore, although the general model has been developed for all possibilities, the leaching model presented here is derived on the assumption that Step 2 is controlling.

Referring to Figure 16.12, assume that dr_c/dt, the rate of movement of the reaction interface at r_c, is small with respect to the diffusion velocity of reactant A, in (16-25), through the porous, leached layer. This is referred to as the

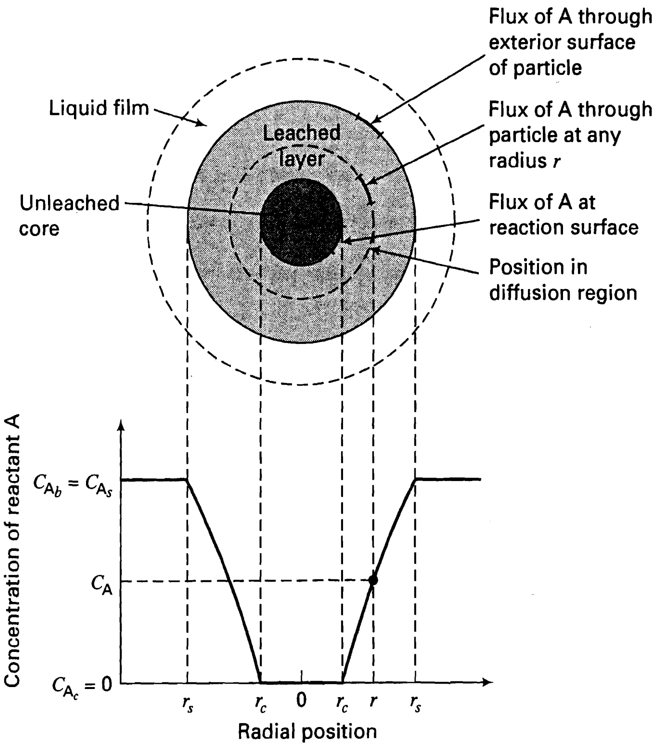


Figure 16.12 Shrinking-core model when diffusion through the leached shell is controlling.

pseudo-steady-state assumption. Although it is valid for the gas–solid case, it is less satisfactory for the liquid–solid case here. The importance of this assumption is that it allows us to neglect the accumulation of reactant A as a function of time in the leached layer as that layer increases in thickness, with the result that the model can be formulated as an ordinary differential equation rather than as a partial differential equation. Thus, the rate of diffusion of reactant A through the porous, leached layer is given by Fick's second law, (3-71), ignoring the term on the left-hand side and replacing the molecular diffusivity with an effective diffusivity:

$$\frac{D_e}{r^2}\frac{d}{dr}\left(r^2\frac{dc_A}{dr}\right) = 0 \qquad (16\text{-}26)$$

with boundary conditions:

$$c_A = c_{A_s} = c_{A_b} \quad \text{at} \quad r = r_s$$

$$c_A = 0 \quad \text{at} \quad r = r_c$$

These boundary conditions hold because the mass-transfer resistance in the liquid film or boundary layer is assumed negligible and the interface reaction is assumed to be instantaneous and complete, respectively.

If (16-26) is integrated twice and the boundary conditions are applied, the result after simplification is

$$c_A = c_{A_b}\left[\frac{1 - \dfrac{r_c}{r}}{1 - \dfrac{r_c}{r_s}}\right] \qquad (16\text{-}27)$$

To obtain a relationship between r_c and time, t, differentiate (16-27) with respect to r and evaluate the differential at $r = r_c$:

$$\left.\frac{dc_A}{dr}\right|_{r=r_c} = \frac{c_{A_b}}{r_c\left(1 - \dfrac{r_c}{r_s}\right)} \qquad (16\text{-}28)$$

The rate of diffusion at $r = r_c$ is given by Fick's first law:

$$n_A = \frac{d\mathcal{N}_A}{dt} = -4\pi r_c^2 D_e\left(\frac{dc_A}{dr}\right)_{r=r_s} \qquad (16\text{-}29)$$

where $\mathcal{N}_A$ = moles of A

Combining (16-28) and (16-29),

$$-\frac{d\mathcal{N}_A}{dt} = \frac{4\pi r_c D_e c_{A_b}}{\left(1 - \dfrac{r_c}{r_s}\right)} \qquad (16\text{-}30)$$

By stoichiometry, from (16-25),

$$\frac{d\mathcal{N}_A}{dt} = \frac{1}{b}\frac{d\mathcal{N}_B}{dt} \qquad (16\text{-}31)$$

By material balance,

$$\frac{d\mathcal{N}_B}{dt} = \frac{\rho_B}{M_B}\frac{d}{dt}\left(\frac{4}{3}\pi r_c^3\right) = \frac{4\pi r_c^2 \rho_B}{M_B}\frac{dr_c}{dt} \qquad (16\text{-}32)$$

where

ρ_B = initial mass of reactant B per unit volume of solid particle

M_B = molecular weight of B

Combining (16-30) with (16-32),

$$\frac{-\rho_B}{M_B}\left(\frac{1}{r_c} - \frac{1}{r_s}\right) r_c^2 dr_c = bD_e c_{A_b} dt \qquad (16\text{-}33)$$

Integration of (16-33) and application of the boundary condition,

$$r_c = r_s \quad \text{at} \quad t = 0$$

gives

$$t = \frac{\rho_B r_s^2}{6D_e b M_B c_{A_b}}\left[1 - 3\left(\frac{r_c}{r_s}\right)^2 + 2\left(\frac{r_c}{r_s}\right)^3\right] \qquad (16\text{-}34)$$

For complete leaching, $r_s = 0$, and (16-34) becomes

$$t = \frac{\rho_B r_s^2}{6D_e b M_B c_{A_b}} \qquad (16\text{-}35)$$

EXAMPLE 16.8

A copper ore containing 2 wt% CuO is to be leached with 0.5-M H_2SO_4. The reaction is

$$\frac{1}{2}\text{CuO}_{(s)} + \text{H}^+_{(aq)} \rightarrow \frac{1}{2}\text{Cu}^{2+}_{(aq)} + \frac{1}{2}\text{H}_2\text{O}_{(aq)} \qquad (1)$$

The leaching process is controlled by the diffusion of hydrogen ions through the leached layer. The effective diffusivity, D_e, of the hydrogen ion has been determined by laboratory tests to be 0.6×10^{-6} cm²/s. The specific gravity of the ore is 2.7. For ore particles of diameter equal to 10 mm, estimate the time required to leach 98% of the copper, assuming that the CuO is uniformly distributed throughout the particles. Also, check the validity of the pseudo-steady-state assumption by comparing the amount of hydrogen ions held up in the liquid in the pores with the amount reacted with CuO.

SOLUTION

If 98% of the cupric oxide is leached, then r_c corresponds to 2% of the particle volume. Thus,

$$\frac{4}{3}\pi r_c^3 = (0.02)\frac{4}{3}\pi r_s^3$$

or

$$r_c = (0.02)^{1/3} r_s = (0.02)^{1/3}(0.5) = 0.136 \text{ cm}$$

$$\rho_B = 0.02(2.7) = 0.054 \text{ g/cm}^3 = \text{density of CuO in the ore}$$

$$M_B = 79.6 = \text{molecular weight of CuO}$$

From (16-25) and (1), $b = 0.5$.

For 0.5-M H_2SO_4, $c_{H_b}^{+} = \dfrac{2(0.5)}{1000} = 0.001 \text{ mol/cm}^3$.

From (16-34), with $r_c/r_s = 0.136/0.500 = 0.272$,

$$t = \frac{(0.054)(0.5)^2}{6(0.6 \times 10^{-6})(0.5)(79.6)(0.001)}[1 - 3(0.272)^2 + 2(0.272)^3]$$

$$= 77{,}000 \text{ sec} = 21.4 \text{ h}$$

Now, check the validity of the pseudo-steady-state assumption.

The specific gravity of CuO is 6.4 g/cm^3.

100 g of ore occupies $100/2.7 = 37.0 \text{ cm}^3$.

The CuO in this amount of ore occupies

$0.02(100)/6.4 = 0.313 \text{ cm}^3$ or 0.845% of the particle volume

Volume of one particle $= \dfrac{4}{3}\pi r_s^3 = \dfrac{4}{3}(3.14)(0.5)^3 = 0.523 \text{ cm}^3$.

Volume of CuO as pores in one particle $= 0.00845(0.523) = 0.0044 \text{ cm}^3$.

Mols of H^+ in pores, based on the bulk concentration to be conservative:

$$0.001(0.0044) = 4.4 \times 10^{-6} \text{ mol}$$

98% of CuO leached in a particle, in mol units:

$$\frac{0.98(0.02)(2.7)(0.523)}{79.6} = 3.5 \times 10^{-4} \text{ mol}$$

which requires 7.0×10^{-4} mol H^+ for reaction.

Because this value is approximately two orders or magnitude larger than the conservative estimate of H^+ in the pores, the pseudo-steady-state assumption is reasonable.

SUMMARY

1. Leaching is similar to liquid–liquid extraction, except that the solute initially resides in a solid. Leaching is widely used to remove solutes from foods and minerals.

2. When leaching is rapid, it can be accomplished in one stage. However, the leached solid will retain surface liquid that contains the solute. To recover most of the solute in the extract, it is desirable to add one or more washing stages in a countercurrent arrangement.

3. Leaching of large solids can be very slow because of very small values of diffusivities in solids. Therefore, it is common to reduce the size of the solids by crushing, grinding, flaking, slicing, etc.

4. Industrial leaching equipment is available for batch or continuous processing. The solids are contacted with the solvent by either percolation or immersion. Large, continuous, countercurrent extractors can process up to 7,000,000 kg/day of food solids.

5. Washing of large flow rates of leached solids is commonly carried out in thickeners that can be designed to produce a clear liquid overflow and a concentrated solids underflow. When a clear overflow is not critical, hydroclones can replace thickeners.

6. An equilibrium-stage model is widely used for continuous, countercurrent systems when leaching is rapid and washing is desirable for high solute recovery. The model assumes that the concentration of the solute in the overflow leaving a stage equals that in the liquid retained on the solid leaving the stage in the underflow.

7. When the ratio of liquid to solids in the underflow is constant form stage to stage, the equilibrium-stage model can be applied algebraically by a modified Kremser method or graphically by a modified McCabe-Thiele method. If the underflow is variable, the graphical method with a curved operating line is applied.

8. When leaching is slow, as with food solids or low-grade ores, leaching calculations must be done on a rate basis. In some cases, the diffusion of solutes in food solids does not obey Fick's law, because of complex membrane and fiber structures.

9. The leaching of low-grade ores by reactive-leaching is conveniently carried out with a shrinking-core diffusion model, using a pseudo-steady-state assumption.

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EXERCISES

Section 16.1

16.1 Using experimental data from pilot-plant tests of soybean extraction by Othmer and Agarwal, summarized at the beginning of this chapter, check the mass balances for oil and hexane around the extractor, assuming the moisture is retained in the flakes, and compute the mass ratio of liquid oil to flakes in the leached solids leaving the extractor.

Section 16.2

16.2 Barium carbonate, which is essentially water insoluble, is to be made by precipitation from an aqueous solution containing 120,000 kg/day of water and 40,000 kg/day of barium sulfide, with the stoichiometric amount of solid sodium carbonate. The reaction also produces a by-product of water-soluble sodium sulfide. The process will be carried out in a continuous, countercurrent system of five thickeners. The reaction will take place completely in the first thickener to which will be fed the solid sodium carbonate, the aqueous solution of barium sulfide, and the overflow from the second thickener. Sufficient fresh water will enter the last thickener so that the overflow from the first thickener will be 10 wt% sodium sulfide, assuming that the underflow from each thickener contains two parts of water per one part of barium carbonate by weight.

(a) Draw a schematic diagram of the process and label it with all the given information.

(b) Determine the kg/day of sodium carbonate required and the kg/day of barium carbonate and sodium sulfide produced by the reaction.

(c) Determine the kg/day of fresh water needed, the wt% of sodium sulfide in the liquid portion of the underflow that leaves each thickener, and the kg/day of sodium sulfide that will remain with the barium carbonate product after it is dried.

16.3 Calcium-carbonate precipitate can be produced by the reaction of an aqueous solution of sodium carbonate and calcium oxide. The by-product is aqueous sodium hydroxide. Following decantation, the slurry leaving the precipitation tank is 5 wt% calcium carbonate, 0.1 wt% sodium hydroxide, and the balance water. One hundred thousand lb/h of this slurry is fed to a two-stage, continuous, countercurrent washing system to be washed with 20,000 lb/h of fresh water. The underflow from each thickener will contain 20 wt% solids. Determine the percent recovery of sodium hydroxide in the extract and wt% sodium hydroxide in the dried, calcium-carbonate product. Based on calculations, is it worthwhile to add a third stage?

16.4 Zinc is to be recovered from an ore containing zinc sulfide. The ore is first roasted with oxygen to produce zinc oxide, which is then leached with aqueous sulfuric acid to produce water-soluble zinc sulfate and an insoluble, worthless residue called gangue. The decanted sludge of 20,000 kg/h contains 5 wt% water, 10 wt% zinc sulfate, and the balance as gangue. This sludge is to be washed with water in a continuous, countercurrent washing system to produce an extract, called a strong solution, of 10 wt% zinc sulfate in water, with a 98% recovery of the zinc sulfate. Assume that the underflow from each washing stage contains, by weight, two parts of water (sulfate-free basis) per part of gangue. Determine the number of stages required.

16.5 Fifty-thousand kg/h of flaked soybeans, containing 20 wt% oil, is to be leached of the oil with the same flow rate of *n*-hexane in a countercurrent-flow system consisting of an ideal leaching stage and three ideal washing stages. Experiments show that the underflow from each stage will contain 0.8 kg liquid/kg soybeans (oil-free basis).

(a) Determine the % recovery of oil in the final extract.

(b) If leaching requires three of the four stages, such that one-third of the leaching occurs in each of these three stages, followed by just one true washing stage, determine the % recovery of oil in the final extract.

16.6 One hundred tons per hour of a feed containing 20 wt% Na_2CO_3 and the balance insoluble solids is to be leached and washed with water in a continuous, countercurrent system. Assume that leaching will be completed in one ideal stage. It is desired to obtain a final extract containing 15 wt% solute, with a 98% recovery of solute. The underflow from each stage will contain 0.5 lb solution/lb insoluble solids. Determine the number of ideal washing stages required.

16.7 Titanium dioxide, which is the most common white pigment in paint, can be produced from the titanium mineral, rutile, by chlorination to $TiCl_4$, followed by oxidation to TiO_2. To purify the insoluble titanium dioxide, it is washed free of soluble impurities in a continuous, countercurrent system of thickeners with water. Two hundred thousand kg/h of 99.9 wt% titanium dioxide pigment is to be produced by washing, followed by filtering and drying. The feed contains 50 wt% TiO_2, 20 wt% soluble salts, and 30 wt% water. The wash liquid is pure water at a flow rate equal to that of the feed on a mass-flow basis.

(a) Determine the number of washing stages required if the underflow from each stage is 0.4 kg solution/kg TiO_2.

(b) Determine the number of washing stages required if the underflow is variable as follows:

Concentration of solute, kg/solute/kg solution	**Retention of solution, kg solution/kg TiO_2**
0.0	0.30
0.2	0.34
0.4	0.38
0.6	0.42

Section 16.3

16.8 Derive (16-20), assuming that $(Y_i)_b$, k_c, m, and a are constants and that $(X_i)_o$ is uniform through the solid.

16.9 Derive (16-24).

16.10 Data of Othmer and Agarwal [1] for the batch extraction of oil from soybeans by oil-free *n*-hexane at 80°F are as follows:

Time, min	Oil content of Soybeans, g/g Dry, Oil-free Soybeans
0	0.203
0.5	0.1559
1	0.1359
2	0.1190
4	0.0981
7	0.0775
12	0.0591
20	0.04197
35	0.03055
60	0.02388
120	0.02107

Determine whether these data are consistent with a constant effective diffusivity of oil in soybeans.

16.11 Estimate the molecular diffusivity of sucrose in water at infinite dilution at 80°C, noting that the value is 0.54×10^{-5} cm^2/s at 25°C. Give reasons for the difference between the value you obtain and the value for effective diffusivity in Example 16.6.

16.12 The sucrose in ground coffee particles of an average diameter of 2 mm is to be extracted with water in a continuous, countercurrent extractor at 25°C. The diffusivity of the sucrose in the particles has been determined to be about 1.0×10^{-6} cm^2/s. Estimate the time in minutes to leach 95% of the sucrose. For a sphere, with $N_{\mathrm{Fo_M}} > 0.10$,

$$E_{\mathrm{ave}} = \frac{6}{\pi^2} \exp\left(\frac{-\pi^2 D_e t}{a^2}\right)$$

16.13 For the conditions of Example 16.8, determine the effect on leaching time of particle size over the range of 0.5 mm to 50 mm.

16.14 For the conditions of Example 16.8, determine the effect of % recovery of copper over the range of 50–100%.

16.15 Repeat Example 16.8, except that the ore contains 3 wt% $\mathrm{Cu_2O}$.

16.16 For the shrinking-core model, if the rate of leaching is controlled by an interface chemical reaction that is first order in the concentration of reactant A, derive the expression,

$$t = \frac{\rho_{\mathrm{B}} r_s}{b M_{\mathrm{B}} k C_{\mathrm{A}_b}} \left(1 - \frac{r_c}{r_s}\right)$$

where k = first-order rate constant.