Liquid-Solid Operations and Equipment

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Nomenclature

Symbol	Definition	SI units	U.S. customary units
c	Specific heat	J/(kg·k)	Btu/(lb·°F)
C	Constant		
C_o	Orifice coefficient	Dimensionless	Dimensionless
d_o	Orifice diameter	m	in
$d_{p,\,max}$	Drop diameter	m	ft
d_t	Pipe diameter	m	in
d_t	Tube diameter	m	ft
D	Impeller diameter	m	ft
D_a	Impeller diameter	m	ft
D_j	Diameter of jacketed vessel	m	ft
D_T	Tank diameter	m	ft
g	Acceleration	m/s²	ft/s²
g_c	Dimensional constant	$g_c = 1$ when using SI units	32.2 (ft·lb)/(lbf·s²)
h	Local individual coefficient of heat transfer, equals $dq/(dA)(\Delta T)$	J/(m²·s·K)	Btu/(h·ft²·°F)
H	Velocity head	m	ft
k	Thermal conductivity	J/(m·s·K)	(Btu·ft)/(h·ft²·°F)
L_p	Diameter of agitator blade	m	ft
N	Agitator rotational speed	s⁻¹, (r/s)	s⁻¹, (r/s)
N_{JS}	Agitator speed for just suspension	s⁻¹	s⁻¹
N_{Re}	$D_a^2 N \rho/\mu$ impeller Reynolds number	Dimensionless	Dimensionless
N_p	Power number = $(q_c P)/\rho N^3 D_a^5$	Dimensionless	Dimensionless
N_Q	Impeller pumping coefficient = Q/ND_a^3	Dimensionless	Dimensionless
N_r	Impeller speed	s⁻¹	s⁻¹
N_t	Impeller speed	s⁻¹	s⁻¹
P	Power	(N·m/s)	ft·lbf/s
Q	Impeller flow rate	m³/s	ft³/s
T	Tank diameter	m	ft
v	Average fluid velocity	m/s	ft/s
v'	Fluid velocity fluctuation	m/s	ft/s
V	Bulk average velocity	m/s	ft/s
Z	Liquid level in tank	m	ft
Greek symbols			
γ	Rate of shear	s⁻¹	s⁻¹
Δp	Pressure drop across orifice		lbf/ft²
μ	Viscosity of liquid at tank temperature	Pa·s	lb/(ft·s)
μ	Stirred liquid viscosity	Pa·s	lb/(ft·s)
μ_b	Viscosity of fluid at bulk temperature	Pa·s	lb/(ft·s)
μ_c	Viscosity, continuous phase	Pa·s	lb/(ft·s)
μ_D	Viscosity of dispersed phase	Pa·s	lb/(ft·s)
μ_f	Viscosity of liquid at mean film temperature	Pa·s	lb/(ft·s)
μ_{wt}	Viscosity at wall temperature	Pa·s	lb/(ft·s)
ρ	Stirred liquid density	g/m³	lb/ft³
ρ	Density of fluid	kg/m³	lb/ft³
ρ_{av}	Density of dispersed phase	kg/m³	lb/ft³
ρ_c	Density	kg/m³	lb/ft³
σ	Interfacial tension	N/m	lbf/ft
Φ_D	Average volume fraction of discontinuous phase	Dimensionless	Dimensionless

PHASE CONTACTING AND LIQUID-SOLID PROCESSING: AGITATION OF LOW-VISCOSITY PARTICLE SUSPENSIONS

GENERAL REFERENCES: Harnby, N., M. F. Edwards, and A. W. Neinow (eds.), *Mixing in the Process Industries,* Butterworth, Stoneham, Mass., 1986. Lo, T. C., M. H. I. Baird, and C. Hanson, *Handbook of Solvent Extraction,* Wiley, New York, 1983. Nagata, S., *Mixing: Principles and Applications,* Kodansha Ltd., Tokyo, Wiley, New York, 1975. Oldshue, J. Y., *Fluid Mixing Technology,* McGraw-Hill, New York, 1983. Tatterson, G. B., *Fluid Mixing and Gas Dispersion in Agitated Tanks,* McGraw-Hill, New York, 1991. Uhl, V. W., and J. B. Gray (eds.), *Mixing,* vols. I and II, Academic Press, New York, 1966; vol. III, Academic Press, Orlando, Fla., 1992. Ulbrecht, J. J., and G. K. Paterson (eds.), *Mixing of Liquids by Mechanical Agitation,* Godon & Breach Science Publishers, New York, 1985.

PROCEEDINGS: *Fluid Mixing,* vol. I, Inst. Chem. Eng. Symp., Ser. No. 64 (Bradford, England), The Institute of Chemical Engineers, Rugby, England, 1984. *Mixing—Theory Related to Practice,* AIChE, Inst. Chem. Eng. Symp. Ser. No. 10 (London), AIChE and The Institute of Chemical Engineers, London, 1965. *Proc. First (1974), Second (1977), Third (1979), Fourth (1982), Fifth (1985), and Sixth (1988) European Conf. on Mixing,* N. G. Coles (ed.), (Cambridge, England) BHRA Fluid Eng., Cranfield, England. *Process Mixing, Chemical and Biochemical Applications,* G. B. Tatterson, and R. V. Calabrese (eds.), AIChE Symp. Ser. No. 286, 1992.

FLUID MIXING TECHNOLOGY

Fluid mixers cut across almost every processing industry including the chemical process industry; minerals, pulp, and paper; waste and water treating and almost every individual process sector. The engineer working with the application and design of mixers for a given process has three basic sources for information. One is published literature, consisting of several thousand published articles and several currently available books, and brochures from equipment vendors. In addition, there may be a variety of in-house experience which may or may not be cataloged, categorized, or usefully available for the process application at hand. Also, short courses are currently available in selected locations and with various course objectives, and a large body of experience and information lies in the hands of equipment vendors.

In the United States, it is customary to design and purchase a mixer from a mixing vendor and purchase the vessel from another supplier. In many other countries, it is more common to purchase the vessel and mixer as a package from one supplier.

In any event, the users of the mixer can issue a mechanical specification and determine the speed, diameter of an impeller, and power with in-house expertise. Or they may issue a processes specification which describes the engineering purpose of the mixing operation and the vendor will supply a description of the mixer process performance as well as prepare a mechanical design.

This section describes fluid mixing technology and is referred to in other sections in this handbook which discuss the use of fluid mixing equipment in their various operating disciplines. This section does not describe paste and dough mixing, which may require planetary and extruder-type mixers, nor the area of dry solid-solid mixing.

It is convenient to divide mixing into five pairs (plus three triplets and one quadruplicate combination) of materials, as shown in Table 18-1. These five pairs are blending (miscible liquids), liquid-solid, liquid-gas, liquid-liquid (immiscible liquids), and fluid motion. There are also four other categories that occur, involving three or four phases. One concept that differentiates mixing requirements is the difference between physical criteria listed on the left side of Table 18-1, in which some degree of sampling can be used to determine the character of the mixture in various parts in the tank, and various definitions of mixing requirements can be based on these physical descriptions. The other category on the right side of Table 18-1 involves chemical and mass-transfer criteria in which rates of mass transfer or chemical reaction are of interest and have many more complexities in expressing the mixing requirements.

The first five classes have their own mixing technologies. Each of these 10 areas has its own mixing technology. There are relationships for the optimum geometry of impeller types, D/T ratios, and tank geometry. They each often have general, overall mixing requirements and different scale-up relationships based on process definitions. In addition, there are many subclassifications, some of which are based on the viscosity of fluids. In the case of blending, we have blending in the viscous region, the transition region, and the turbulent region. Since any given mixer designed for a process may be required to do several different parts of these 10 categories, it must be a compromise of the geometry and other requirements for the total process result and may not optimize any one particular process component. If it turns out that one particular process requirement is so predominant that all the other requirements are satisfied as a consequence, then it is possible to optimize that particular process step. Often, the only process requirement is in one of these 10 areas, and the mixer can be designed and optimized for that one step only.

As an example of the complexity of fluid mixing, many batch processes involve adding many different materials and varying the liquid level over wide ranges in the tank, have different temperatures and shear rate requirements, and obviously need experience and expert attention to all of the requirements. Superimpose the requirements for sound mechanical design, including drives, fluid seals, and rotating shafts, means that the concepts presented here are merely a beginning to the overall, final design.

A few general principles are helpful at this point before proceeding to the examination of equipment and process details. For any given impeller geometry, speed, and diameter, the impeller draws a certain amount of power. This power is 100 percent converted to heat. In low-viscosity mixing (defined later), this power is used to generate a *macro-scale* regime in which one typically has the visual observation of flow pattern, swirls, and other surface phenomena. However, these flow patterns are primarily energy transfer agents that transfer the power down to the micro scale. The macro-scale regime involves the pumping capacity of the impeller as well as the total circulating capacity throughout the tank and it is an important part of the overall mixer design. The micro-scale area in which the power is dissipated does not care much which impeller is used to generate the energy dissipation. In contrast, in high-viscosity processes, there is a continual progress of energy dissipation from the macro scale down to the micro scale.

There is a wide variety of impellers using *fluidfoil principles,* which are used when flow from the impeller is predominant in the process requirement and macro- or micro-scale shear rates are a subordinate issue.

Scale-up involves selecting mixing variables to give the desired performance in both pilot and full scale. This is often difficult (sometimes

TABLE 18-1 Classification System for Mixing Processes

Physical	Components	Chemical, mass transfer
Blending	Blending	Chemical reactions
Suspension	Solid-liquid	Dissolving, precipitation
Dispersion	Gas-liquid	Gas absorption
	Solid-liquid-gas	
Emulsions	Liquid-liquid	Extraction
	Liquid-liquid-solid	
	Gas-liquid-liquid	
	Gas-liquid-liquid-solid	
Pumping	Fluid motion	Heat transfer

impossible) using geometric similarity, so that the use of nongeometric impellers in the pilot plant compared to the impellers used in the plant often allows closer modeling of the mixing requirements to be achieved.

Computational fluid mixing allows the modeling of flow patterns in mixing vessels and some of the principles on which this is based in current techniques are included.

INTRODUCTORY FLUID MECHANICS

The fluid mixing process involves three different areas of viscosity which affect flow patterns and scale-up, and two different scales within the fluid itself: macro scale and micro scale. Design questions come up when looking at the design and performance of mixing processes in a given volume. Considerations must be given to proper impeller and tank geometry as well as the proper speed and power for the impeller. Similar considerations come up when it is desired to scale up or scale down, and this involves another set of mixing considerations.

If the fluid discharge from an impeller is measured with a device that has a high-frequency response, one can track the velocity of the fluid as a function of time. The velocity at a given point in time can then be expressed as an average velocity v plus fluctuating component v'. Average velocities can be integrated across the discharge of the impeller, and the pumping capacity normal to an arbitrary discharge plane can be calculated. This arbitrary discharge plane is often defined as the plane bounded by the boundaries of the impeller blade diameter and height. Because there is no casing, however, an additional 10 to 20 percent of flow typically can be considered as the primary flow from an impeller.

The velocity gradients between the average velocities operate only on larger particles. Typically, these larger-size particles are greater than 1000 μm. This is not a proven definition, but it does give a feel for the magnitudes involved. This defines macro-scale mixing. In the turbulent region, these macro-scale fluctuations can also arise from the finite number of impeller blades. These set up velocity fluctuations that can also operate on the macro scale.

Smaller particles see primarily only the fluctuating velocity component. When the particle size is much less than 100 μm, the turbulent properties of the fluid become important. This is the definition of the physical size for micro-scale mixing.

All of the power applied by a mixer to a fluid through the impeller appears as heat. The conversion of power to heat is through viscous shear and is approximately 2542 Btu/h/hp. Viscous shear is present in turbulent flow only at the micro-scale level. As a result, the power per unit volume is a major component of the phenomena of micro-scale mixing. At a 1-μm level, in fact, it doesn't matter what specific impeller design is used to supply the power.

Numerous experiments show that power per unit volume in the zone of the impeller (which is about 5 percent of the total tank volume) is about 100 times higher than the power per unit volume in the rest of the vessel. Making some reasonable assumptions about the fluid mechanics parameters, the root-mean-square (rms) velocity fluctuation in the zone of the impeller appears to be approximately 5 to 10 times higher than in the rest of the vessel. This conclusion has been verified by experimental measurements.

The ratio of the rms velocity fluctuation to the average velocity in the impeller zone is about 50 percent with many open impellers. If the rms velocity fluctuation is divided by the average velocity in the rest of the vessel, however, the ratio is on the order of 5 percent. This is also the level of rms velocity fluctuation to the mean velocity in pipeline flow. There are phenomena in micro-scale mixing that can occur in mixing tanks that do not occur in pipeline reactors. Whether this is good or bad depends upon the process requirements.

Figure 18-1 shows velocity versus time for three different impellers. The differences between the impellers are quite significant and can be important for mixing processes.

All three impellers are calculated for the same impeller flow Q and the same diameter. The A310 (Fig. 18-2) draws the least power and has the least velocity fluctuations. This gives the lowest micro-scale turbulence and shear rate. The A200 (Fig. 18-3) shows increased velocity
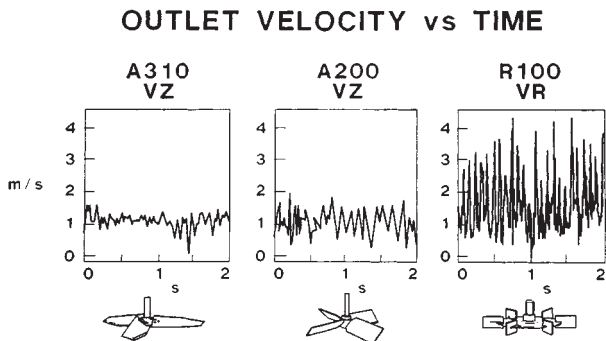
FIG. 18-1 Velocity fluctuations versus time for equal total pumping capacity from three different impellers.

fluctuations and draws more power. The R100 (Fig. 18-4) draws the most power and has the highest micro-scale shear rate. The proper impeller should be used for each individual process requirement.

Scale-up/Scale-down   Two aspects of scale-up frequently arise. One is building a model based on pilot-plant studies that develop an understanding of the process variables for an existing full-scale mixing installation. The other is taking a new process and studying it in the pilot plant in such a way that pertinent scale-up variables are worked out for a new mixing installation.

There are a few principles of scale-up that can indicate which approach to take in either case. Using geometric similarity, the macro-scale variables can be summarized as follows:

• Blend and circulation times in the large tank will be much longer than in the small tank.

FIG. 18-2 An A310 impeller.

FIG. 18-4   Flat-blade turbine.
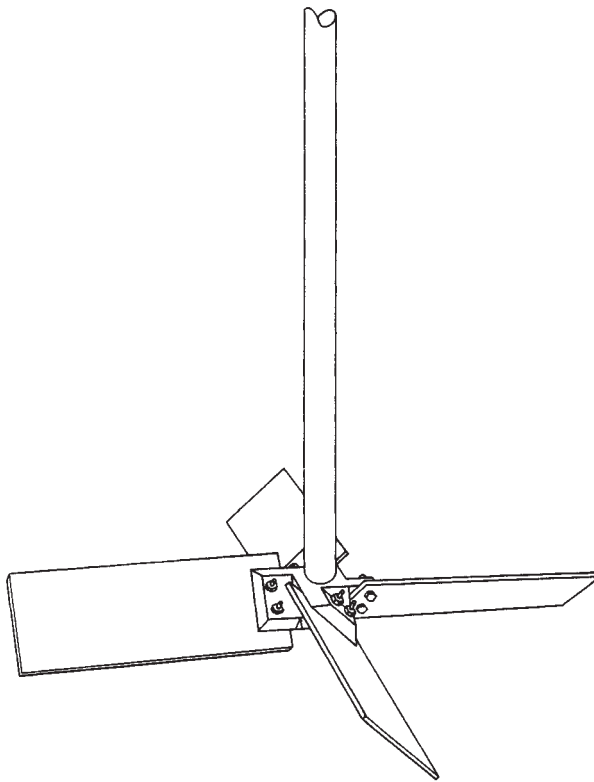
FIG. 18-3   Pitched-blade turbine.

• Maximum impeller zone shear rate will be higher in the larger tank, but the average impeller zone shear rate will be lower; therefore, there will be a much greater variation in shear rates in a full-scale tank than in a pilot unit.

• Reynolds numbers in the large tank will be higher, typically on the order of 5 to 25 times higher than those in a small tank.

• Large tanks tend to develop a recirculation pattern from the impeller through the tank back to the impeller. This results in a behavior similar to that for a number of tanks in a series. The net result is that the mean circulation time is increased over what would be predicted from the impeller pumping capacity. This also increases the standard deviation of the circulation times around the mean.

• Heat transfer is normally much more demanding on a large scale. The introduction of helical coils, vertical tubes, or other heat-transfer devices causes an increased tendency for areas of low recirculation to exist.

• In gas-liquid systems, the tendency for an increase in the gas superficial velocity upon scale-up can further increase the overall circulation time.

What about the micro-scale phenomena? These are dependent primarily on the energy dissipation per unit volume, although one must also be concerned about the energy spectra. In general, the energy dissipation per unit volume around the impeller is approximately 100 times higher than in the rest of the tank. This results in an rms velocity fluctuation ratio to the average velocity on the order of 10:1 between the impeller zone and the rest of the tank.

Because there are thousands of specific processes each year that involve mixing, there will be at least hundreds of different situations requiring a somewhat different pilot-plant approach. Unfortunately, no set of rules states how to carry out studies for any specific program, but here are a few guidelines that can help one carry out a pilot-plant program.
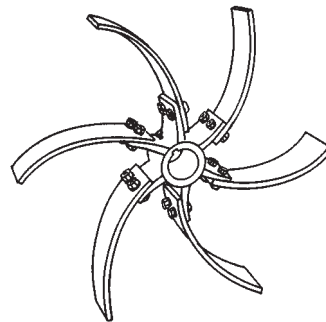
• For any given process, one takes a qualitative look at the possible role of fluid shear stresses. Then one tries to consider pathways related to fluid shear stress that may affect the process. If there are none, then this extremely complex phenomenon can be dismissed and the process design can be based on such things as uniformity, circulation time, blend time, or velocity specifications. This is often the case in the blending of miscible fluids and the suspension of solids.

• If fluid shear stresses are likely to be involved in obtaining a process result, then one must qualitatively look at the scale at which the shear stresses influence the result. If the particles, bubbles, droplets, or fluid clumps are on the order of 1000 μm or larger, the variables are macro scale and average velocities at a point are the predominant variable.

When macro-scale variables are involved, every geometric design variable can affect the role of shear stresses. They can include such items as power, impeller speed, impeller diameter, impeller blade shape, impeller blade width or height, thickness of the material used to make the impeller, number of blades, impeller location, baffle location, and number of impellers.

Micro-scale variables are involved when the particles, droplets, baffles, or fluid clumps are on the order of 100 μm or less. In this case, the critical parameters usually are power per unit volume, distribution of power per unit volume between the impeller and the rest of the tank, rms velocity fluctuation, energy spectra, dissipation length, the smallest micro-scale eddy size for the particular power level, and viscosity of the fluid.

• The overall circulating pattern, including the circulation time and the deviation of the circulation times, can never be neglected. No matter what else a mixer does, it must be able to circulate fluid throughout an entire vessel appropriately. If it cannot, then that mixer is not suited for the task being considered.

Qualitative and, hopefully, quantitative estimates of how the process result will be measured must be made in advance. The evaluations must allow one to establish the importance of the different steps in a process, such as gas-liquid mass transfer, chemical reaction rate, or heat transfer.

• It is seldom possible, either economically or timewise, to study every potential mixing variable or to compare the performance of many impeller types. In many cases, a process needs a specific fluid regime that is relatively independent of the impeller type used to generate it. Because different impellers may require different geometries to achieve an optimum process combination, a random choice of only one diameter of each of two or more impeller types may not tell what is appropriate for the fluid regime ultimately required.

• Often, a pilot plant will operate in the viscous region while the commercial unit will operate in the transition region, or alternatively, the pilot plant may be in the transition region and the commercial unit in the turbulent region. Some experience is required to estimate the difference in performance to be expected upon scale-up.

• In general, it is not necessary to model Z/T ratios between pilot and commercial units.

• In order to make the pilot unit more like a commercial unit in macro-scale characteristics, the pilot unit impeller must be designed

to lengthen the blend time and to increase the maximum impeller zone shear rate. This will result in a greater range of shear rates than is normally found in a pilot unit.

MIXING EQUIPMENT

There are three types of mixing flow patterns that are markedly different. The so-called axial-flow turbines (Fig. 18-3) actually give a flow coming off the impeller of approximately 45°, and therefore have a recirculation pattern coming back into the impeller at the hub region of the blades. This flow pattern exists to an approximate Reynolds number of 200 to 600 and then becomes radial as the Reynolds number decreases. Both the R100 and A200 impellers normally require four baffles for an effective flow pattern. These baffles typically are ¹⁄₁₂ of the tank diameter and width.

Radial-flow impellers include the flat-blade disc turbine, Fig. 18-4, which is labeled an R100. This generates a radial flow pattern at all Reynolds numbers. Figure 18-17 is the diagram of Reynolds number/power number curve, which allows one to calculate the power knowing the speed and diameter of the impeller. The impeller shown in Fig. 18-4 typically gives high shear rates and relatively low pumping capacity.

The current design of fluidfoil impellers includes the A310 (Fig. 18-2), as well as several other impellers of that type commonly referred to as *high-efficiency impellers, hydrofoil,* and other descriptive names to illustrate that they are designed to maximize flow and minimize shear rate. These impellers typically require two baffles, but are normally used with three, since three gives a more stable flow pattern. Since most industrial mixing processes involve pumping capacity and, to a lesser degree, fluid shear rate, the fluidfoil impellers are now used on the majority of the mixer installations. There is now an additional family of these fluidfoil impellers, which depend upon different solidity ratios to operate in various kinds of fluid mixing systems. Figure 18-5 illustrates four of these impellers. The solidity ratio is the ratio of total blade area to a circle circumscribing the impeller and, as viscosity increases, higher values of the solidity ratios are more effective in providing an axial flow pattern rather than a radial flow pattern. Also the A315-type provides an effective area of preventing gas bypassing through the hub of the impeller by having exceptionally wide blades. Another impeller of that type is the Prochem Maxflo T.

Small Tanks   For tanks less than 1.8 m in diameter, the clamp or flanged mounted angular, off-center axial-flow impeller without baffles should be used for a wide range of process requirements (refer to Fig. 18-14). The impellers currently used are the fluidfoil type. Since small impellers typically operate at low Reynolds numbers, often in the transition region, the fluidfoil impeller should be designed to give good flow characteristics over a range of Reynolds numbers, probably on the order of 50 to 500. The Z/T ratio should be 0.75 to 1.5. The volume of liquid should not exceed 4 m³.

Close-Clearance Impellers   There are two close-clearance impellers. They are the *anchor impeller* (Fig. 18-6) and the *helical*

FIG. 18-6   Anchor impeller.

impeller (Fig. 18-7), which operate near the tank wall and are particularly effective in pseudoplastic fluids in which it is desirable to have the mixing energy concentrated out near the tank wall where the flow pattern is more effective than with the open impellers that were covered earlier.

Axial-Flow Impellers   Axial-flow impellers include all impellers in which the blade makes an angle of less than 90° with the plane of rotation. Propellers and pitched-blade turbines, as illustrated in Figs. 18-8 and 18-3, are representative axial-flow impellers.
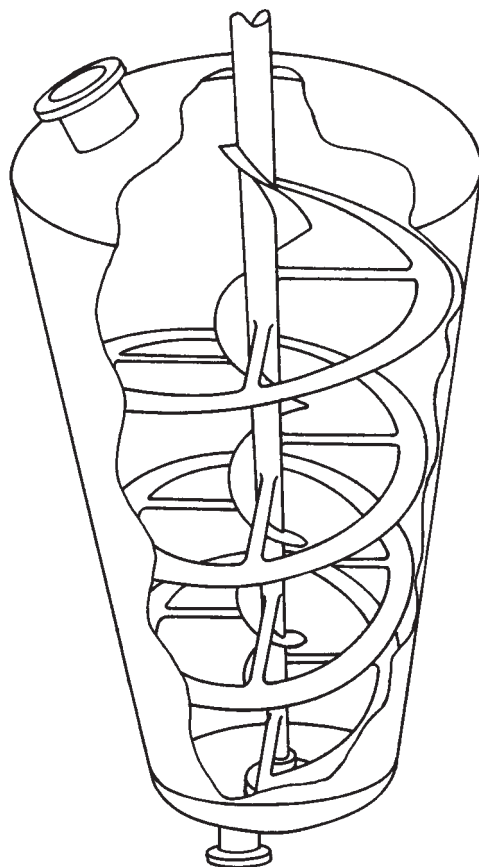
FIG. 18-7   Helical mixer for high-viscosity fluid.

FIG. 18-5   The solidity ratio for four different impellers of the axial-flow fluidfoil type.
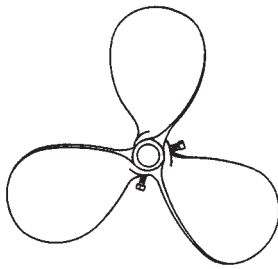
FIG. 18-8   Marine-type mixing impeller.

FIG. 18-10   Side-entering propeller mixer.

Portable mixers may be clamped on the side of an open vessel in the angular, off-center position shown in Fig. 18-14 or bolted to a flange or plate on the top of a closed vessel with the shaft in the same angular, off-center position. This mounting results in a strong top-to-bottom circulation.

Two basic speed ranges are available: 1150 or 1750 r/min with direct drive and 350 or 420 r/min with a gear drive. The high-speed units produce higher velocities and shear rates (Fig. 18-9) in the impeller discharge stream and a lower circulation rate throughout the vessel than the low-speed units. For suspension of solids, it is common to use the gear-driven units, while for rapid dispersion or fast reactions the high-speed units are more appropriate.

Axial-flow impellers may also be mounted near the bottom of the cylindrical wall of a vessel as shown in Fig. 18-10. Such side-entering agitators are used to blend low-viscosity fluids [<0.1 Pa·s (100 cP)] or to keep slowly settling sediment suspended in tanks as large as some 4000 m³ (10⁶ gal). Mixing of paper pulp is often carried out by side-entering propellers.

Pitched-blade turbines (Fig. 18-3) are used on top-entering agitator shafts instead of propellers when a high axial circulation rate is desired and the power consumption is more than 2.2 kW (3 hp). A pitched-blade turbine near the upper surface of liquid in a vessel is effective for rapid submergence of floating particulate solids.

Radial-Flow Impellers   Radial-flow impellers have blades which are parallel to the axis of the drive shaft. The smaller multiblade ones are known as *turbines*; larger, slower-speed impellers, with two or four blades, are often called *paddles.* The diameter of a turbine is normally between 0.3 and 0.6 of the tank diameter. Turbine impellers come in a variety of types, such as curved-blade and flat-blade, as illustrated in Fig. 18-4. Curved blades aid in starting an impeller in settled solids.

For processes in which corrosion of commonly used metals is a problem, glass-coated impellers may be economical. A typical modified curved-blade turbine of this type is shown in Fig. 18-11.

Close-Clearance Stirrers   For some pseudoplastic fluid systems stagnant fluid may be found next to the vessel walls in parts remote from propeller or turbine impellers. In such cases, an "anchor" impeller may be used (Fig. 18-6). The fluid flow is principally circular or helical (see Fig. 18-7) in the direction of rotation of the anchor. Whether substantial axial or radial fluid motion also occurs depends on the fluid viscosity and the design of the upper blade-supporting spokes. Anchor agitators are used particularly to obtain improved heat transfer in high-consistency fluids.

Unbaffled Tanks   If a low-viscosity liquid is stirred in an unbaffled tank by an axially mounted agitator, there is a tendency for a swirling flow pattern to develop regardless of the type of impeller. Figure 18-12 shows a typical flow pattern. A vortex is produced owing to centrifugal force acting on the rotating liquid. In spite of the presence of a vortex, satisfactory process results often can be obtained in an unbaffled vessel. However, there is a limit to the rotational speed that may be used, since once the vortex reaches the impeller, severe air entrainment may occur. In addition, the swirling mass of liquid often generates an oscillating surge in the tank, which coupled with the deep vortex may create a large fluctuating force acting on the mixer shaft.

FIG. 18-9   High shear rate impeller.
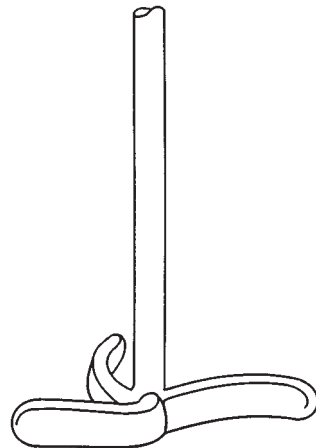
FIG. 18-11   Glass-steel impeller. (*The Pfaudler Company.*)
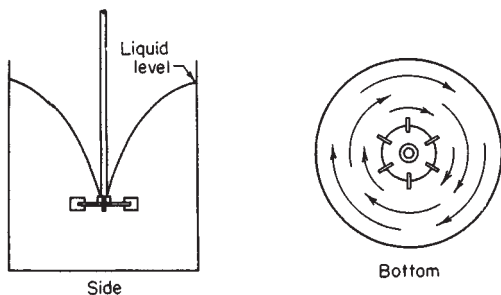
FIG. 18-12 Typical flow pattern for either axial- or radial-flow impellers in an unbaffled tank.

Vertical velocities in a vortexing low-viscosity liquid are low relative to circumferential velocities in the vessel. Increased vertical circulation rates may be obtained by mounting the impeller off center, as illustrated in Fig. 18-13. This position may be used with either turbines or propellers. The position is critical, since too far or too little off center in one direction or the other will cause greater swirling, erratic vortexing, and dangerously high shaft stresses. Changes in viscosity and tank size also affect the flow pattern in such vessels. Off-center mountings have been particularly effective in the suspension of paper pulp.

With axial-flow impellers, an angular off-center position may be used. The impeller is mounted approximately 15° from the vertical, as shown in Fig. 18-14.

The angular off-center position used with fluidfoil units is usually limited to impellers delivering 2.2 kW (3 hp) or less. The unbalanced fluid forces generated by this mounting can become severe with higher power.

Baffled Tanks For vigorous agitation of thin suspensions, the tank is provided with baffles which are flat vertical strips set radially along the tank wall, as illustrated in Figs. 18-15 and 18-16. Four baffles are almost always adequate. A common baffle width is one-tenth to one-twelfth of the tank diameter (radial dimension). For agitating slurries, the baffles often are located one-half of their width from the vessel wall to minimize accumulation of solids on or behind them.

For Reynolds numbers greater than 2000 baffles are commonly used with turbine impellers and with on-centerline axial-flow impellers. The flow patterns illustrated in Figs. 18-15 and 18-16 are quite different, but in both cases the use of baffles results in a large top-to-bottom circulation without vortexing or severely unbalanced fluid forces on the impeller shaft.

Off-center top — entering propeller position

FIG. 18-14 Typical flow pattern with a propeller in angular off-center position without baffles.

In the transition region [Reynolds numbers, Eq. (18-1), from 10 to 10,000], the width of the baffle may be reduced, often to one-half of standard width. If the circulation pattern is satisfactory when the tank is unbaffled but a vortex creates a problem, partial-length baffles may be used. These are standard-width and extend downward from the surface into about one-third of the liquid volume.

In the region of laminar flow ($N_{Re} < 10$), the same power is consumed by the impeller whether baffles are present or not, and they are seldom required. The flow pattern may be affected by the baffles, but not always advantageously. When they are needed, the baffles are usually placed one or two widths radially off the tank wall, to allow fluid to circulate behind them and at the same time produce some axial deflection of flow.

FLUID BEHAVIOR IN MIXING VESSELS

Impeller Reynolds Number The presence or absence of turbulence in an impeller-stirred vessel can be correlated with an impeller Reynolds number defined

$$N_{Re} = \frac{D_a^2 N \rho}{\mu} \tag{18-1}$$

FIG. 18-13 Flow pattern with a paper-stock propeller, unbaffled; vertical off-center position.

FIG. 18-15 Typical flow pattern in a baffled tank with a propeller or an axial-flow turbine positioned on center.
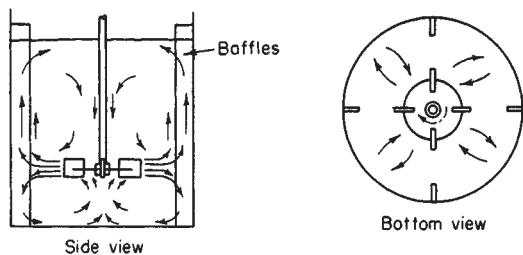
FIG. 18-16 Typical flow pattern in a baffled tank with a turbine positioned on center.

where N = rotational speed, r/s; D_a = impeller diameter, m (ft); ρ = fluid density, kg/m³ (lb/ft³); and μ = viscosity, Pa·s [lb/(ft·s)]. Flow in the tank is turbulent when $N_{Re} > 10,000$. Thus viscosity alone is not a valid indication of the type of flow to be expected. Between Reynolds numbers of 10,000 and approximately 10 is a transition range in which flow is turbulent at the impeller and laminar in remote parts of the vessel; when $N_{Re} < 10$, flow is laminar only.

Not only is the type of flow related to the impeller Reynolds number, but also such process performance characteristics as mixing time, impeller pumping rate, impeller power consumption, and heat- and mass-transfer coefficients can be correlated with this dimensionless group.

Relationship between Fluid Motion and Process Performance   Several phenomena which can be used to promote various processing objectives occur during fluid motion in a vessel.

1. Shear stresses are developed in a fluid when a layer of fluid moves faster or slower than a nearby layer of fluid or a solid surface. In laminar flow, the shear stress is equal to the product of fluid viscosity and velocity gradient or rate of shear. Under laminar-flow conditions, shear forces are larger than inertial forces in the fluid.

With turbulent flow, shear stress also results from the behavior of transient random eddies, including large-scale eddies which decay to small eddies or fluctuations. The scale of the large eddies depends on equipment size. On the other hand, the scale of small eddies, which dissipate energy primarily through viscous shear, is almost independent of agitator and tank size.

The shear stress in the fluid is much higher near the impeller than it is near the tank wall. The difference is greater in large tanks than in small ones.

2. Inertial forces are developed when the velocity of a fluid changes direction or magnitude. In turbulent flow, inertia forces are larger than viscous forces. Fluid in motion tends to continue in motion until it meets a solid surface or other fluid moving in a different direction. Forces are developed during the momentum transfer that takes place. The forces acting on the impeller blades fluctuate in a random manner related to the scale and intensity of turbulence at the impeller.

3. The interfacial area between gases and liquids, immiscible liquids, and solids and liquids may be enlarged or reduced by these viscous and inertia forces when interacting with interfacial forces such as surface tension.

4. Concentration and temperature differences are reduced by bulk flow or circulation in a vessel. Fluid regions of different composition or temperature are reduced in thickness by bulk motion in which velocity gradients exist. This process is called bulk diffusion or Taylor diffusion (Brodkey, in Uhl and Gray, op. cit., vol. 1, p. 48). The turbulent and molecular diffusion reduces the difference between these regions. In laminar flow, Taylor diffusion and molecular diffusion are the mechanisms of concentration- and temperature-difference reduction.

5. Equilibrium concentrations which tend to develop at solid-liquid, gas-liquid, or liquid-liquid interfaces are displaced or changed by molecular and turbulent diffusion between bulk fluid and fluid adjacent to the interface. Bulk motion (Taylor diffusion) aids in this mass-transfer mechanism also.

Turbulent Flow in Stirred Vessels   Turbulence parameters such as intensity and scale of turbulence, correlation coefficients, and

energy spectra have been measured in stirred vessels. However, these characteristics are not used directly in the design of stirred vessels.

Fluid Velocities in Mixing Equipment   Fluid velocities have been measured for various turbines in baffled and unbaffled vessels. Typical data are summarized in Uhl and Gray, op. cit., vol. 1, chap. 4. Velocity data have been used for calculating impeller discharge and circulation rates but are not employed directly in the design of mixing equipment.
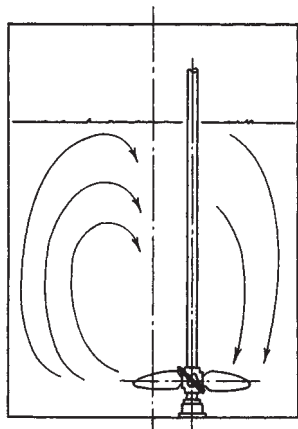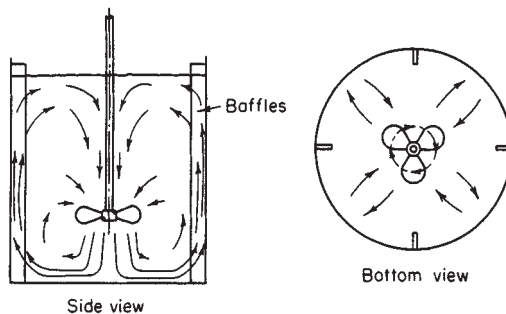
Impeller Discharge Rate and Fluid Head for Turbulent Flow When fluid viscosity is low and flow is turbulent, an impeller moves fluids by an increase in momentum from the blades which exert a force on the fluid. The blades of rotating propellers and turbines change the direction and increase the velocity of the fluids.

The pumping rate or discharge rate of an impeller is the flow rate perpendicular to the impeller discharge area. The fluid passing through this area has velocities proportional to the impeller peripheral velocity and velocity heads proportional to the square of these velocities at each point in the impeller discharge stream under turbulent-flow conditions. The following equations relate velocity head, pumping rate, and power for geometrically similar impellers under turbulent-flow conditions:

$$Q = N_Q N D_a^3 \qquad (18\text{-}2)$$

$$H = \frac{N_p N^2 D_a^2}{N_Q g} \qquad (18\text{-}3)$$

$$P = N_p \rho N^3 \left(\frac{D_a^5}{g_c} \right) \qquad (18\text{-}4)$$

$$P = \frac{\rho H Q g}{g_c} \qquad (18\text{-}5)$$

where Q = impeller discharge rate, m³/s (ft³/s); N_Q = discharge coefficient, dimensionless; H = velocity head, m (ft); N_p = power number, dimensionless; P = power, (N·m)/s [(ft·lbf)/s]; g_c = dimensional constant, 32.2 (ft·lb)/(lbf·s²)(g_c = 1 when using SI units); and g = gravitational acceleration, m/s² (ft/s²).

The discharge rate Q has been measured for several types of impellers, and discharge coefficients have been calculated. The data of a number of investigators are reviewed by Uhl and Gray (op. cit., vol. 1, chap. 4). N_Q is 0.4 to 0.5 for a propeller with pitch equal to diameter at $N_{Re} = 10^5$. For turbines, N_Q ranges from 0.7 to 2.9, depending on the number of blades, blade-height-to-impeller-diameter ratio, and impeller-to-vessel-diameter ratio. The effects of these geometric variables are not well defined.

Power consumption has also been measured and correlated with impeller Reynolds number. The velocity head for a mixing impeller can be calculated, then, from flow and power data, by Eq. (18-3) or Eq. (18-5).

The velocity head of the impeller discharge stream is a measure of the maximum force that this fluid can exert when its velocity is changed. Such inertia forces are higher in streams with higher discharge velocities. Shear rates and shear stresses are also higher under these conditions in the smallest eddies. If a higher discharge velocity is desired at the same power consumption, a smaller-diameter impeller must be used at a higher rotational speed. According to Eq. (18-4), at a given power level $N \propto D_a^{-5/3}$ and $ND_a \propto D_a^{-2/3}$. Then, $H \propto D_a^{-4/3}$ and $Q \propto D_a^{4/3}$.

An impeller with a high fluid head is one with high peripheral velocity and discharge velocity. Such impellers are useful for (1) rapid reduction of concentration differences in the impeller discharge stream (rapid mixing), (2) production of large interfacial area and small droplets in gas-liquid and immiscible-liquid systems, (3) solids deagglomeration, and (4) promotion of mass transfer between phases.

The impeller discharge rate can be increased at the same power consumption by increasing impeller diameter and decreasing rotational speed and peripheral velocity so that $N^3 D_a^5$ is a constant (Eq. 18-4)]. Flow goes up, velocity head and peripheral velocity go down, but impeller torque T_Q goes up. At the same torque, $N^2 D_a^5$ is constant, $P \propto D_a^{-5/2}$, and $Q \propto D_a^{1/2}$. Therefore, increasing impeller diameter at constant torque increases discharge rate at lower power consumption. At the same discharge rate, ND_a^3 is constant, $P \propto D_a^{-4}$, and $T_Q \propto D_a^{-1}$.

Therefore, power and torque decrease as impeller diameter is increased at constant Q.

A large-diameter impeller with a high discharge rate is used for (1) short times to complete mixing of miscible liquid throughout a vessel, (2) promotion of heat transfer, (3) reduction of concentration and temperature differences in all parts of vessels used for constant-environment reactors and continuous averaging, and (4) suspension of particles of relatively low settling rate.

Laminar Fluid Motion in Vessels   When the impeller Reynolds number is less than 10, the flow induced by the impeller is laminar. Under these conditions, the impeller drags fluid with it in a predominantly circular pattern. If the impeller blades curve back, there is a viscous drag flow toward the tips of these blades. Under moderate-viscosity conditions in laminar flow, centrifugal force acting on the fluid layer dragged in a circular path by the rotating impeller will move fluid in a radial direction. This centrifugal effect causes any gas accumulated behind a rotating blade to move to the axis of impeller rotation. Such radial-velocity components are small relative to tangential velocity.

For turbines at Reynolds numbers less than 100, toroidal stagnant zones exist above and below the turbine periphery. Interchange of liquid between these regions and the rest of the vessel is principally by molecular diffusion.

Suspensions of fine solids may have pseudoplastic or plastic-flow properties. When they are in laminar flow in a stirred vessel, motion in remote parts of the vessel where shear rates are low may become negligible or cease completely. To compensate for this behavior of slurries, large-diameter impellers or paddles are used, with $(D_a/D_T) > 0.6$, where D_T is the tank diameter. In some cases, for example, with some anchors, $D_a > 0.95 \, D_T$. Two or more paddles may be used in deep tanks to avoid stagnant regions in slurries.

In laminar flow ($N_{Re} < 10$), $N_p \propto 1/N_{Re}$ and $P \propto \mu N^2 D_a^3$. Since shear stress is proportional to rotational speed, shear stress can be increased at the same power consumption by increasing N proportionally to $D_a^{-3/2}$ as impeller diameter D_a is decreased.

Fluid circulation probably can be increased at the same power consumption and viscosity in laminar flow by increasing impeller diameter and decreasing rotational speed, but the relationship between Q, N, and D_a for laminar flow from turbines has not been determined.

As in the case of turbulent flow, then, small-diameter impellers ($D_a < D_T/3$) are useful for (1) rapid mixing of dry particles into liquids, (2) gas dispersion in slurries, (3) solid-particle deagglomeration, and (4) promoting mass transfer between solid and liquid phases. If stagnant regions are a problem, large impellers must be used and rotational speed and power increased to obtain the required results. Small continuous-processing equipment may be more economical than batch equipment in such cases.

Likewise, large-diameter impellers ($D_a > D_T/2$) are useful for (1) avoiding stagnant regions in slurries, (2) short mixing times to obtain uniformity throughout a vessel, (3) promotion of heat transfer, and (4) laminar continuous averaging of slurries.

Vortex Depth   In an unbaffled vessel with an impeller rotating in the center, centrifugal force acting on the fluid raises the fluid level at the wall and lowers the level at the shaft. The depth and shape of such a vortex (Rieger, Ditl, and Novak, *Chem. Eng. Sci.*, **34**, 397 (1978)] depend on impeller and vessel dimensions as well as rotational speed.

Power Consumption of Impellers   Power consumption is related to fluid density, fluid viscosity, rotational speed, and impeller diameter by plots of power number ($g_c P/\rho N^3 D_a^5$) versus Reynolds number ($D_a^2 N\rho/\mu$). Typical correlation lines for frequently used impellers operating in newtonian liquids contained in baffled cylindrical vessels are presented in Fig. 18-17. These curves may be used also for operation of the respective impellers in unbaffled tanks when the Reynolds number is 300 or less. When N_{Re} is greater than 300, however, the power consumption is lower in an unbaffled vessel than indicated in Fig. 18-17. For example, for a six-blade disk turbine with $D_T/D_a = 3$ and $D_a/W_i = 5$, $N_p = 1.2$ when $N_{Re} = 10^4$. This is only about one-fifth of the value of N_p when baffles are present.

Additional power data for other impeller types such as anchors, curved-blade turbines, and paddles in baffled and unbaffled vessels are available in the following references: Holland and Chapman, op.
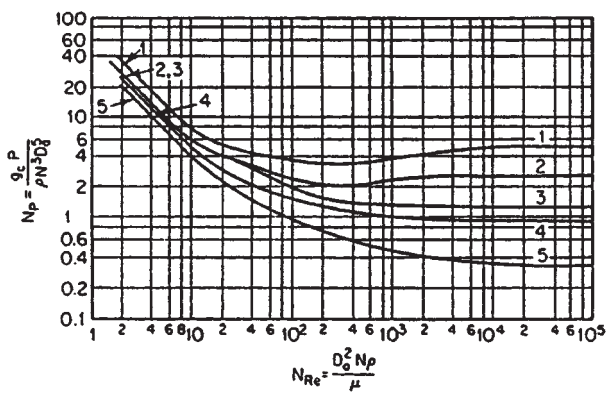
FIG. 18-17   Impeller power correlations: curve 1, six-blade turbine, $D_a/W_i = 5$, like Fig. 18-4 but with six blades, four baffles, each $D_T/12$; curve 2, vertical-blade, open turbine with six straight blades, $D_a/W_i = 8$, four baffles each $D_T/12$; curve 3, 45° pitched-blade turbine like Fig. 18-3 but with six blades, $D_a/W_i = 8$, four baffles, each $D_T/12$; curve 4, propeller, pitch equal to $2D_a$, four baffles, each $0.1D_T$, also same propeller in angular off-center position with no baffles; curve 5, propeller, pitch equal to D_a, four baffles each $0.1D_T$, also same propeller in angular off-center position as in Fig. 18-14 with no baffles. D_a = impeller diameter, D_T = tank diameter, g_c = gravitational conversion factor, N = impeller rotational speed, P = power transmitted by impeller shaft, W_i = impeller blade height, μ = viscosity of stirred liquid, and ρ = density of stirred mixture. Any set of consistent units may be used, but N must be rotations (rather than radians) per unit time. In the SI system, g_c is dimensionless and unity. [Curves 4 and 5 from Rushton, Costich, and Everett, *Chem. Eng. Prog.*, **46**, 395, 467 (1950), by permission; curves 2 and 3 from Bates, Fondy, and Corpstein, *Ind. Eng. Chem. Process Des. Dev.*, **2**, 310 (1963), by permission of the copyright owner, the American Chemical Society.]

cit., chaps. 2, 4, Reinhold, New York, 1966; and Bates, Fondy, and Fenic, in Uhl and Gray, op. cit., vol. 1, chap. 3.

Power consumption for impellers in pseudoplastic, Bingham plastic, and dilatant nonnewtonian fluids may be calculated by using the correlating lines of Fig. 18-17 if viscosity is obtained from viscosity-shear rate curves as described here. For a pseudoplastic fluid, viscosity decreases as shear rate increases. A Bingham plastic is similar to a pseudoplastic fluid but requires that a minimum shear stress be exceeded for any flow to occur. For a dilatant fluid, viscosity increases as shear rate increases.

The appropriate shear rate to use in calculating viscosity is given by one of the following equations when a propeller or a turbine is used (Bates et al., in Uhl and Gray, op. cit., vol. 1, p. 149):

For dilatant liquids,

$$\dot{\gamma} = 13N \left(\frac{D_a}{D_T} \right)^{0.5} \qquad (18\text{-}6)$$

For pseudoplastic and Bingham plastic fluids,

$$\dot{\gamma} = 10N \qquad (18\text{-}7)$$

where $\dot{\gamma}$ = average shear rate, s^{-1}.

The shear rate calculated from impeller rotational speed is used to identify a viscosity from a plot of viscosity versus shear rate determined with a capillary or rotational viscometer. Next N_{Re} is calculated, and N_p is read from a plot like Fig. 18-17.

DESIGN OF AGITATION EQUIPMENT

Selection of Equipment   The principal factors which influence mixing-equipment choice are (1) the process requirements, (2) the flow properties of the process fluids, (3) equipment costs, and (4) construction materials required.

Ideally, the equipment chosen should be that of the lowest total cost which meets all process requirements. The total cost includes depreciation on investment, operating cost such as power, and maintenance costs. Rarely is any more than a superficial evaluation based on this

principle justified, however, because the cost of such an evaluation often exceeds the potential savings that can be realized. Usually optimization is based on experience with similar mixing operations. Often the process requirements can be matched with those of a similar operation, but sometimes tests are necessary to identify a satisfactory design and to find the minimum rotational speed and power.

There are no satisfactory specific guides for selecting mixing equipment because the ranges of application of the various types of equipment overlap and the effects of flow properties on process performance have not been adequately defined. Nevertheless, what is frequently done in selecting equipment is described in the following paragraphs.

Top-Entering Impellers   For vessels less than 1.8 m (6 ft) in diameter, a clamp- or flange-mounted, angular, off-center fluidfoil impeller with no baffles should be the initial choice for meeting a wide range of process requirements (Fig. 18-14). The vessel straight-side-height-to-diameter ratio should be 0.75 to 1.5, and the volume of stirred liquid should not exceed 4 m³ (about 1000 gal).

For suspension of free-settling particles, circulation of pseudoplastic slurries, and heat transfer or mixing of miscible liquids to obtain uniformity, a speed of 350 or 420 r/min should be stipulated. For dispersion of dry particles in liquids or for rapid initial mixing of liquid reactants in a vessel, an 1150- or 1750- r/min propeller should be used at a distance $D_T/4$ above the vessel bottom. A second propeller can be added to the shaft at a depth D_a below the liquid surface if the submergence of floating liquids or particulate solids is otherwise inadequate. Such propeller mixers are readily available up to 2.2 kW (3 hp) for off-center sloped-shaft mounting.

Propeller size, pitch, and rotational speed may be selected by model tests, by experience with similar operations, or, in a few cases, by published correlations of performance data such as mixing time or heat transfer. The propeller diameter and motor power should be the minimum which meet process requirements.

If agitation is required for a vessel less than 1.8 m (6 ft) in diameter and the same operations will be scaled up to a larger vessel ultimately, the equipment type should be the same as that expected in the larger vessel.

Axial-Flow Fluidfoil Impellers   For vessel volumes of 4 to 200 m³ (1000 to 50,000 gal), a turbine mixer mounted coaxially within the vessel with four or more baffles should be the initial choice. Here also the vessel straight-side-height-to-diameter ratio should be 0.75 to 1.5. Four vertical baffles should be fastened perpendicularly to the vessel wall with a gap between baffle and wall equal to $D_T/24$ and a radial baffle width equal to $D_T/12$.

For suspension of rapidly settling particles, the impeller turbine diameter should be $D_T/3$ to $D_T/2$. A clearance of less than one-seventh of the fluid depth in the vessel should be used between the lower edge of the turbine blade tips and the vessel bottom. As the viscosity of a suspension increases, the impeller diameter should be increased. This diameter may be increased to 0.6 D_T and a second impeller added to avoid stagnant regions in pseudoplastic slurries. Moving the baffles halfway between the impeller periphery and the vessel wall will also help avoid stagnant fluid near the baffles.

As has been shown, power consumption is decreased and turbine discharge rate is increased as impeller diameter is increased at constant torque (in the completely turbulent regime). This means that for a stipulated discharge rate, more efficient operation is obtained (lower power and torque) with a relatively large impeller operating at a relatively low speed ($N \propto D_a^{-3}$). Conversely, if power is held constant, decreasing impeller diameter results in increasing peripheral velocity and decreasing torque. Thus at a stipulated power level the rapid, efficient initial mixing of reactants identified with high peripheral velocity can be achieved by a relatively small impeller operating at a relatively high speed ($N \propto D_a^{-5/3}$).

For circulation and mixing to obtain uniformity, the impeller should be located at one-third of the liquid depth above the vessel bottom unless rapidly settling material or a need to stir a nearly empty vessel requires a lower impeller location.

Side-Entering Impellers   For vessels greater than 4 m³ (1000 gal), a side-entering propeller agitator (Fig. 18-9) may be more economical than a top-mounted impeller on a centered vertical shaft.

For vessels greater than 38 m³ (10,000 gal), the economic attractiveness of side-entering impellers increases. For vessels larger than 380 m³ (100,000 gal), units may be as large as 56 kW (75 hp), and two or even three may be installed in one tank. For the suspension of slow-settling particles or the maintenance of uniformity in a viscous slurry of small particles, the diameter and rotational speed of a side-entering agitator must be selected on the basis of model tests or experience with similar operations.

When abrasive solid particles must be suspended, maintenance costs for the submerged shaft seal of a side-entering propeller may become high enough to make this type of mixer an uneconomical choice.

Jet Mixers   Continuous recycle of the contents of a tank through an external pump so arranged that the pump discharge stream appropriately reenters the vessel can result in a flow pattern in the tank which will produce a slow mixing action [Fossett, *Trans. Inst. Chem. Eng.,* **29,** 322 (1951)].

Large Tanks   Most large vessels (over 4 m³) require a heavy-duty drive. About two-thirds of the mixing requirements industrially involve flow, circulation, and other types of pumping capacity requirements, including such applications as blending and solid suspension. There often is no requirement for any marked level of shear rate, so the use of the fluidfoil impellers is most common. If additional shear rate is required over what can be provided by the fluidfoil impeller, the axial-flow turbine (Fig. 18-3) is often used, and if extremely high shear rates are required, the flat-blade turbine (Rushton turbine) (Fig. 18-4) is required. For still higher shear rates, there is an entire variety of high-shear-rate impellers, typified by that shown in Fig. 18-10 that are used.

The fluidfoil impellers in large tanks require only two baffles, but three are usually used to provide better flow pattern asymmetry. These fluidfoil impellers provide a true axial flow pattern, almost as though there was a draft tube around the impeller. Two or three or more impellers are used if tanks with high D/T ratios are involved. The fluidfoil impellers do not vortex vigorously even at relatively low coverage so that if gases or solids are to be incorporated at the surface, the axial-flow turbine is often required and can be used in combination with the fluidfoil impellers also on the same shaft.

BLENDING

If the blending process is between two or more fluids with relatively low viscosity such that the blending is not affected by fluid shear rates, then the difference in blend time and circulation between small and large tanks is the only factor involved. However, if the blending involves wide disparities in the density of viscosity and surface tension between the various phases, then a certain level of shear rate may be required before blending can proceed to the required degree of uniformity.

The role of viscosity is a major factor in going from the turbulent regime, through the transition region, into the viscous regime and the change in the role of energy dissipation discussed previously. The role of non-newtonian viscosities comes into the picture very strongly since that tends to markedly change the type of influence of impellers and determines the appropriate geometry that is involved.

There is the possibility of misinterpretation of the difference between circulation time and blend time. Circulation time is primarily a function of the pumping capacity of the impeller. For axial-flow impellers, a convenient parameter, but not particularly physically accurate, is to divide the pumping capacity of the impeller by the cross-sectional area of the tank to give a superficial liquid velocity. This is sometimes used by using the total volume of flow from the impeller including entrainment of the tank to obtain a superficial liquid velocity.

As the flow from an impeller is increased from a given power level, there will be a higher fluid velocity and therefore a shorter circulation time. This holds true when dealing with any given impeller. This is shown in Fig. 18-18, which shows that circulation time versus D/T decreases. A major consideration is when increasing D/T becomes too large and actually causes the curve to reverse. This occurs somewhere around 0.45, ±0.05, so that using impellers of D/T ratios of 0.6 to 0.8
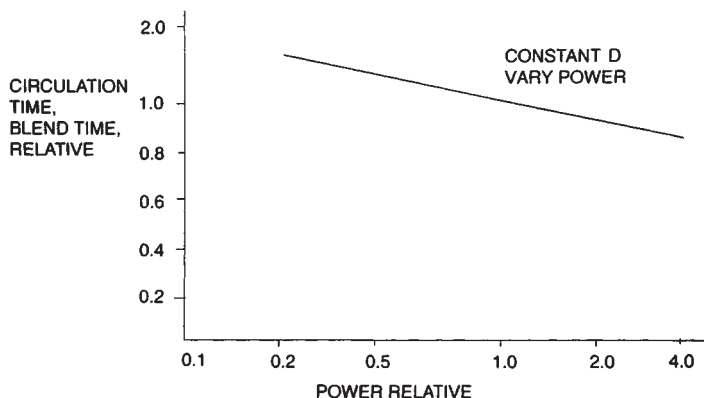
FIG. 18-18 Effect of D/T ratio on two different impellers on the circulation time and the blend time.

is often counterproductive for circulation time. They may be useful for the blending or motion of pseudoplastic fluids.

When comparing different impeller types, an entirely different phenomenon is important. In terms of circulation time, the phenomena shown in Figs. 18-18 and 18-19 still apply with the different impellers shown in Fig. 18-5. When it comes to blending another factor enters the picture. When particles A and B meet each other as a result of shear rates, there has to be sufficient shear stress to cause A and B to blend, react, or otherwise participate in the process.

It turns out that in low-viscosity blending the actual result does depend upon the measuring technique used to measure blend time. Two common techniques, which do not exhaust the possibilities in reported studies, are to use an acid-base indicator and inject an acid or base into the system that will result in a color change. One can also put a dye into the tank and measure the time for color to arrive at uniformity. Another system is to put in a conductivity probe and inject a salt or other electrolyte into the system. With any given impeller type at constant power, the circulation time will increase with the D/T ratio of the impeller. Figure 18-18 shows that both circulation time and blend time decrease as D/T increases. The same is true for impeller speed. As impeller speed is increased with any impeller, blend time and circulation time are decreased (Fig. 18-19).

However, when comparing different impeller types at the same power level, it turns out that impellers that have a higher pumping capacity will give decreased circulation time, but all the impellers, regardless of their pumping efficiency, give the same blend time at the same power level and same diameter. This means that circulation time must be combined with shear rate to carry out a blending experiment which involves chemical reactions or interparticle mixing (Fig. 18-20).

For other situations in low-viscosity blending, the fluid in tanks may become stratified. There are few studies on that situation, but Oldshue (op. cit.) indicates the relationship between some of the variables. The important difference is that blend time is inversely proportional to power, not impeller flow, so that the exponents are quite different for a stratified tank. This situation occurs more frequently in the petroleum industry, where large petroleum storage tanks become stratified either by filling techniques or by temperature fluctuations.

There is a lot of common usage of the terms *blend time, mixing time,* and *circulation time.* There are differences in concept and interpretation of these different "times." For any given experiment, one must pick a definition of *blend time* to be used. As an example, if one is measuring the fluctuation of concentration after an addition of material to the tank, then one can pick an arbitrary definition of blending such as reducing the fluctuations below a certain level. This often is chosen as a fluctuation equal to 5% of the original fluctuation when the feed material is added. This obviously is a function of the size of the probe used to measure these fluctuations, which often is on the order of 500 to 1000 μm.

At the micro-scale level, there really is no way to measure concentration fluctuations. Resort must be made to other qualitative interpretation of results for either a process or a chemical reaction study.

High-Viscosity Systems All axial-flow impellers become radial flow as Reynolds numbers approach the viscous region. Blending in

FIG. 18-19 Effect of impeller speed and power for the same diameter on circulation time and blend time for a particular impeller.

FIG. 18-20 At constant power and constant impeller diameter, three different impellers give the same blend time but different circulation times.

the transition and low-viscosity system is largely a measure of fluid motion throughout the tank. For close-clearance impellers, the anchor and helical impellers provide blending by having an effective action at the tank wall, which is particularly suitable for pseudoplastic fluids.

Figure 18-21 gives some data on the circulation time of the helical impeller. It has been observed that it takes about three circulation times to get one blend time being the visual uniformity of a dye added to the material. This is a macro-scale blending definition.

Axial-flow turbines are often used in blending pseudoplastic materials, and they are often used at relatively large D/T ratios, from 0.5 to 0.7, to adequately provide shear rate in the majority of the batch particularly in pseudoplastic material. These impellers develop a flow pattern which may or may not encompass an entire tank, and these areas of motion are sometimes referred to as *caverns*. Several papers describe the size of these caverns relative to various types of mixing phenomena. An effective procedure for the blending of pseudoplastic fluids is given in Oldshue (op. cit.).

Chemical Reactions   Chemical reactions are influenced by the uniformity of concentration both at the feed point and in the rest of the tank and can be markedly affected by the change in overall blend time and circulation time as well as the micro-scale environment. It is possible to keep the ratio between the power per unit volume at the impeller and in the rest of the tank relatively similar on scale-up, but many details need to be considered when talking about the reaction conditions, particularly where they involve selectivity. This means that reactions can take different paths depending upon chemistry and fluid mechanics, which is a major consideration in what should be examined. The method of introducing the reagent stream can be projected in several different ways depending upon the geometry of the impeller and feed system.

Chemical reactions normally occur in the micro-scale range. In turbulent flow, almost all of the power dissipation occurs eventually in the micro-scale regime because that is the only place where the scale of the fluid fluctuations is small enough that viscous shear stress exists. At approximately 100 μm, the fluid does not know what type of impeller is used to generate the power; continuing down to 10 μm and, even further, to chemical reactions, the actual impeller type is not a major variable as long as the proper macro-scale regime has been provided throughout the entire tank. The intensity of the mixing environment in the micro-scale regime can be related to a series of variables in an increasing order of complexity. Since all of the power is ultimately dissipated in the micro-scale regime, the power per unit volume throughout the tank is one measure of the overall measure of micro-scale mixing and the power dissipation at individual volumes in the tank is another way of expressing the influence. In general, the power per unit

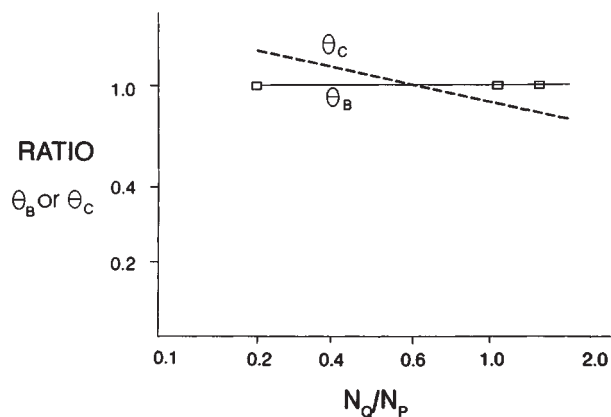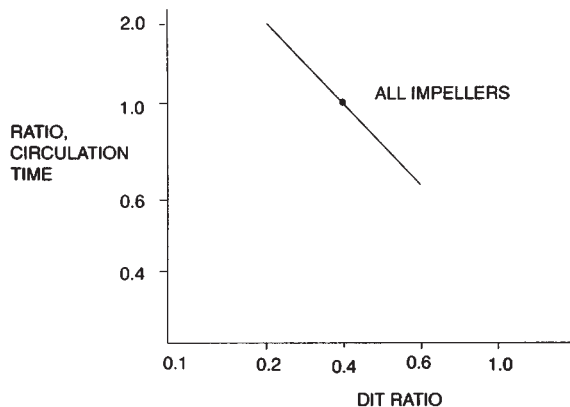volume dissipated around an impeller zone can be 100 times higher than the power dissipated throughout the remainder of the tank.

The next level of complexity is to look at the rms velocity fluctuation, which is typically 50 percent of the mean velocity around the impeller zone and about 5 percent of the mean velocity in the rest of the vessel. This means that the feed introduction point for either a single reactant or several reactants can be of extreme importance. It seems that the selectivity of competing or consecutive chemical reactions can be a function of the rms velocity fluctuations in the feed point if the chemical reactants remain constant and involve an appropriate relationship to the time between the rms velocity fluctuations. There are three common ways of introducing reagents into a mixing vessel. One is to let them drip on the surface. The second is to use some type of introduction pipe to bring the material into various parts of the vessel. The third is to purposely bring them in and around the impeller zone. Generally, all three methods have to be tried before determining the effect of feed location.

Since chemical reactions are on a scale much below 1 μm, and it appears that the Komolgoroff scale of isotropic turbulence turns out to be somewhere between 10 and 30 μm, other mechanisms must play a role in getting materials in and out of reaction zones and reactants in and out of those zones. One cannot really assign a shear rate magnitude to the area around a micro-scale zone, and it is primarily an environment that particles and reactants witness in a real scale.

The next level of complexity looks at the kinetic energy of turbulence. There are several models that are used to study the fluid mechanics, such as the Kε model. One can also put the velocity measurements through a spectrum analyzer to look at the energy at various wave numbers.

In the viscous regime, chemical reactants become associated with each other through viscous shear stresses. These shear stresses exist at all scales (macro to micro) and until the power is dissipated continuously through the entire spectrum. This gives a different relationship for power dissipation than in the case of turbulent flow.

Solid-Liquid   The most-used technique to study solid suspension, as documented in hundreds of papers in the literature, is called the *speed for just suspension*, N_{JS}. The original work was done in 1958 by Zwietering and this is still the most extensive range of variables, although other investigators have added to it considerably.

This particular technique is suitable only for laboratory investigation using tanks that are transparent and well illuminated. It does not lend itself to evaluation of the opaque tanks, nor is it used in any study of large-scale tanks in the field. It is a very minimal requirement for uniformity, and definitions suggested earlier are recommended for use in industrial design.

Some Observations on the Use of N_{JS}   With D/T ratios of less than 0.4, uniformity throughout the rest of the tank is minimal. In D/T ratios greater than 0.4, the rest of the tank has a very vigorous fluid motion with marked approach to complete uniformity before N_{JS} is reached.

Much of the variation in N_{JS} can be reduced by using P_{JS}, which is the power in the just-suspended state. This also gives a better feel for the comparison of various impellers based on the energy requirement rather than speed, which has no economic relevance.

The overall superficial fluid velocity, mentioned earlier, should be proportional to the settling velocity of the solids if that were the main mechanism for solid suspension. If this were the case, the requirement for power if the settling velocity were doubled should be eight times. Experimentally, it is found that the increase in power is more nearly four times, so that some effect of the shear rate in macro-scale turbulence is effective in providing uplift and motion in the system.

Picking up the solids at the bottom of the tank depends upon the eddies and velocity fluctuations in the lower part of the tank and is a different criterion from the flow pattern required to keep particles suspended and moving in various velocity patterns throughout the remainder of the vessel. This leads to the variables in the design equation and a relationship that is quite different when these same variables are studied in relation to complete uniformity throughout the mixing vessel.

Another concern is the effect of multiple particle sizes. In general, the presence of fine particles will affect the requirements of suspen-
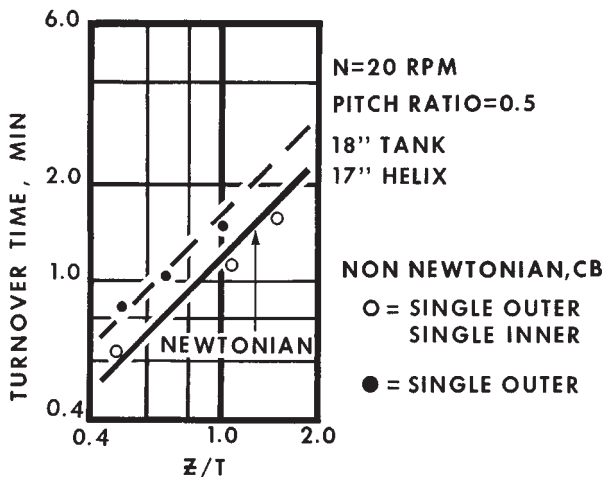
FIG. 18-21   Effect of impeller speed on circulation time for a helical impeller in the Reynolds number arranged less than 10.

sion of larger particles. The fine particles act largely as a potential viscosity-increasing agent and give a similar result to what would happen if the viscosity of the continuous phase were increased.

Another phenomenon is the increase in power required with percent solids, which makes a dramatic change at approximately 40 percent by volume, and then dramatically changes again as we approach the ultimate weight percent of settled solids. This phenomenon is covered by Oldshue (op. cit.), who describes conditions required for mixing slurries in the 80 to 100 percent range of the ultimate weight percent of settled solids.

Solids suspension in general is not usually affected by blend time or shear-rate changes in the relatively low to medium solids concentration in the range from 0 to 40 percent by weight. However, as solids become more concentrated, the effect of solids concentration on power required gives a change in criterion from the settling velocity of the individual particles in the mixture to the apparent viscosity of the more concentrated slurry. This means that we enter into an area where the blending of non-newtonian fluid regions affects the shear rates and plays a marked role.

The suspension of a single solid particle should depend primarily on the upward velocity at a given point and also should be affected by the uniformity of this velocity profile across the entire tank cross section. There are upward velocities in the tank and there also must be corresponding downward velocities.

In addition to the effect of the upward velocity on a settling particle, there is also the random motion of the micro-scale environment, which does not affect large particles very much but is a major factor in the concentration and uniformity of particles in the transition and micro-scale size range.

Using a draft tube in the tank for solids suspension introduces another, different set of variables. There are other relationships that are very much affected by scale-up in this type of process, as shown in Fig. 18-22. Different scale-up problems exist whether the impeller is pumping up or down within the draft tube.

Solid Dispersion   If the process involves the dispersion of solids in a liquid, then we may either be involved with breaking up agglomerates or possibly physically breaking or shattering particles that have a low cohesive force between their components. Normally, we do not think of breaking up ionic bonds with the shear rates available in mixing machinery.

If we know the shear stress required to break up a particle, we can then determine the shear rate required from the machinery by various viscosities with the equation:

$$\text{Shear stress} = \text{viscosity (shear rate)}$$
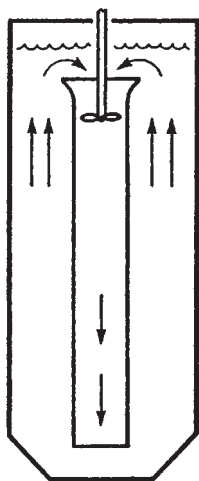
FIG. 18-22   Typical draft tube circulator, shown here for down-pumping mode for the impeller in the draft tube.

The shear rate available from various types of mixing and dispersion devices is known approximately and also the range of viscosities in which they can operate. This makes the selection of the mixing equipment subject to calculation of the shear stress required for the viscosity to be used.

In the equation referred to above, it is assumed that there is 100 percent transmission of the shear rate in the shear stress. However, with the slurry viscosity determined essentially by the properties of the slurry, at high concentrations of slurries there is a slippage factor. Internal motion of particles in the fluids over and around each other can reduce the effective transmission of viscosity efficiencies from 100 percent to as low as 30 percent.

Animal cells in biotechnology do not normally have tough skins like those of fungal cells and they are very sensitive to mixing effects. Many approaches have been and are being tried to minimize the effect of increased shear rates on scale-up. These include encapsulating the organism in or on microparticles and/or conditioning cells selectively to shear rates. In addition, traditional fermentation processes have maximum shear-rate requirements in which cells become progressively more and more damaged until they become motile.

Solid-Liquid Mass Transfer   There is potentially a major effect of both shear rate and circulation time in these processes. The solids can either be fragile or rugged. We are looking at the slip velocity of the particle and also whether we can break up agglomerates of particles which may enhance the mass transfer. When the particles become small enough, they tend to follow the flow pattern, so the slip velocity necessary to affect the mass transfer becomes less and less available.

What this shows is that, from the definition of off-bottom motion to complete uniformity, the effect of mixer power is much less than from going to on-bottom motion to off-bottom suspension. The initial increase in power causes more and more solids to be in active communication with the liquid and has a much greater mass-transfer rate than that occurring above the power level for off-bottom suspension, in which slip velocity between the particles of fluid is the major contributor (Fig. 18-23).

Since there may well be chemical or biological reactions happening on or in the solid phase, depending upon the size of the process participants, macro- or micro-scale effects may or may not be appropriate to consider.

In the case of living organisms, their access to dissolved oxygen throughout the tank is of great concern. Large tanks in the fermentation industry often have a Z/T ratio of 2:1 to 4:1; thus, top-to-bottom blending can be a major factor. Some biological particles are facultative and can adapt and reestablish their metabolisms at different dissolved-oxygen levels. Other organisms are irreversibly destroyed by sufficient exposure to low dissolved-oxygen levels.

GAS-LIQUID SYSTEMS

Gas-Liquid Dispersion   This involves physical dispersion of gas bubbles by the impeller, and the effect of gas flow on the impeller.
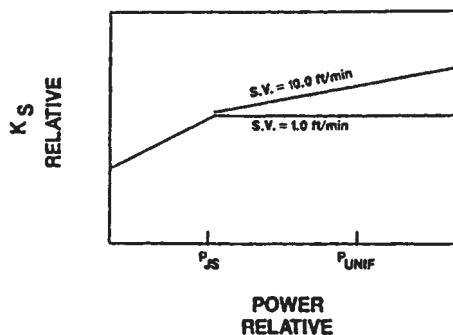
FIG. 18-23   Relative change in solid-liquid mass-transfer ratio with three different suspension levels, i.e., on-bottom motion, off-bottom motion, and complete uniformity.

The observation of the physical appearance of a tank undergoing gas-liquid mass transfer can be helpful but is not a substitute for mass-transfer data on the actual process. The mixing vessel can have four regimes of visual comparisons between gas bubbles and flow patterns. A helpful parameter is the ratio between the power given up by the gas phase and the power introduced by the mixing impeller. In general, if the power in the gas stream (calculated as the expansion energy from the gas expanding from the sparging area to the top of the tank, shown in Fig. 18-24) is greater, there will be considerable blurping and entrainment of liquid drops by a very violent explosion of gas bubbles at the surface. If the power level is more than the expanding gas energy, then the surface action will normally be very coalescent and uniform by comparison, and the gas will be reasonably well distributed throughout the remainder of the tank. With power levels up to 10 to 100 times the gas energy, the impeller will cause a more uniform and vigorous dispersion of the gas bubbles and smaller gas bubbles in the vessel.

In the 1960s and before, most gas-liquid operations were conducted using flat-blade turbines as shown in Fig. 18-4. These impellers required input of approximately three times the energy in the gas stream before they completely control the flow pattern. This was usually the case, and the mass-transfer characteristics were comparable to what would be expected. One disadvantage of the radial-flow impeller is that it is a very poor blending device so blend time is very long compared to that in pilot-scale experiments and compared to the fluidfoil impeller types often used currently. Using curvature of the blades to modify the tendency of gas bubbles to streamline the back of the flat-blade turbine gives a different characteristic to the power drawn by the impeller at a given gas rate compared to no gas rate, but it seems to give quite similar mass transfer at power levels similar to those of the flat-blade design. In order to improve the blending and solid-suspension characteristics, fluidfoil impellers (typified by the A315, Fig. 18-25) have been introduced in recent years and they have many of the advantages and some of the disadvantages of the flat-blade turbine. These impellers typically have a very high solidity ratio, on the order of 0.85 or more, and produce a strong axial downflow at low gas rate. As the gas rate increases, the flow pattern becomes more radial due to the upflow of the gas counteracting the downward flow of the impeller.

Mass-transfer characteristics on large-scale equipment seem to be quite similar, but the fluidfoil impellers tend to release a larger-
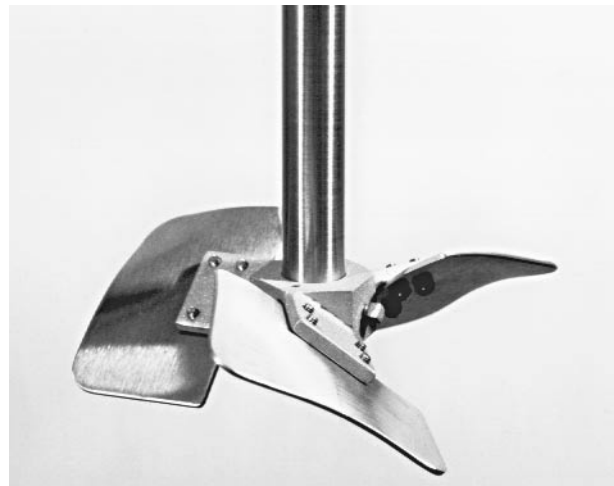
FIG. 18-25   An impeller designed for gas-liquid dispersion and mass transfer of the fluidfoil type, i.e., A315.

diameter bubble than is common with the radial-flow turbines. The blend time is one-half or one-third as long, and solid-suspension characteristics are better so that there have been notable improved process results with these impellers. This is particularly true if the process requires better blending and there is solid suspension. If this is not the case, the results from these impellers can be negative compared to radial-flow impellers.

It is very difficult to test these impellers on a small scale, since they provide better blending on a pilot scale where blending is already very effective compared to the large scale. Caution is recommended if it is desirable to study these impellers in pilot-scale equipment.

Gas-Liquid Mass Transfer   Gas-liquid mass transfer normally is correlated by means of the mass-transfer coefficient $K_g a$ versus power level at various superficial gas velocities. The superficial gas velocity is the volume of gas at the average temperature and pressure at the midpoint in the tank divided by the area of the vessel. In order to obtain the partial-pressure driving force, an assumption must be made of the partial pressure in equilibrium with the concentration of gas in the liquid. Many times this must be assumed, but if Fig. 18-26 is obtained in the pilot plant and the same assumption principle is used in evaluating the mixer in the full-scale tank, the error from the assumption is limited.
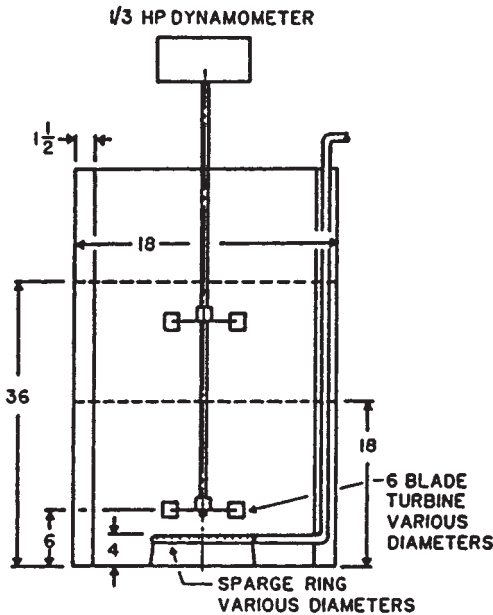
FIG. 18-24   Typical arrangement of Rushton radial-flow R100 flat-blade turbine with typical sparge ring for gas-liquid mass transfer.
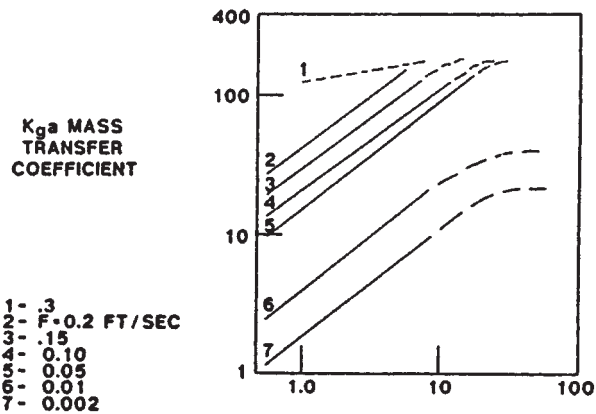
FIG. 18-26   Typical curve for mass transfer coefficient $K_g a$ as a function of mixer power and superficial gas velocity.

In the plant-size unit, Fig. 18-26 must be translated into a mass-transfer-rate curve for the particular tank volume and operating condition selected. Every time a new physical condition is selected, a different curve similar to that of Fig. 18-27 is obtained.

Typical exponents on the effect of power and gas rate on $K_g a$ tend to be around 0.5 for each variable, ±0.1.

Viscosity markedly changes the picture and, usually, increasing viscosity lowers the mass-transfer coefficient. For the common application of waste treating and for some of the published data on biological slurries, data for $k_L a$ (shown in Fig. 18-28) is obtained in the literature. For a completely new gas or liquid of a liquid slurry system, Fig. 18-26 must be obtained by an actual experiment.

Liquid-Gas-Solid Systems   Many gas-liquid systems contain solids that may be the ultimate recipient of the liquid-gas-solid mass transfer entering into the process result. Examples are biological processes in which the biological solids are the user of the mass transfer of the mixing-flow patterns, various types of slurries reactors in which the solids either are being reactive or there may be extraction or dissolving taking place, or there may be polymerization or precipitation of solids occurring.

Normally there must be a way of determining whether the mass-transfer rate with the solids is the key controlling parameter or the gas-liquid mass transfer rate.

In general, introduction of a gas stream to a fluid will increase the blend time because the gas-flow patterns are counterproductive to the typical mixer-flow patterns. In a similar vein, the introduction of a gas stream to a liquid-solid suspension will decrease the suspension uniformity because the gas-flow pattern is normally counterproductive to the mixer-flow pattern. Many times the power needed for the gas-liquid mass transfer is higher than the power needed for solid suspension, and the effect of the gas flow on the solid suspensions are of little concern. On the other hand, if power levels are relatively low and solid-suspension characteristics are critical—examples being the case of activated sludge reactors in the waste-treating field or biological solid reactors in the hydrometallurgical field—then the effect of the gas-flow pattern of the mixing system can be quite critical to the overall design.

Another common situation is batch hydrogenation, in which pure hydrogen is introduced to a relatively high pressure reactor and a decision must be made to recycle the unabsorbed gas stream from the top of the reactor or use a vortexing mode for an upper impeller to incorporate the gas from the surface.

Loop Reactors   For some gas-liquid-solid processes, a recirculating loop can be an effective reactor. These involve a relatively high horsepower pumping system and various kinds of nozzles, baffles, and turbulence generators in the loop system. These have power levels
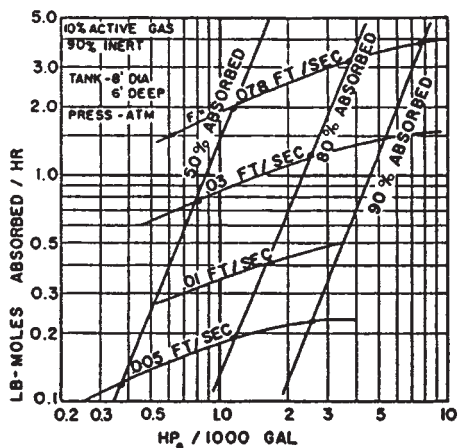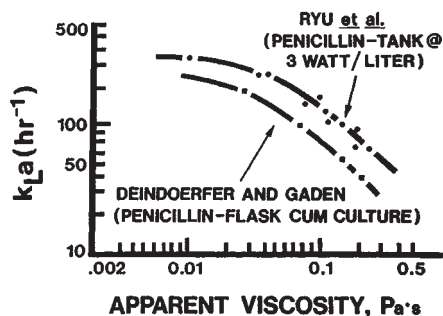
FIG. 18-28   Usually, the gas-liquid mass-transfer coefficient, $K_g a$, is reduced with increased viscosity. This shows the effect of increased concentration of microbial cells in a fermentation process.

anywhere from 1 to 10 times higher than the power level in a typical mixing reactor, and may allow the retention time to be less by a factor of 1 to 10.

LIQUID-LIQUID CONTACTING

Emulsions   Almost every shear rate parameter affects liquid-liquid emulsion formation. Some of the effects are dependent upon whether the emulsion is both dispersing and coalescing in the tank, or whether there are sufficient stabilizers present to maintain the smallest droplet size produced for long periods of time. Blend time and the standard deviation of circulation times affect the length of time it takes for a particle to be exposed to the various levels of shear work and thus the time it takes to achieve the ultimate small particle size desired.

The prediction of drop sizes in liquid-liquid systems is difficult. Most of the studies have used very pure fluids as two of the immiscible liquids, and in industrial practice there almost always are other chemicals that are surface-active to some degree and make the prediction of absolute drop sizes very difficult. In addition, techniques to measure drop sizes in experimental studies have all types of experimental and interpretation variations and difficulties so that many of the equations and correlations in the literature give contradictory results under similar conditions. Experimental difficulties include dispersion and coalescence effects, difficulty of measuring actual drop size, the effect of visual or photographic studies on where in the tank you can make these observations, and the difficulty of using probes that measure bubble size or bubble area by light or other sample transmission techniques which are very sensitive to the concentration of the dispersed phase and often are used in very dilute solutions.

It is seldom possible to specify an initial mixer design requirement for an absolute bubble size prediction, particularly if coalescence and dispersion are involved. However, if data are available on the actual system, then many of these correlations could be used to predict relative changes in drop size conditions with changes in fluid properties or impeller variables.

STAGEWISE EQUIPMENT: MIXER-SETTLERS

Introduction   Insoluble liquids may be brought into direct contact to cause transfer of dissolved substances, to allow transfer of heat, and to promote chemical reaction. This subsection concerns the design and selection of equipment used for conducting this type of liquid-liquid contact operation.

Objectives   There are four principal purposes of operations involving the direct contact of immiscible liquids. The purpose of a particular contact operation may involve any one or any combination of the following objectives:

1. *Separation of components in solution.*   This includes the ordinary objectives of liquid extraction, in which the constituents of a solution are separated by causing their unequal distribution between two insoluble liquids, the washing of a liquid with another to remove small

amounts of a dissolved impurity, and the like. The theoretical principles governing the phase relationships, material balances, and number of ideal stages or transfer units required to bring about the desired changes are to be found in Sec. 15. Design of equipment is based on the quantities of liquids and the efficiency and operating characteristics of the type of equipment selected.

2. *Chemical reaction.* The reactants may be the liquids themselves, or they may be dissolved in the insoluble liquids. The kinetics of this type of reaction are treated in Sec. 4.

3. *Cooling or heating a liquid by direct contact with another.* Although liquid-liquid-contact operations have not been used widely for heat transfer alone, this technique is one of increasing interest. Applications also include cases in which chemical reaction or liquid extraction occurs simultaneously.

4. *Creating permanent emulsions.* The objective is to disperse one liquid within another in such finely divided form that separation by settling either does not occur or occurs extremely slowly. The purpose is to prepare the emulsion. Neither extraction nor chemical reaction between the liquids is ordinarily sought.

Liquid-liquid contacting equipment may be generally classified into two categories: **stagewise** and **continuous** (**differential**) contact.

The function of a stage is to contact the liquids, allow equilibrium to be approached, and to make a mechanical separation of the liquids. The contacting and separating correspond to mixing the liquids, and settling the resulting dispersion; so these devices are usually called **mixer-settlers.** The operation may be carried out in batch fashion or with continuous flow. If batch, it is likely that the same vessel will serve for both mixing and settling, whereas if continuous, separate vessels are usually but not always used.

Mixer-Settler Equipment The equipment for extraction or chemical reaction may be classified as follows:

I. Mixers
    A. Flow or line mixers
        1. Mechanical agitation
        2. No mechanical agitation
    B. Agitated vessels
        1. Mechanical agitation
        2. Gas agitation
II. Settlers
    A. Nonmechanical
        1. Gravity
        2. Centrifugal (cyclones)
    B. Mechanical (centrifuges)
    C. Settler auxiliaries
        1. Coalescers
        2. Separator membranes
        3. Electrostatic equipment

In principle, at least, any mixer may be coupled with any settler to provide the complete stage. There are several combinations which are especially popular. Continuously operated devices usually, but not always, place the mixing and settling functions in separate vessels. Batch-operated devices may use the same vessel alternately for the separate functions.

Flow or Line Mixers

Definition Flow or line mixers are devices through which the liquids to be contacted are passed, characterized principally by the very small time of contact for the liquids. They are used only for continuous operations or semibatch (in which one liquid flows continuously and the other is continuously recycled). If holding time is required for extraction or reaction, it must be provided by passing the mixed liquids through a vessel of the necessary volume. This may be a long pipe of large diameter, sometimes fitted with segmental baffles, but frequently the settler which follows the mixer serves. The energy for mixing and dispersing usually comes from pressure drop resulting from flow.

There are many types, and only the most important can be mentioned here. [See also Hunter, in Dunstan (ed.), *Science of Petroleum,* vol. 3, Oxford, New York, 1938, pp. 1779–1797.] They are used fairly extensively in treating petroleum distillates, in vegetable-oil, refining, in extraction of phenol-bearing coke-oven liquors, in some metal extractions, and the like. Kalichevsky and Kobe (*Petroleum Refining*

with Chemicals, Elsevier, New York, 1956) discuss detailed application in the refining of petroleum.

Jet Mixers These depend upon impingement of one liquid on the other to obtain a dispersion, and one of the liquids is pumped through a small nozzle or orifice into a flowing stream of the other. Both liquids are pumped. They can be used successfully only for liquids of low interfacial tension. See Fig. 18-29 and also Hunter and Nash [*Ind. Chem.,* **9,** 245, 263, 317 (1933)]. Treybal (*Liquid Extraction,* 2d ed., McGraw-Hill, New York, 1963) describes a more elaborate device. For a study of the extraction of antibiotics with jet mixers, see Anneskova and Boiko, *Med. Prom. SSSR,* **13**(5), 26 (1959). Insonation with ultrasound of a toluene-water mixture during methanol extraction with a simple jet mixer improves the rate of mass transfer, but the energy requirements for significant improvement are large [Woodle and Vilbrandt, *Am. Inst. Chem. Eng. J.,* **6,** 296 (1960)].

Injectors The flow of one liquid is induced by the flow of the other, with only the majority liquid being pumped at relatively high velocity. Figure 18-30 shows a typical device used in semibatch fashion for washing oil with a recirculated wash liquid. It is installed directly in the settling drum. See also Hampton (U.S. Patent 2,091,709, 1933), Sheldon (U.S. Patent 2,009,347, 1935), and Ng (U.S. Patent 2,665,975, 1954). Folsom [*Chem. Eng. Prog.,* **44,** 765 (1948)] gives a good review of basic principles. The most thorough study for extraction is provided by Kafarov and Zhukovskaya [*Zh. Prikl. Khim.,* **31,** 376 (1958)], who used very small injectors. With an injector measuring 73 mm from throat to exit, with 2.48-mm throat diameter, they extracted benzoic acid and acetic acid from water with carbon tetrachloride at the rate of 58 to 106 L/h, to obtain a stage efficiency $E = 0.8$ to 1.0. Data on flow characteristics are also given. Boyadzhiev and Elenkov [*Collect. Czech. Chem. Commun.,* **31,** 4072 (1966)] point out that the presence of surface-active agents exerts a profound influence on drop size in such devices.

Orifices and Mixing Nozzles Both liquids are pumped through constrictions in a pipe, the pressure drop of which is partly utilized to create the dispersion (see Fig. 18-31). Single nozzles or several in series may be used. For the orifice mixers, as many as 20 orifice plates each with 13.8-kPa (2-lb/in²) pressure drop may be used in series [Morell and Bergman, *Chem. Metall. Eng.,* **35,** 211 (1928)]. In the Dualayer process for removal of mercaptans from gasoline, 258 m³/h (39,000 bbl/day) of oil and treating solution are contacted with 68.9-kPa (10-lb/in²) pressure drop per stage [Greek et al., *Ind. Eng. Chem.,* **49,** 1938 (1957)]. Holland et al. [*Am. Inst. Chem. Eng. J.,* **4,** 346 (1958); **6,** 615 (1960)] report on the interfacial area produced between two immiscible liquids entering a pipe (diameter 0.8 to 2.0 in) from an orifice, $\gamma_D = 0.02$ to 0.20, at flow rates of 0.23 to 4.1 m³/h (1 to 18 gal/min). At a distance 17.8 cm (7 in) downstream from the orifice,

$$a_{av} = \frac{0.179}{\sigma g_c} (C_O^2 \, \Delta p)^{0.75} \left(\frac{\sigma \sqrt{g_c \rho_{av}}}{\mu_D} \right)^{0.158} \left[\left(\frac{d_t}{d_O} \right)^4 - 1 \right]^{0.117} \gamma_D^{0.878} \quad (18\text{-}8)$$

where a_{av} = interfacial surface, cm²/cm³; C_O = orifice coefficient, dimensionless; d_t = pipe diameter, in; d_O = orifice diameter, in; g_c =
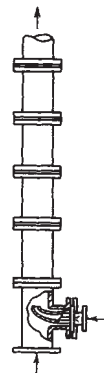
FIG. 18-29 Elbow jet mixer.
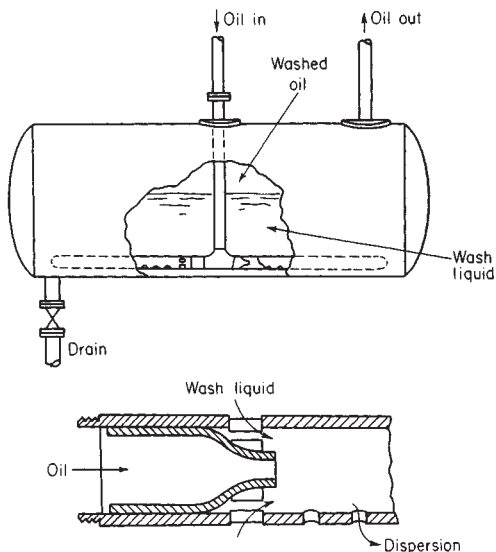
FIG. 18-30 Injector mixer. (*Ayres, U.S. Patent 2,531,547, 1950.*)

gravitational conversion factor, (32.2 lbm·ft)/(lbf·s²); Δp = pressure drop across orifice, lbf/ft²; μ_D = viscosity of dispersed phase, lbm/(ft·s); ρ_{av} = density of dispersed phase, lbm/ft; and σ = interfacial tension, lbf/ft. See also Shirotsuka et al. [*Kagaku Kogaku*, **25**, 109 (1961)].

Valves Valves may be considered to be adjustable orifice mixers. In desalting crude petroleum by mixing with water, Hayes et al. [*Chem. Eng. Prog.*, **45**, 235 (1949)] used a globe-valve mixer operating at 110- to 221-kPa (16- to 32-lb/in²) pressure drop for mixing 66 m³/h (416 bbl/h) oil with 8 m³/h (50 bbl/h) water, with best results at the lowest value. Simkin and Olney [*Am. Inst. Chem. Eng. J.*, **2**, 545 (1956)] mixed kerosine and white oil with water, using 0.35- to 0.62-kPa (0.05- to 0.09-lb/in²) pressure drop across a 1-in gate valve, at 22-m³/h (10-gal/min) flow rate for optimum separating conditions in a cyclone, but higher pressure drops were required to give good extractor efficiencies.

Pumps Centrifugal pumps, in which the two liquids are fed to the suction side of the pump, have been used fairly extensively, and they offer the advantage of providing interstage pumping at the same time. They have been commonly used in the extraction of phenols from coke-oven liquors with light oil [Gollmar, *Ind. Eng. Chem.*, **39**, 596, 1947); Carbone, *Sewage Ind. Wastes*, **22**, 200 (1950)], but the intense shearing action causes emulsions with this low-interfacial-tension system. Modern plants use other types of extractors. Pumps are useful in
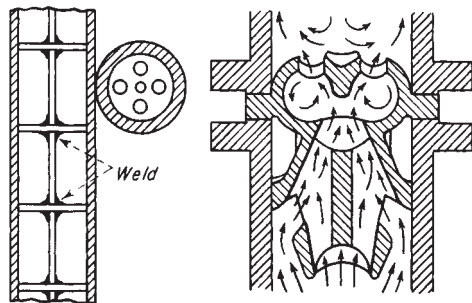
the extraction of slurries, as in the extraction of uranyl nitrate from acid-uranium-ore slurries [*Chem. Eng.*, **66**, 30 (Nov. 2, 1959)]. Shaw and Long [*Chem. Eng.*, **64**(11), 251 (1957)] obtain a stage efficiency of 100 percent ($E = 1.0$) in a uranium-ore-slurry extraction with an open impeller pump. In order to avoid emulsification difficulties in these extractions, it is necessary to maintain the organic phase continuous, if necessary by recycling a portion of the settled organic liquid to the mixer.

Agitated Line Mixer See Fig. 18-32. This device, which combines the features of orifice mixers and agitators, is used extensively in treating petroleum and vegetable oils. It is available in sizes to fit ½- to 10-in pipe. The device of Fig. 18-33, with two impellers in separate stages, is available in sizes to fit 4- to 20-in pipe.

Packed Tubes Cocurrent flow of immiscible liquids through a packed tube produces a one-stage contact, characteristic of line mixers. For flow of isobutanol-water[*] through a 0.5-in diameter tube packed with 6 in of 3-mm glass beads, Leacock and Churchill [*Am. Inst. Chem. Eng. J.*, **7**, 196 (1961)] find

$$k_C a_{av} = c_1 L_C^{0.5} L_D \tag{18-9}$$

$$k_D a_{av} = c_2 L_C^{0.75} L_D^{0.75} \tag{18-10}$$

where c_1 = 0.00178 using SI units and 0.00032 using U.S. customary units; and c_2 = 0.0037 using SI units and 0.00057 using U.S. customary units. These indicate a stage efficiency approaching 100 percent. Organic-phase holdup and pressure drop for larger pipes similarly packed are also available [Rigg and Churchill, ibid., **10**, 810 (1964)].

Pipe Lines The principal interest here will be for flow in which one liquid is dispersed in another as they flow cocurrently through a pipe (stratified flow produces too little interfacial area for use in liquid extraction or chemical reaction between liquids). Drop size of dispersed phase, if initially very fine at high concentrations, increases as the distance downstream increases, owing to coalescence [see Holland, loc. cit.; Ward and Knudsen, *Am. Inst. Chem. Eng. J.*, **13**, 356 (1967)]; or if initially large, decreases by breakup in regions of high shear [Sleicher, ibid., **8**, 471 (1962); *Chem. Eng. Sci.*, **20**, 57 (1965)]. The maximum drop size is given by (Sleicher, loc. cit.)

[*] Isobutanol dispersed: L_D = 3500 to 27,000; water continuous; L_C = 6000 to 32,000 in pounds-mass per hour-square foot (to convert to kilograms per second-square meter, multiply by 1.36×10^{-3}).

FIG. 18-31 Orifice mixer and nozzle mixer.
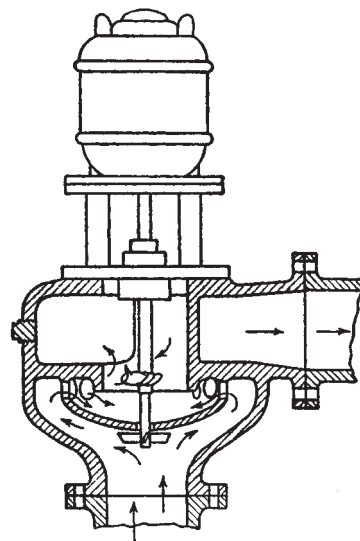
FIG. 18-32 Nettco Corp. Flomix.
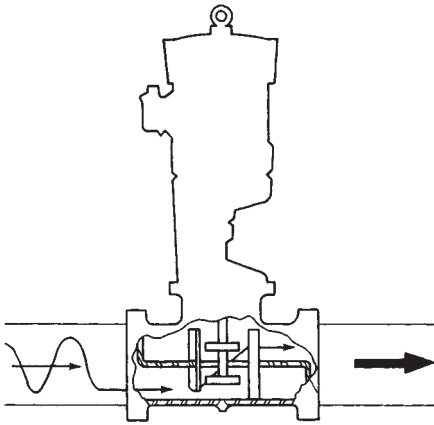
FIG. 18-33   Lightnin line blender. (*Mixing Equipment Co., Inc., with permission.*)

$$\frac{d_{p,\max}\rho_C V^2}{\sigma g_c}\sqrt{\frac{\mu_C V}{\sigma g_c}} = C\left[1 + 0.7\left(\frac{\mu_D V}{\sigma g_c}\right)^{0.7}\right] \qquad (18\text{-}11)$$

where $C = 43$ ($d_t = 0.013$ m or 0.0417 ft) or 38 ($d_t = 0.038$ m or 0.125 ft), with $d_{p,av} = d_{p,\max}/4$ for high flow rates and $d_{p,\max}/13$ for low velocities.

Extensive measurements of the rate of mass transfer between *n*-butanol and water flowing in a 0.008-m (0.314-in) ID horizontal pipe are reported by Watkinson and Cavers [*Can. J. Chem. Eng.,* **45,** 258 (1967)] in a series of graphs not readily reproduced here. Length of a transfer unit for either phase is strongly dependent upon flow rate and passes through a pronounced maximum at an organic-water phase ratio of 0.5. In energy (pressure-drop) requirements and volume, the pipe line compared favorably with other types of extractors. Boyadzhiev and Elenkov [*Chem. Eng. Sci.,* **21,** 955 (1966)] concluded that, for the extraction of iodine between carbon tetrachloride and water in turbulent flow, drop coalescence and breakup did not influence the extraction rate. Yoshida et al. [*Coal Tar* (Japan), **8,** 107 (1956)] provide details of the treatment of crude benzene with sulfuric acid in a 1-in diameter pipe, $N_{Re} = 37,000$ to 50,000. Fernandes and Sharma [*Chem. Eng. Sci.,* **23,** 9 (1968)] used cocurrent flow downward of two liquids in a pipe, agitated with an upward current of air.

The pipe has also been used for the transfer of heat between two immiscible liquids in cocurrent flow. For hydrocarbon oil-water, the heat-transfer coefficient is given by

$$\frac{U a_{av} d_t^2}{v k_{to}} = \frac{\gamma_D N_{We,t}^{6/5}}{\dfrac{k_{to}}{0.415 k_{tC}} + \dfrac{k_{to}}{0.173 k_{tD}}} \qquad (18\text{-}12)$$

for $\gamma_D = 0$ to 0.2. Additional data for $\gamma_D = 0.4$ to 0.8 are also given. Data for stratified flow are given by Wilke et al. [*Chem. Eng. Prog.,* **59,** 69 (1963)] and Grover and Knudsen [*Chem. Eng. Prog.,* **51,** *Symp. Ser.* **17,** 71 (1955)].

Mixing in Agitated Vessels   Agitated vessels may frequently be used for either batch or continuous service and for the latter may be sized to provide any holding time desired. They are useful for liquids of any viscosity up to 750 Pa·s (750,000 cP), although in contacting two liquids for reaction or extraction purposes viscosities in excess of 0.1 Pa·s (100 cP) are only rarely encountered.

Mechanical Agitation   This type of agitation utilizes a rotating impeller immersed in the liquid to accomplish the mixing and dispersion. There are literally hundreds of devices using this principle, the major variations being found when chemical reactions are being carried out. The basic requirements regarding shape and arrangement of the vessel, type and arrangement of the impeller, and the like are essentially the same as those for dispersing finely divided solids in liquids, which are fully discussed in Sec. 18.

The following summary of operating characteristics of mechanically agitated vessels is confined to the data available on liquid-liquid contacting.

Phase Dispersed   There is an ill-defined upper limit to the volume fraction of dispersed liquid which may be maintained in an agitated dispersion. For dispersions of organic liquids in water [Quinn and Sigloh, *Can. J. Chem. Eng.,* **41,** 15 (1963)],

$$\gamma_{Do,\max} = \gamma' + \left(\frac{C}{N^3}\right) \qquad (18\text{-}13)$$

where γ' is a constant, asymptotic value, and C is a constant, both depending in an unestablished manner upon the system physical properties and geometry. Thus, inversion of a dispersion may occur if the agitator speed is increased. With systems of low interfacial tension ($\sigma' = 2$ to 3 mN/m or 2 to 3 dyn/cm), γ_D as high as 0.8 can be maintained. Selker and Sleicher [*Can. J. Chem. Eng.,* **43,** 298 (1965)] and Yeh et al. [*Am. Inst. Chem. Eng. J.,* **10,** 260 (1964)] feel that the viscosity ratio of the liquids alone is important. Within the limits in which either phase can be dispersed, for *batch operation* of baffled vessels, that phase in which the impeller is immersed when at rest will normally be continuous [Rodger, Trice, and Rushton, *Chem. Eng. Prog.,* **52,** 515 (1956); Laity and Treybal, *Am. Inst. Chem. Eng. J.,* **3,** 176 (1957)]. With water dispersed, *dual emulsions* (continuous phase found as small droplets within larger drops of dispersed phase) are possible. In *continuous operation,* the vessel is first filled with the liquid to be continuous, and agitation is then begun, after which the liquid to be dispersed is introduced.

Uniformity of Mixing   This refers to the gross uniformity throughout the vessel and not to the size of the droplets produced. For *unbaffled vessels, batch, with an air-liquid interface,* Miller and Mann [*Trans. Am. Inst. Chem. Eng.,* **40,** 709 (1944)] mixed water with several organic liquids, measuring uniformity of mixing by sampling the tank at various places, comparing the percentage of dispersed phase found with that in the tank as a whole. A power application of 200 to 400 W/m³ [(250 to 500 ft·lb)/(min·ft³)] gave maximum and nearly uniform performance for all. See also Nagata et al. [*Chem. Eng. (Japan),* **15,** 59 (1951)].

For *baffled vessels operated continuously, no air-liquid interface,* flow upward, light liquid dispersed [Treybal, *Am. Inst. Chem. Eng. J.,* **4,** 202 (1958)], the average fraction of dispersed phase in the vessel $\gamma_{D,av}$ is less than the fraction of the dispersed liquid in the feed mixture, unless the impeller speed is above a certain critical value which depends upon vessel geometry and liquid properties. Thornton and Bouyatiotis [*Ind. Chem.,* **39,** 298 (1963); *Inst. Chem. Eng. Symp. Liquid Extraction,* Newcastle-upon-Tyne, April 1967] have presented correlations of data for a 17.8-cm (7-in) vessel, but these do not agree with observations on 15.2- and 30.5-cm (6- and 12-in) vessels in Treybal's laboratory. See also Kovalev and Kagan [*Zh. Prikl. Khim.,* **39,** 1513 (1966)] and Trambouze [*Chem. Eng. Sci.,* **14,** 161 (1961)]. Stemerding et al. [*Can. J. Chem. Eng.,* **43,** 153 (1965)] present data on a large mixing tank [15 m³ (530 ft³)] fitted with a marine-type propeller and a draft tube.

Drop Size and Interfacial Area   The drops produced have a size range [Sullivan and Lindsey, *Ind. Eng. Chem. Fundam.,* **1,** 87 (1962); Sprow, *Chem. Eng. Sci.,* **22,** 435 (1967); and Chen and Middleman, *Am. Inst. Chem. Eng. J.,* **13,** 989 (1967)]. The average drop size may be expressed as

$$d_{p,av} = \frac{\sum n_i d_{pi}^3}{\sum n_i d_{pi}^2} \qquad (18\text{-}14)$$

and if the drops are spherical,

$$a_{av} = \frac{6\gamma_{D,av}}{d_{p,av}} \qquad (18\text{-}15)$$

The drop size varies locally with location in the vessel, being smallest at the impeller and largest in regions farthest removed from the impeller owing to coalescence in regions of relatively low turbulence

intensity [Schindler and Treybal, *Am. Inst. Chem. Eng. J.,* **14,** 790 (1968); Vanderveen, U.S. AEC UCRL-8733, 1960]. Interfacial area and hence average drop size have been measured by light transmittance, light scattering, direct photography, and other means. Typical of the resulting correlations is that of Thornton and Bouyatiotis (*Inst. Chem. Eng. Symp. Liquid Extraction,* Newcastle-upon-Tyne, April 1967) for a 17.8-cm- (7-in-) diameter baffled vessel, six-bladed flat-blade turbine, d_i = 6.85 cm (0.225 ft), operated full, for organic liquids (σ' = 8.5 to 34, ρ_D = 43.1 to 56.4, μ_D = 1.18 to 1.81) dispersed in water, in the absence of mass transfer, and under conditions giving nearly the vessel-average $d_{p,\text{av}}$:

$$\frac{d_{p,\text{av}}}{d_p^0} = 1 + 1.18\phi_D \left(\frac{\sigma^2 g_c^2}{d_p^0 \mu_c^2 g}\right)\left(\frac{\mu_c^4 g}{\Delta\rho\, \sigma^3 g_c^3}\right)^{0.62}\left(\frac{\Delta\rho}{\rho_c}\right)^{0.05} \quad (18\text{-}16)$$

where d_p^0 is given by

$$\frac{(d_p^0)^3 \rho_C^2 g}{\mu_c^2} = 29.0\left(\frac{P^3 g_c^3}{v^3 \rho_c^2 \mu_c g^4}\right)^{-0.32}\left(\frac{\rho_C \sigma^3 g_c^3}{\mu_c^4 g}\right)^{0.14} \quad (18\text{-}17)$$

Caution is needed in using such correlations, since those available do not generally agree with each other. For example, Eq. (21-28) gives $d_{p,\text{av}}$ = 4.78(10^{-4}) ft for a liquid pair of properties a' = 30, ρ_C = 62.0, ρ_D = 52.0, μ_C = 2.42, μ_D = 1.94, $\gamma_{D,\text{av}}$ = 0.20 in a vessel T = Z = 0.75, a turbine impeller d_i = 0.25 turning at 400 r/min. Other correlations provide 3.28(10^{-4}) [Thornton and Bouyatiotis, *Ind. Chem.,* **39,** 298 (1963)], 8.58(10^{-4}) [Calderbank, *Trans. Inst. Chem. Eng. (London),* **36,** 443 (1958)], 6.1(10^{-4}) [Kafarov and Babinov, *Zh. Prikl. Khim,* **32,** 789 (1959)], and 2.68(10^{-3}) (Rushton and Love, paper at AIChE, Mexico City, September 1967). See also Vermeulen et al. [*Chem. Eng. Prog.,* **51,** 85F (1955)], Rodgers et al. [ibid., **52,** 515 (1956); U.S. AEC ANL-5575 (1956)], Rodrigues et al. [*Am. Inst. Chem. Eng. J.,* **7,** 663 (1961)], Sharma et al. [*Chem. Eng. Sci.,* **21,** 707 (1966); **22,** 1267 (1967)], and Kagan and Kovalev [*Khim. Prom.,* **42,** 192 (1966)]. For the effect of absence of baffles, see Fick et al. (U.S. AEC UCRL-2545, 1954) and Schindler and Treybal [*Am. Inst. Chem. Eng. J.,* **14,** 790 (1968)]. The latter have observations during mass transfer.

Coalescence Rates   The droplets coalesce and redisperse at rates that depend upon the vessel geometry, N, $\gamma_{D,\text{av}}$, and liquid properties. The few measurements available, made with a variety of techniques, do not as yet permit quantitative estimates of the coalescence frequency v. Madden and Damarell [*Am. Inst. Chem. Eng. J.,* **8,** 233 (1962)] found for baffled vessels that v varied as $N^{2.2}\gamma_{D,\text{av}}^{0.5}$, and this has generally been confirmed by Groothius and Zuiderweg [*Chem. Eng. Sci.,* **19,** 63 (1964)], Miller et al. [*Am. Inst. Chem. Eng. J.,* **9,** 196 (1963)], and Howarth [ibid., **13,** 1007 (1967)], although absolute values of v in the various studies are not well related. Hillestad and Rushton (paper at AIChE, Columbus, Ohio, May 1966), on the other hand, find v to vary as $N^{0.73}\gamma_{D,\text{av}}$ for impeller Weber numbers $N_{\text{We},i}$ below a certain critical value and as $N^{-3.5}\gamma_{D,\text{av}}^{1.58}$ for higher Weber numbers. The influence of liquid properties is strong. There is clear evidence [Groothius and Zuiderweg, loc. cit.; *Chem. Eng. Sci.,* **12,** 288 (1960)] that coalescence rates are enhanced by mass transfer from a drop to the surrounding continuum and retarded by transfer in the reverse direction. See also Howarth [*Chem. Eng. Sci.,* **19,** 33 (1964)]. For a theoretical treatment of drop breakage and coalescence and their effects, see Valentas and Amundsen [*Ind. Eng. Chem. Fundam.,* **5,** 271, 533 (1966); **7,** 66 (1968)], Gal-Or and Walatka [*Am. Inst. Chem. Eng. J.,* **13,** 650 (1967)], and Curl [ibid., **9,** 175 (1963)].

In calculating the power required for mixers, a reasonable estimate of the average density and viscosity for a two-phase system is satisfactory.

Solids are often present in liquid streams either as a part of the processing system or as impurities that come along and have to be handled in the process. One advantage of mixers in differential contact equipment is the fact that they can handle slurries in one or both phases. In many industrial leaching systems, particularly in the minerals processing industry, coming out of the leach circuit is a slurry with a desired material involved in the liquid but a large amount of solids contained in the stream. Typically, the solids must be separated out by filtration or centrifugation, but there has always been a desire to try a direct liquid-liquid extraction with an immiscible liquid contact with this often highly concentrated slurry leach solution. The major prob-

lem with this approach is loss of organic material going out with the highly concentrated liquid slurry.

Data are not currently available on the dispersion with the newer fluidfoil impellers, but they are often used in industrial mixer-settler systems to maintain dispersion when additional resonance time holdup is required, after an initial dispersion is made by a radial- or axial-flow turbine.

Recent data by Calabrese[5] indicates that the sauter mean drop diameter can be correlated by equation and is useful to compare with other predictions indicated previously.

As an aside, when a large liquid droplet is broken up by shear stress, it tends initially to elongate into a dumbbell shape, which determines the particle size of the two large droplets formed. Then, the neck in the center between the ends of the dumbbell may explode or shatter. This would give a debris of particle sizes which can be quite different than the two major particles produced.

Liquid-Liquid Extraction   The actual configuration of mixers in multistage mixer-settlers and/or multistage columns is summarized in Section 15. A general handbook on this subject is *Handbook of Solvent Extraction* by Lowe, Beard, and Hanson. This handbook gives a comprehensive review of this entire operation as well.

In the liquid-liquid extraction area, in the mining industry, coming out of the leach tanks is normally a slurry, in which the desired mineral is dissolved in the liquid phase. To save the expense of separation, usually by filtration or centrifugation, attempts have been made to use a resident pump extraction system in which the organic material is contacted directly with the slurry. The main economic disadvantage to this proposed system is the fact that considerable amounts of organic liquid are entrained in the aqueous slurry system, which, after the extraction is complete, is discarded. In many systems this has caused an economic loss of solvent into this waste stream.

LIQUID-LIQUID-SOLID SYSTEMS

Many times solids are present in one or more phases of a solid-liquid system. They add a certain level of complexity in the process, especially if they tend to be a part of both phases, as they normally will do. Approximate methods need to be worked out to estimate the density of the emulsion and determine the overall velocity of the flow pattern so that proper evaluation of the suspension requirements can be made. In general, the solids will behave as though they were a fluid of a particular average density and viscosity and won't care much that there is a two-phase dispersion going on in the system. However, if solids are being dissolved or precipitated by participating in one phase and not the other, then they will be affected by which phase is dispersed or continuous, and the process will behave somewhat differently than if the solids migrate independently between the two phases within the process.

FLUID MOTION

Pumping   Some mixing applications can be specified by the pumping capacity desired from the impeller with a certain specified geometry in the vessel. As mentioned earlier, this sometimes is used to describe a blending requirement, but circulation and blending are two different things. The major area where this occurs is in draft tube circulators or pump-mix mixer settlers. In draft tube circulators (shown in Fig. 18-22), the circulation occurs through the draft tube and around the annulus and for a given geometry, the velocity head required can be calculated with reference to various formulas for geometric shapes. What is needed is a curve for head versus flow for the impeller, and then the system curve can be matched to the impeller curve. Adding to the complexity of this system is the fact that solids can settle out and change the character of the head curve so that the impeller can get involved in an unstable condition which has various degrees of erratic behavior depending upon the sophistication of the impeller and inlet and outlet vanes involved. These draft tube circulators often involve solids, and applications are often for precipitation or crystallization in these units. Draft tube circulators

can either have the impeller pump up in the draft tube and flow down the annulus or just the reverse. If the flow is down the annulus, then the flow has to make a 180° turn where it comes back at the bottom of the tank into the draft tube again. This is a very sensitive area, and special baffles must be used to carefully determine how the fluid will make this turn since many areas of constriction are involved in making this change in direction.

When pumping down the draft tube, flow normally makes a more troublefree velocity change to a flow going up the annulus. Since the area of the draft tube is markedly less than the area of the annulus, pumping up the draft tube requires less flow to suspend solids of a given settling velocity than does pumping down the draft tube.

Another example is to eliminate the interstage pump between mixing and settling stages in the countercurrent mixer-settler system. The radial-flow impeller typically used is placed very close to an orifice at the bottom of the mixing tank and can develop heads from 12 to 18 in. All the head-loss terms in the mixer and settler circuit have to be carefully calculated because they come very close to that 12- to 18-in range when the passages are very carefully designed and streamlined. If the mixing tank gets much above 10 ft in depth, then the heads have to be higher than the 12- to 18-in range and special designs have to be worked on which have the potential liability of increasing the shear rate acting on the dispersed phase to cause more entrainment and longer settling times. In these cases, it is sometimes desirable to put the mixer system outside the actual mixer tank and have it operate in a single phase or to use multiple impellers, each one of which can develop a portion of the total head required.

Heat Transfer   In general, the fluid mechanics of the film on the mixer side of the heat transfer surface is a function of what happens at that surface rather than the fluid mechanics going on around the impeller zone. The impeller largely provides flow across and adjacent to the heat-transfer surface and that is the major consideration of the heat-transfer result obtained. Many of the correlations are in terms of traditional dimensionless groups in heat transfer, while the impeller performance is often expressed as the impeller Reynolds number.

The fluidfoil impellers (shown in Fig. 18-2) usually give more flow for a given power level than the traditional axial- or radial-flow turbines. This is also thought to be an advantage since the heat-transfer surface itself generates the turbulence to provide the film coefficient and more flow should be helpful. This is true to a limited degree in jacketed tanks (Fig. 18-34), but in helical coils (Fig. 18-35), the
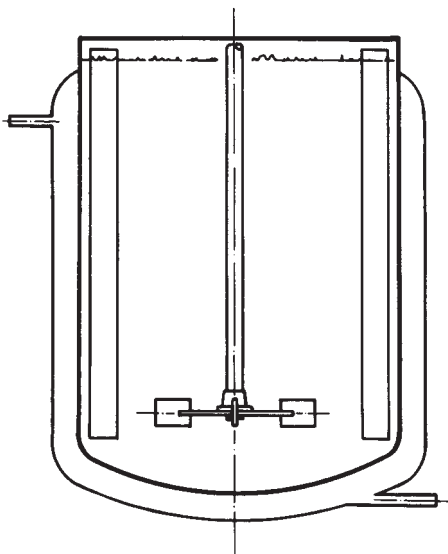
FIG. 18-34   Typical jacket arrangement for heat transfer.
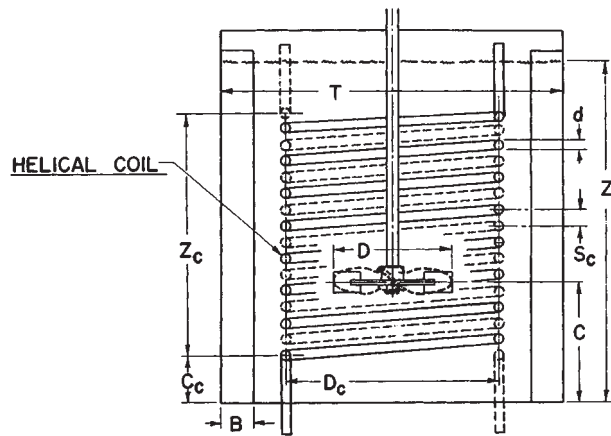
FIG. 18-35   Typical arrangement of helical coil at mixing vessel for heat transfer.

extreme axial flow of these impellers tends to have the first or second turn in the coil at the bottom of the tank blank off the flow from the turns above it in a way that (at the same power level) the increased flow from the fluidfoil impeller is not helpful. It best gives the same coefficient as with the other impellers and on occasion can cause a 5 to 10 percent reduction in the heat-transfer coefficient over the entire coil.

JACKETS AND COILS OF AGITATED VESSELS

Most of the correlations for heat transfer from the agitated liquid contents of vessels to jacketed walls have been of the form:

$$\frac{hD_j}{k} = a \left(\frac{L_p^2 N_r \rho}{\mu} \right)^b \left(\frac{c\mu}{k} \right)^{1/3} \left(\frac{\mu_b}{\mu_w} \right)^m \tag{18-18}$$

The film coefficient h is for the inner wall; D_j is the inside diameter of the mixing vessel. The term $L_p^2 N_r \rho / \mu$ is the Reynolds number for mixing in which L_p is the diameter and N_r the speed of the agitator. Recommended values of the constants a, b, and m are given in Table 18-2.

A wide variety of configurations exists for coils in agitated vessels. Correlations of data for heat transfer to helical coils have been of two forms, of which the following are representative:

$$\frac{hD_j}{k} = 0.87 \left(\frac{L_p^2 N_t \rho}{\mu} \right)^{0.62} \left(\frac{c\mu}{k} \right)^{1/3} \left(\frac{\mu_b}{\mu_w} \right)^{0.14} \tag{18-19}$$

TABLE 18-2   Values of Constants for Use in Eq. (18-18)

Agitator	a	b	m	Range of Reynolds number
Paddle[a]	0.36	2/3	0.21	$300–3 \times 10^5$
Pitched-blade turbine[b]	0.53	2/3	0.24	80–200
Disk, flat-blade turbine[c]	0.54	2/3	0.14	$40–3 \times 10^5$
Propeller[d]	0.54	2/3	0.14	2×10^3 (one point)
Anchor[b]	1.0	1/2	0.18	10–300
Anchor[b]	0.36	2/3	0.18	300–40,000
Helical ribbon[e]	0.633	1/2	0.18	$8–10^5$

[a]Chilton, Drew, and Jebens, *Ind. Eng. Chem.*, **36**, 510 (1944), with constant *m* modified by Uhl.
[b]Uhl, *Chem. Eng. Progr., Symp. Ser.* 17, **51**, 93 (1955).
[c]Brooks and Su, *Chem. Eng. Progr.*, **55**(10), 54 (1959).
[d]Brown et al., *Trans. Inst. Chem. Engrs.* (*London*), **25**, 181 (1947).
[e]Gluz and Pavlushenko, *J. Appl. Chem. U.S.S.R.*, **39**, 2323 (1966).

where the agitator is a paddle, the Reynolds number range is 300 to 4×10^5 [Chilton, Drew, and Jebens, *Ind. Eng. Chem.,* **36,** 510 (1944)], and

$$\frac{hD_o}{k} = 0.17 \left(\frac{L_p^2 N_r \rho}{\mu}\right)^{0.67} \left(\frac{c\mu}{k}\right)^{0.37} \left(\frac{L_p}{D_j}\right)^{0.1} \left(\frac{D_o}{D_j}\right)^{0.5} \quad (18\text{-}20)$$

where the agitator is a disk flat-blade turbine, and the Reynolds number range is 400 to $(2)(10^5)$ [Oldshue and Gretton, *Chem. Eng. Prog.,* **50,** 615 (1954)]. The term D_o is the outside diameter of the coil tube.

The most comprehensive correlation for heat transfer to vertical baffle-type coils is for a disk flat-blade turbine over the Reynolds number range 10^3 to $(2)(10^6)$:

$$\frac{hD_o}{k} = 0.09 \left(\frac{L_p^2 N_r \rho}{\mu}\right)^{0.65} \left(\frac{c\mu}{k}\right)^{1/3} \left(\frac{L_p}{D_j}\right)^{1/3} \left(\frac{2}{n_b}\right)^{0.2} \left(\frac{\mu}{\mu_f}\right)^{0.4} \quad (18\text{-}21)$$

where n_b is the number of baffle-type coils and μ_f is the fluid viscosity at the mean film temperature [Dunlop and Rushton, *Chem. Eng. Prog. Symp. Ser.* 5, **49,** 137 (1953)].

Chapman and Holland (*Liquid Mixing and Processing in Stirred Tanks,* Reinhold, New York, 1966) review heat transfer to low-viscosity fluids in agitated vessels. Uhl ["Mechanically Aided Heat Transfer," in Uhl and Gray (eds.), *Mixing: Theory and Practice,* vol. I, Academic, New York, 1966, chap. V] surveys heat transfer to low- and high-viscosity agitated fluid systems. This review includes scraped-wall units and heat transfer on the jacket and coil side for agitated vessels.

LIQUID-LIQUID-GAS-SOLID SYSTEMS

This is a relatively unusual combination, and one of the more common times it exists is in the fermentation of hydrocarbons with aerobic microorganisms in an aqueous phase. The solid phase is a microorganism which is normally is in the aqueous phase and is using the organic phase for food. Gas is supplied to the system to make the fermentation aerobic. Usually the viscosities are quite low, percent solids is also modest, and there are no special design conditions required when this particular gas-liquid-liquid-solid combination occurs. Normally, average properties for the density of viscosity of the liquid phase are used. In considering that the role the solids play in the system is adequate, there are cases of other processes which consist of four phases, each of which involves looking at the particular properties of the phases to see whether there are any problems of dispersion, suspension, or emulsification.

COMPUTATIONAL FLUID DYNAMICS

There are several software programs that are available to model flow patterns of mixing tanks. They allow the prediction of flow patterns based on certain boundary conditions. The most reliable models use accurate fluid mechanics data generated for the impellers in question and a reasonable number of modeling cells to give the overall tank flow pattern. These flow patterns can give velocities, streamlines, and localized kinetic energy values for the systems. Their main use at the present time is to look at the effect of making changes in mixing variables based on doing certain things to the mixing process. These programs can model velocity, shear rates, and kinetic energy, but probably cannot adapt to the actual chemistry of diffusion or mass-transfer kinetics of actual industrial process at the present time.

Relatively uncomplicated transparent tank studies with tracer fluids or particles can give a similar feel for the overall flow pattern. It is important that a careful balance be made between the time and expense of calculating these flow patterns with computational fluid dynamics compared to their applicability to an actual industrial process. The future of computational fluid dynamics appears very encouraging and a reasonable amount of time and effort put forth in this regard can yield immediate results as well as potential for future process evaluation.

Figures 18-36, 18-37, and 18-38 show some approaches. Figure 18-36 shows velocity vectors for an A310 impeller. Figure 18-37 shows contours of kinetic energy of turbulence. Figure 18-38 uses a particle trajectory approach with neutral buoyancy particles.
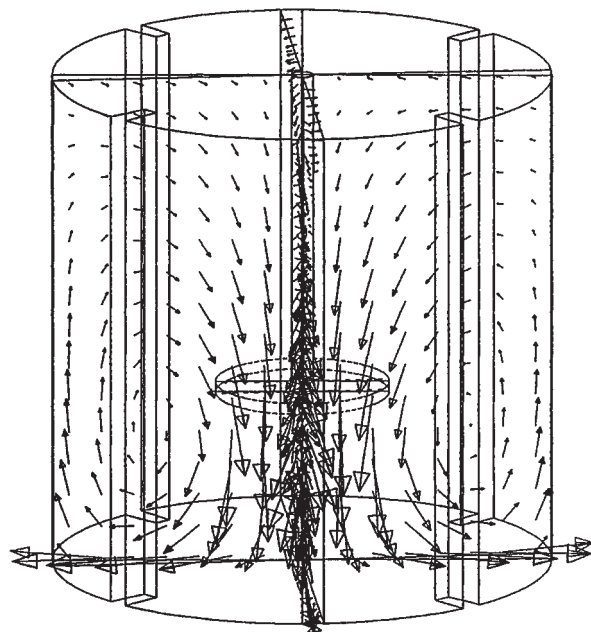
FIG. 18-36 Laser scan.
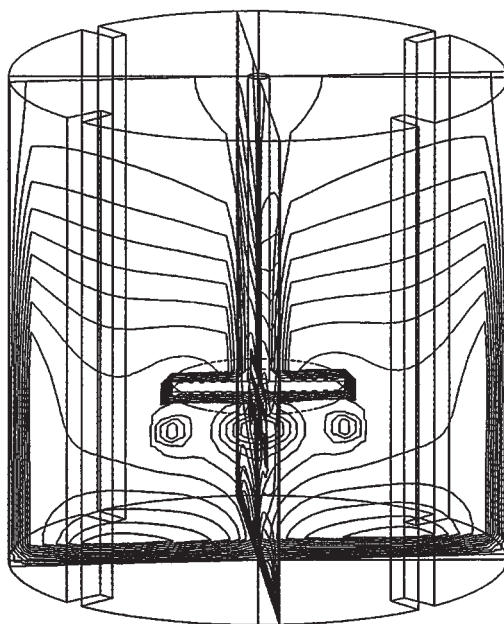
FIG. 18-37 Laser scan.
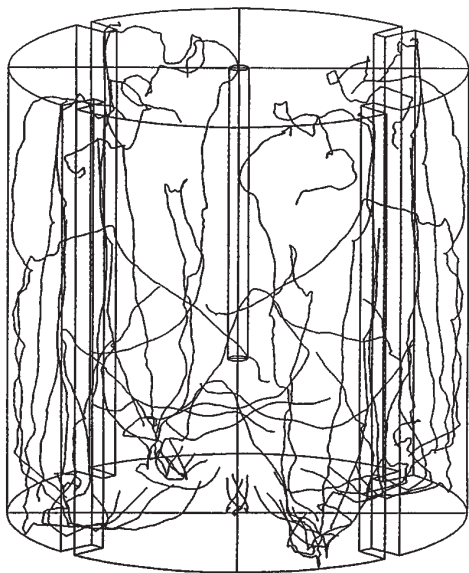
FIG. 18-38   Laser scan.

Numerical fluid mechanics can define many of the fluid mechanics parameters for an overall reactor system. Many of the models break up the mixing tank into small microcells. Suitable material and mass-transfer balances between these cells throughout the reactor are then made. This can involve long and massive computational requirements. Programs are available that can give reasonably acceptable models of experimental data taken in mixing vessels. Modeling the three-dimensional aspect of a flow pattern in a mixing tank can require a large amount of computing power.

Most modeling codes are a time-averaging technique. Depending upon the process, a time-dependent technique may be more suitable. Time-dependent modeling requires much more computing power than does time averaging.

GENERAL REFERENCES

1. J. Y. Oldshue, "Mixing '89," *Chemical Engineering Progress,* **85**(5): 33–42 (1989).
2. J. C. Middleton, *Proc. 3d European Conf. on Mixing,* 4/89, BHRA, pp. 15–36.
3. J. Y. Oldshue, T. A. Post, R. J. Weetman, "Comparison of Mass Transfer Characteristics of Radial and Axial Flow Impellers," *BHRA Proc. 6th European Conf. on Mixing,* 5/88.
4. A. W. Neinow, B. Buckland, R. J. Weetman, *Mixing XII Research Conference,* Potosi, Mo., 8/89.
5. R. Calabrese et al., *AIChE J.* **32:** 657, 677 (1986).
6. T. N. Zwietering, *Chemical Engineering Science,* **8**(3): 244–253 (1958).
7. J. Y. Oldshue, *Chemical Engineering Progress,* "Mixing of Slurries Near the Ultimate Settled Solids Concentration," **77**(5): 95–98 (1981).

PASTE AND VISCOUS-MATERIAL MIXING

GENERAL REFERENCES: *Dry Solids, Paste and Dough Mixing Equipment Testing Procedure,* American Institute of Chemical Engineers, New York, 1979. Fischer, *Chem. Eng.* **69**(3): 52 (1962). Irving and Saxton, "Mixing of High Viscosity Materials," in Uhl and Gray, *Mixing Theory and Practice,* vol. 2, Academic, New York, 1967, chap. 8. Mohr, in Bernhardt, *Processing of Thermoplastic Materials,* Reinhold, New York, 1967, chap. 3. Parker, *Chem. Eng.* **71**(12): 166 (1964). Rauwendaal, *Mixing in Polymer Processing,* Marcel Dekker, 1991. Tadmor and Gogos, *Principles of Polymer Processing,* Wiley, New York, 1979.

INTRODUCTION

Thick mixtures with viscosities greater than 10 Pa·s are not readily mixed in conventional stirred pots with either propeller or turbine agitators. The high viscosity may be due to that of the matrix fluid itself, to a high slurry concentration, or to interactions between components.

Because of the high viscosity, the mixing Reynolds number (Re = $D^2\rho N/\mu$) may be well below 100. Mixing occurs as a consequence of laminar shearing and stretching forces, and turbulence plays no part. Relative motion of an agitator stretches and deforms the material between itself and the vessel wall. As a layer of fluid gets stretched into thinner layers, the striations diminish and the shear forces tear solid agglomerates apart until apparent homogeneity is obtained. When solids are present, it may be necessary to reduce the particle size of the solids, even down to submicron size, such as in pigment dispersion.

Mixers for high-viscosity materials generally have a small high shear zone (to minimize dissipative heat effects) and rely on the impeller to circulate all of the mixer contents past the high shear zone. It may be necessary to take special steps to eliminate any stagnant zones or perhaps to avoid material riding around on mixing blades without being reincorporated into the matrix.

Most paste and high-viscosity mixtures are nonnewtonian, with viscosity dropping with shear rate. Consequently, increasing impeller speed may be counterproductive, as the transmitted shear drops rapidly and an isolated hole may be created in the central mass without circulation of the bulk material in the remainder of the vessel.

The relative viscosities of the materials being mixed can be very important. Karam and Bellinger [*Ind. Eng. Chem. Fund.* **7:** 576 (1981)] and Grace [*Engr. Fndn. Mixing Research Conf.* Andover, N.H., 1973] have shown that there is a maximum viscosity ratio (μ dispersed/μ continuous equal to about 4) above which droplets can no longer be dispersed by shear forces. The only effective dispersing mechanism for high-viscosity-ratio mixtures is elongational flow.

Equipment for viscous mixing usually has a small clearance between impeller and vessel walls, a relatively small volume, and a high power per unit volume. Intermeshing blades or stators may be present to prevent material from cylindering on the rotating impeller.

Blade shape can have a significant impact on the mixing process. A scraping profile will be useful if heat transfer is important, whereas a smearing profile will be more effective for dispersion. Ease of cleaning and ease of discharge may also be important.

BATCH MIXERS

Change-Can Mixers   Change-can mixers are vertical batch mixers in which the container is a separate unit easily placed in or removed from the frame of the machine. They are available in capacities of about 4 to 1500 L (1 to 400 gal). The commonest type is the pony mixer. Separate cans allow the batch to be carefully measured or weighed before being brought to the mixer itself. The mixer also may serve to transport the finished batch to the next operation or to storage. The identity of each batch is preserved, and weight checks are easily made.

Change cans are relatively inexpensive. A good supply of cans allows cleaning to be done in a separate department, arranged for efficient cleaning. In paint and ink plants, where mixing precedes milling or grinding and where there may be a long run of the same formulation and color, the cans may be used for an extended period without cleaning, as long as no drying out or surface oxidation occurs.

In most change-can mixers, the mixing elements are raised from the can by either a vertical lift or a tilting head; in others, the can is

dropped away from the mixing elements. After separation the mixing elements drain into the can, and the blades can be wiped down. With the can out of the way, complete cleaning in the blades and their supports is simple. If necessary, blades may be cleaned by rotating them in solvent.

Intimate mixing is accomplished in change-can mixers in two ways. One method is to have the mixing-unit assembly revolve in a planetary motion so that the rotating blades sweep the entire circumference of the can (Fig. 18-39). The other is to mount the can on a rotating turntable so that all parts of the can wall pass fixed scraper blades or the agitator blades at a point of minimum clearance.

A type of heavy-duty planetary change-can mixer has been used extensively for processing critical solid-propellant materials. In a design offered by APV Chemical Machinery Inc., the mixer blades pass through all portions of the can volume, and the two blades wipe each other, thus assuring no unmixed portions. A dead spot under the mixer blades is avoided by having both blades off the centerline of the can. The cans fit tightly enough so that mixing can be achieved under vacuum or pressure. There is no contact between the glands and the material being mixed. Charging ports located in the housing directly above the mixing can make it possible to charge materials to the mixer with the can in the operating position. This type of mixer is available in sizes of 0.5 L (about 1 pt) to 1.6 m³ (420 gal), involving power input of 0.2 to 75 kW (0.25 to 100 hp).

Helical-Blade Mixers   Helical mixers are now available in a variety of configurations. The mixing element may be in the form of a conical or a cylindrical helix. It may be a ribbon spaced radially from the shaft by spokes or a screw consisting of a helical surface that is continuous from the shaft to the periphery of the helix. A venerable example of the latter type is the soap crutcher, in which the screw is mounted in a draft tube. Close screw-tube clearance and a high rotational speed result in rapid motion of the material and high shear. The screw lifts the material through the tube, and gravity returns it to the bottom of the tank. If the tank has well-rounded corners, this kind of mixer may be used for fibrous materials. Heavy paper pulp containing 16 to 18 percent solids is uniformly bleached in large mixers of this type.

A double helix shortens mixing time but requires more power. The disadvantages of the higher torque requirement are frequently offset by the better mixing and heat transfer.

A vertical helical ribbon blender can be combined with an axial screw of smaller diameter (Fig. 18-25). Such mixers are used in polymerization reactions in which uniform blending is required but in which high-shear dispersion is not a factor. Addition of the inner flight contributes little more turnover in mixing newtonian fluids but significantly shortens the mixing time in nonnewtonian systems and adds negligibly to the impeller power [Coyle et al., *Am. Inst. Chem. Eng. J.,* **15,** 903 (1970)].

Double-Arm Kneading Mixers   The universal mixing and kneading machine consists of two counterrotating blades in a rectangular trough curved at the bottom to form two longitudinal half cylinders and a saddle section (Fig. 18-40). The blades are driven by gearing at either or both ends. The oldest style empties through a bottom door or valve and is still in use when 100 percent discharge or thorough cleaning between batches is not an essential requirement. More commonly, however, double-arm mixers are tilted for discharge. The tilting mechanism may be manual, mechanical, or hydraulic.

A variety of blade shapes has evolved. The mixing action is a combination of bulk movement, smearing, stretching, folding, dividing, and recombining as the material is pulled and squeezed against blades, saddle, and sidewalls. The blades are pitched to achieve end-to-end circulation. Rotation is usually such that material is drawn down over the saddle. Clearances are as close as 1 mm (0.04 in).

The blades may be tangential or overlapping. Tangential blades are run at different speeds, with the advantages of faster mixing from constant change of relative position, greater wiped heat-transfer area per unit volume, and less riding of material above the blades. Overlapping blades can be designed to avoid buildup of sticky material on the blades.

The agitator design most widely used is the sigma blade (Fig. 18-41a). The sigma-blade mixer is capable of starting and operating with either liquids or solids or a combination of both. Modifications in blade-face design have been introduced to increase particular effects, such as shredding or wiping. The sigma blade has good mixing action, readily discharges materials which do not stick to the blades, and is relatively easy to clean when sticky materials are being processed.

The dispersion blade (Fig. 18-41b) was developed particularly to provide compressive shear higher than that achieved with standard

FIG. 18-39   Change-can mixer. (*Charles Ross & Son Co.*)
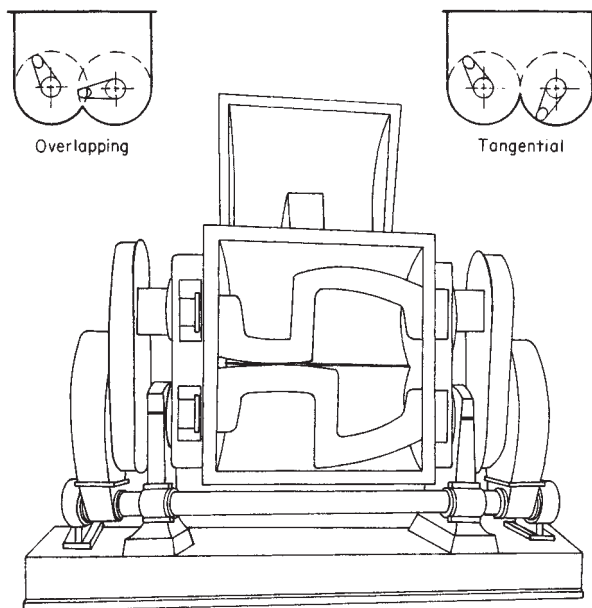
FIG. 18-40   Double-arm kneader mixer. (*APV Baker Perkins Inc.*)
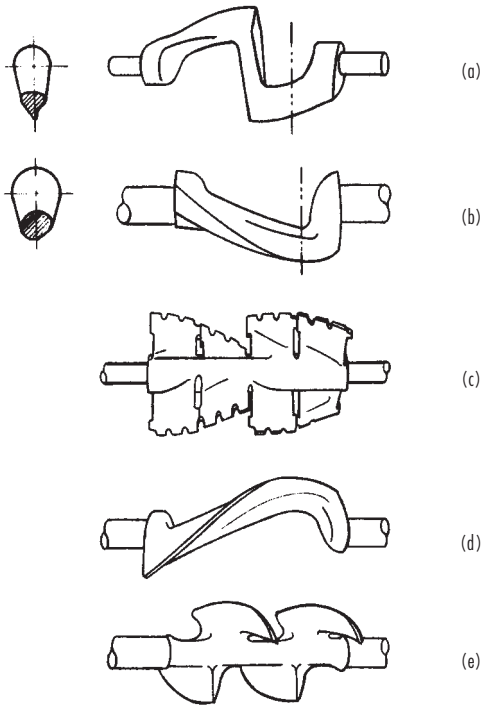
FIG. 18-41 Agitator blades for double-arm kneaders: (*a*) sigma; (*b*) dispersion; (*c*) multiwiping overlap; (*d*) single-curve; (*e*) double-naben. (*APV Baker Perkins, Inc.*)

TABLE 18-3 Characteristics of Double-Arm Kneading Mixers*

| Size number | Capacity, U.S. gal | | Typical supplied horsepower | | Floor space, ft |
	Working	Maximum	Sigma blade, MWOL blade	Dispersion blade	
4	0.7	1	1	2	1 × 3
6	2.3	3.5	2	5	2 × 3
8	4.5	7	5	7.5	3 × 4
11	10	15	15	20	5 × 6
12	20	30	25	40	6 × 6
14	50	75	30	60	6 × 8
15	100	150	50	100	8 × 10
16	150	225	60	150	9 × 11
17	200	300	75	200	9 × 13
18	300	450	100	—	10 × 14
20	500	750	150	—	11 × 16
21	600	900	175	—	12 × 16
22	750	1125	225	—	12 × 17
23	1000	1500	300	—	14 × 18

*Data from APV Baker Perkins, Inc. To convert feet to meters, multiply by 0.3048; to convert gallons to cubic meters, multiply by 3.78×10^{-3}; and to convert horsepower to kilowatts, multiply by 0.746.

sigma blades. The blade face wedges material between itself and the trough, rather than scraping the trough, and is particularly suited for dispersing fine particles in a viscous mass. Rubbery materials have a tendency to ride the blades, and a ram is frequently used to keep the material in the mixing zone.

Multiwiping overlapping (MWOL) blades (Fig. 18-41*c*) are commonly used for mixtures which start tough and rubberlike, inasmuch as the blade cuts the material into small pieces before plasticating it.

The single-curve blade (Fig. 18-41*d*) was developed for incorporating fiber reinforcement into plastics. In this application, the individual fibers (e.g., sisal or glass) must be wetted with polymer without incurring undue fiber breakage.

Many other blade designs have been developed for specific applications. The double-naben blade (Fig. 18-41*e*) is a good blade for mixes which "ride," that is, form a lump which bridges across the sigma blade.

Double-arm mixers are available from several suppliers (e.g., Paul O. Abbe, Inc.; Littleford Day; Jaygo, Inc.; Charles Ross & Son Co.; Teledyne Readco). Options include vacuum design, cored blades, jacketed trough, choice of cover design, and a variety of seals and packing glands. Power requirements vary from ⅙ to 2 hp/gal of capacity. Table 18-3 lists specifications and space requirements for typical tilting-type, double-ended-drive, double-arm mixers. The working capacity is generally at or near the top of the blades, and the total capacity is the volume contained when the mixer is filled level with the top of the trough.

Figure 18-42 provides a guide for typical applications. Individual formulation changes may require more power than indicated in the figure. Parker [*Chem. Eng.*, **72**(18), 121 (1965)] has described in greater detail how to select double-arm mixers.

Screw-Discharge Batch Mixers A variant of the sigma-blade mixer is now available with an extrusion-discharge screw located in the saddle section. During the mixing cycle the screw moves the material within the reach of the mixing blades, thereby accelerating the

mixing process. At discharge time, the direction of rotation of the screw is reversed and the mixed material is extruded through suitable die openings in the side of the machine. The discharge screw is driven independently of the mixer blades by a separate drive.

Working capacities range from 4 to 3800 L (1 to 1000 gal), with up to 300 kW (400 hp). This type of kneader is offered by most of the double-arm-kneader manufacturers. It is particularly suitable when a heel from the prior batch can be left without detriment to succeeding batches.

Intensive Mixers

Banbury Mixer Preeminent in the field of high-intensity mixers, with power input up to 6000 kW/m³ (30 hp/gal), is the Banbury mixer, made by the Farrel Co. (Fig. 18-43). It is used mainly in the plastics and rubber industries. The top of the charge is confined by an air-operated ram cover mounted so that it can be forced down on the charge. The clearance between the rotors and the walls is extremely small, and it is
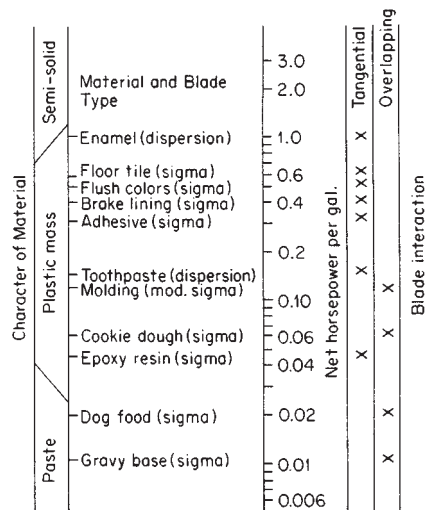
FIG. 18-42 Typical application and power for double-arm kneaders. To convert horsepower per gallon to kilowatts per cubic meter, multiply by 197.3. [*Parker*, Chem. Eng. **72**(18): 125 (1965); *excerpted by special permission of the copyright owner, McGraw-Hill, Inc.*]
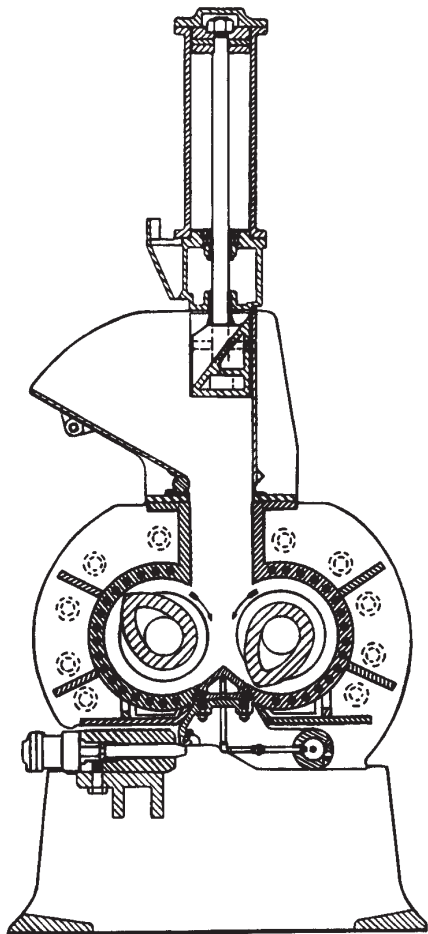
here that the mixing action takes place. The operation of the rotors of a Banbury at different speeds enables one rotor to drag the stock against the rear of the other and thus help clean ingredients from this area.

The extremely high power consumption of the machines operating at speeds of 40 r/min or lower calls for rotor shafts of large diameter. The combination of heavy shafts, stubby blades, close clearances, and the confined charge limits the Banbury mixer to small batches. The production rate is increased as much as possible by using powerful drives and rotating the blades at the highest speed that the material will stand. The friction produced in the confined space is great, and with heat-sensitive materials cooling may be the limiting factor. Recent innovations include a drop door, four-wing rotors which can provide 30 percent greater power than the older two-wing rotors, and separable gear housings. Equipment is available from laboratory size to a mixer capable of handling a 450-kg (1000-lb) charge and applying 2240 kW (3000 hp).

High-Intensity Mixer.   Mixers such as that shown in Fig. 18-44 combine a high shear zone with a fluidized vortex mixing action. Blades at the bottom of the vessel scoop the batch upward at peripheral speeds of about 40 m/s (130 ft/s). The high shear stress (to $20,000 \ s^{-1}$) and blade impact easily reduce agglomerates and aid intimate dispersion. Since the energy input is high [200 kW/m^3 (about 8 hp/ft^3)], even powdery material is heated rapidly.

Mixers of this type are available in sizes from 4 to 2000 L (1 to 500 gal), consuming from 1.5 to 375 kW (2 to 500 hp).

These mixers are particularly suited for rapid mixing of powders and granules with liquids, for dissolving resins or solids in liquids, or for removal of volatiles from pastes under vacuum. Scale-up is usually on the basis of maintaining constant peripheral velocity of the impeller.

Roll Mills   Roll mills can provide exceedingly high localized shear while retaining extended surface for temperature control.

Two-Roll Mills   These mills contain two parallel rolls mounted in a heavy frame with provision for accurately regulating the pressure and distance between the rolls. As one pass between the rolls does little blending and only a small amount of work, the mills are practically always used as batch mixers. Only a small amount of material is in the high-shear zone at any one time.

To increase the wiping action, the rolls are usually operated at different speeds. The material passing between the rolls is returned to the feed point by the rotation of the rolls. If the rolls are at different temperatures, the material usually will stick to the hotter roll and return to the feed point as a thick layer.

FIG. 18-43   Banbury mixer. (*Farrel Co.*)
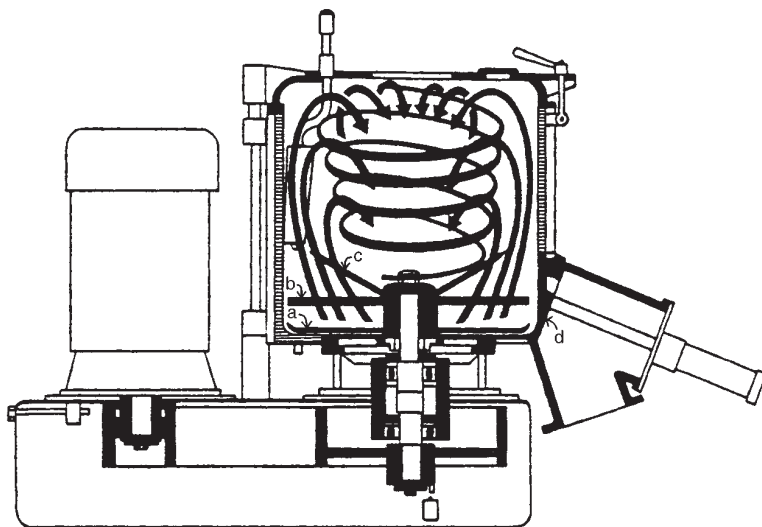
FIG. 18-44   High-intensity mixer: (*a*) bottom scraper; (*b*) fluidizing tool; (*c*) horn tool; (*d*) flush-mounted discharge valve. (*Henschel Mixers America, Inc.*)

At the end of the period of batch mixing, heavy materials may be discharged by dropping between the rolls, while thin mixes may be removed by a scraper bar pressing against the descending surface of one of the rolls.

Two-roll mills are used mainly for preparing color pastes for the ink, paint, and coating industries. There are a few applications in heavy-duty blending of rubber stocks, for which corrugated and masticating rolls are often used.

Miscellaneous Batch Mixers

Bulk Blenders   Many of the mixers used for solids blending (Sec. 19) are also suitable for some liquid-solids blending. **Ribbon blenders** can be used for such tasks as wetting out or coating a powder. When the final paste product is not too fluid, other solids-handling equipment finds frequent use.

Plow Mixers   Plow mixers such as the **Littleford** (Littleford Day) and the **Marion** (Rapids Machinery Co.) machines can be used for either batch or continuous mixing. Plow-shaped heads arranged on the horizontal shaft rotate at high speed, hurling the material throughout the free space of the vessel. Additional intermixing and blending occur as the impellers plow through the solids bed. Special high-speed choppers (3600 r/min) can be installed to break up lumps and aid liquid incorporation. The choppers also disperse fine particles throughout viscous materials to provide a uniform suspension. The mixer is available in sizes of 40 L to 40 m³ (10 to 10,000 gal) of working capacity.

Cone and Screw Mixers   The **Nauta mixer** of Fig. 18-45 (Day Mixing) utilizes an orbiting action of a helical screw rotating on its own axis to carry material upward, while revolving about the centerline of the cone-shaped shell near the wall for top-to-bottom circulation. Reversing the direction of screw rotation aids discharge of pasty materials. Partial batches are mixed in the Nauta type of mixer as efficiently as full loads. These mixers, available in sizes of 40 L to 40 m³ (10 to 10,000 gal), achieve excellent low-energy blending, with some hydraulic shear dispersion. At constant speed, both mixing time and power scale up with the square root of volume.

Pan Muller Mixers   These mixers can be used if the paste is not too fluid or too sticky. The main application of muller mixers is now in the foundry industry, in mixing small amounts of moisture and binder materials with sand particles for both core and molding sand. In paste processing, pan-and-plow mixers are used principally for mixing putty and clay pastes, while muller mixers handle such diversified materials as clay, storage-battery paste, welding-rod coatings, and chocolate coatings.

In muller mixers the rotation of the circular pan or of the plows brings the material progressively into the path of the mullers, where the intensive action takes place. Figure 18-46 shows one type of mixer, in which the mullers and plows revolve around a stationary turret in a stationary pan. The outside plow moves material from the crib wall to the path of the following muller; the inside plow moves it from the central turret to the path of the other muller. The mullers crush the material, breaking down lumps and aggregates.

Standard muller mixers range in capacity from a fraction of a cubic foot to more than 1.8 m³ (60 ft³), with power requirements ranging from 0.2 to 56 kW (⅓ to 75 hp). A continuous muller design employs two intersecting and communicating cribs, each with its own mullers and plows. At the point of intersection of the two crib bodies, the outside plows give an approximately equal exchange of material from one crib to the other, but material builds up in the first crib until the feed rate and the discharge rate of material from the gate in the second crib are equal. The residence time is regulated by adjusting the outlet gate.

CONTINUOUS MIXERS

Some of the batch mixers previously described can be converted for continuous processing. Product uniformity may be poor because of the broad residence time distribution. If the different ingredients can be accurately metered, various continuous mixers are available. Continuous mixers generally consist of a closely fitted agitator element rotating within a stationary housing.

Single-Screw Mixers   Because of the growth of the plastics industry, use of extruders such as that depicted in Fig. 18-47 are now
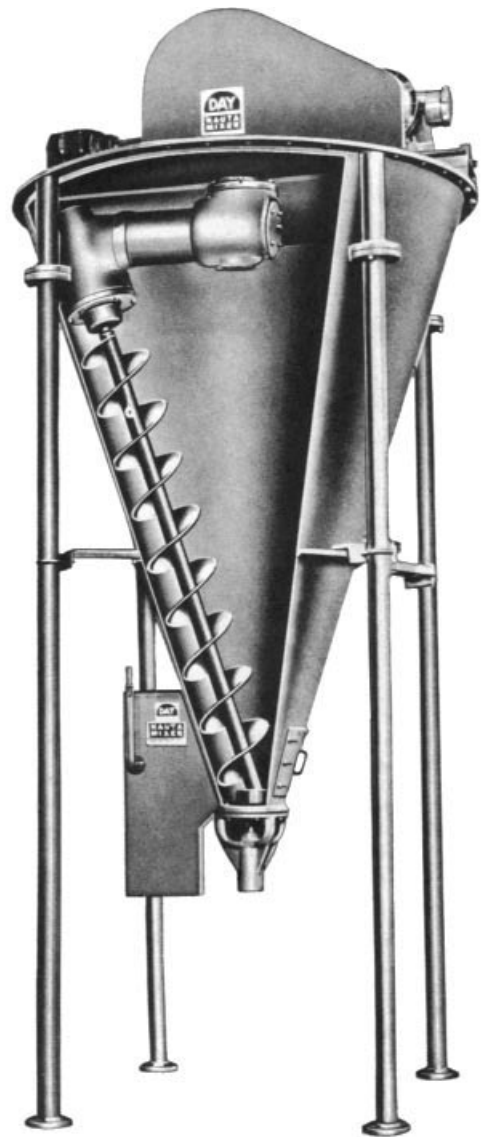
FIG. 18-45   Nauta mixer. (*Littleford Day.*)

very widespread. The quality and usefulness of the product may well depend on how uniformly the various additives, stabilizers, fillers, etc., have been incorporated. The extruder combines the process functions of melting the base resin, mixing in the additives, and developing the pressure required for shaping the product into pellets, sheet, or profiles. Dry ingredients, sometimes premixed in a batch blender, are fed into the feed throat where the channel depth is deepest. As the root diameter of the screw is increased, the plastic is melted by a combination of friction and heat transfer from the barrel. Shear forces can be very high, especially in the melting zone, and the mixing is primarily a laminar shearing action.

Single-screw extruders can be built with a long length-to-diameter ratio to permit a sequence of process operations, such as staged addition of various ingredients. Capacity is determined by diameter, length, and power. Although the majority of extruders are in the 25- to 200-mm-diameter range, much larger units have been made for specific applications such as polyethylene homogenization. Mixing
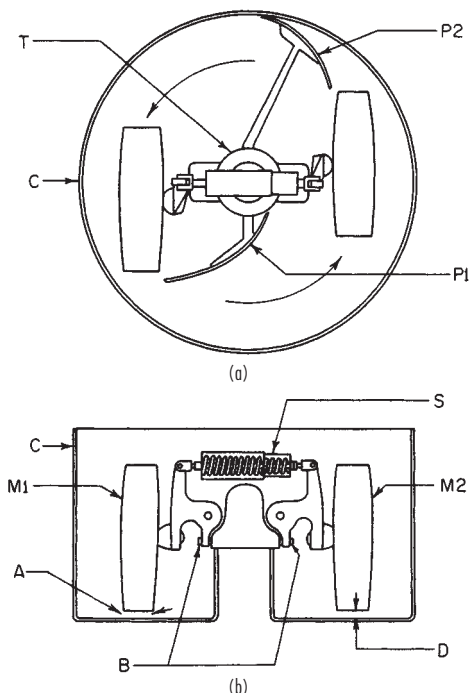
FIG. 18-46 Pan muller: (*a*) plan view; (*b*) sectional elevation. [*Bullock,* Chem. Eng. Prog. *51: 243 (1955), by permission.*]

enhancers (Fig. 18-48) are utilized to provide both elongational reorienting and shearing action to provide for both dispersive and distributive mixing.

The maximum power (*P,* kW) being supplied for single-screw extruders varies with screw diameter (*D,* mm) approximately as follows:

$$P = 5.3 \times 10^{-3} \, D^{2.25}$$

The power required for most polymer mixing applications varies from 0.15 to 0.3 kWh/kg.

Rietz Extruder   This extruder, shown schematically in Fig. 18-49, has orifice plates and baffles along the vessel. The rotor carries multiple blades with a forward pitch, generating the head for extrusion through the orifice plates as well as battering the material to break up agglomerates between the baffles. Typical applications include wet granulation of pharmaceuticals, blending color in bar soap, and mixing and extruding cellulose materials. The Extructor is available in rotor diameters up to 600 mm (24 in) and in a power range of 5 to 112 kW (7 to 150 hp).

Twin-Screw Extruders   With two screws in a figure-eight barrel, advantage can be taken of the interaction between the screws as well as between the screw and the barrel. Twin-screw machines are used in continuous melting, mixing, and homogenizing of different polymers with various additives, or to carry out the intimate mixing required for reactions in which at least one of the components is of high viscosity. The screws can be tangential or intermeshing, and the latter either co- or counterrotating. Tangential designs allow variability in channel depth and permit longer lengths.

Counterrotating intermeshing screws provide a dispersive milling action between the screws and behave like a positive displacement device with the ability to generate pressure more efficiently than any other extruder.

The most common type of twin-screw mixing extruder is the corotating intermeshing variety (APV, Berstorff, Davis Standard, Leistritz, Werner & Pfleiderer). The two keyed or splined shafts are fitted with pairs of slip-on kneading or conveying elements, as shown in Fig. 18-50. The arrays of these elements can be varied to provide a wide range of mixing effects. The barrel sections are also segmented to allow for optimum positioning of feed ports, vents, barrel valves, etc. The barrels may be heated electrically or with oil or steam and cooled with air or water.

Each pair of kneading paddles causes an alternating compression and expansion effect which massages the contents and provides a combination of shearing and elongational mixing actions. The corotating twin-screw mixers are available in sizes ranging from 15 to 300 mm, with length-to-diameter ratios up to 50 and throughput capacities up to 25,000 kg/h. Screw speeds can be high (to 500 r/min in the smaller-production-size extruders), and residence times for mixing are usually under 2 min.

Farrel Continuous Mixer   This mixer (Fig. 18-51) consists of rotors similar in cross section to the Banbury batch mixer. The first section of the rotor acts as a screw conveyor, propelling the feed ingredients to the mixing section. The mixing action is a combination of intensive shear, between rotor and chamber wall, kneading between the rotors, and a rolling action of the material itself. The amount and quality of mixing are controlled by adjustment of speed, feed rates, and discharge-orifice opening. Units are available in five sizes with mixing-chamber volumes ranging up to 0.12 m³ (4.2 ft³). At 200 r/min, the power range is 5 to 2200 kW (7 to 3000 hp).

Miscellaneous Continuous Mixers

Trough-and-Screw Mixers   These mixers usually consist of single or twin rotors which continually turn the feed material over as it
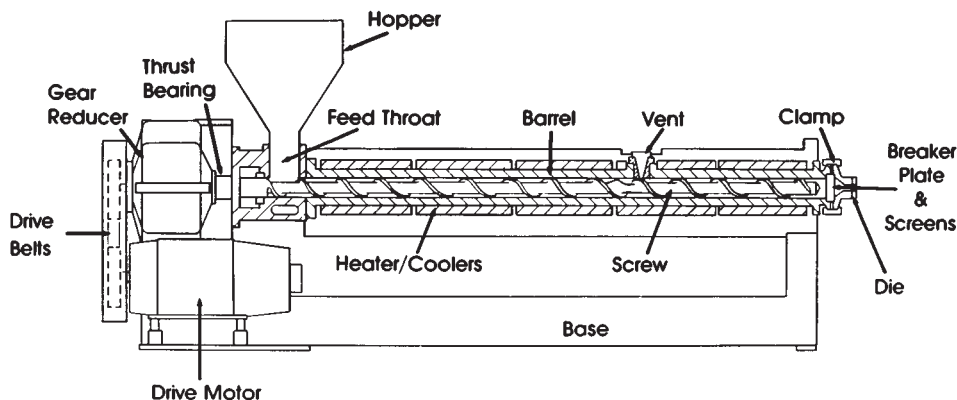
FIG. 18-47 Single-screw extruder. (*Davis Standard.*)
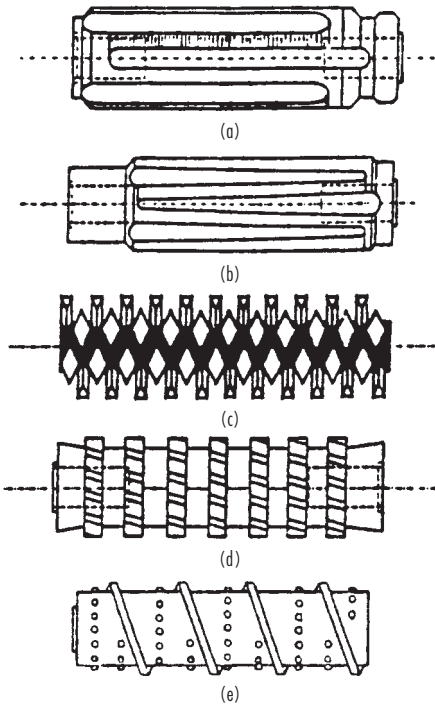
FIG. **18-48** Mixing enhancers for single-screw extruders: (a) Maddock (straight); (b) Maddock (tapered); (c) pineapple; (d) gear; (e) pin.
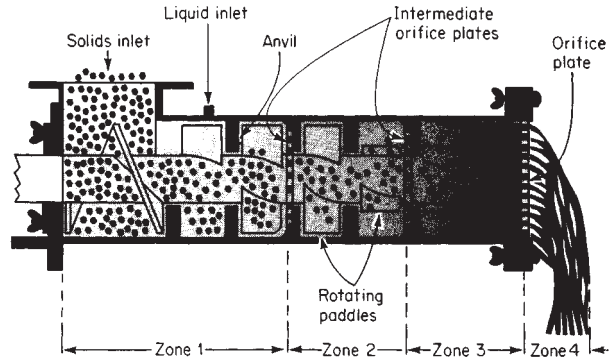
FIG. **18-49** Rietz Extruder. (*Bepex Corporation.*)

progresses toward the discharge end. Some have been designed with extensive heat-transfer area. The continuous-screw **Holo-Flite Processor** (Fig. 18-52; Denver Sala) is used primarily for heat transfer, since the hollow screws present extended surface without contributing much shear. Two or four screws may be used. Bethlehem Corp.'s **Porcupine Processor** also has heat-transfer media going through the flights of the rotor, but the agitator flights are cut to provide a folding action on the process mass. Breaker-bar assemblies, consisting of fingers extending toward the shaft, are frequently used to improve agitation.

Another type of trough-and-screw mixer with a large volume available for mixing is the AP Conti (List AG) machine shown in Fig. 18-53. These self-cleaning-type mixers are particularly appropriate when
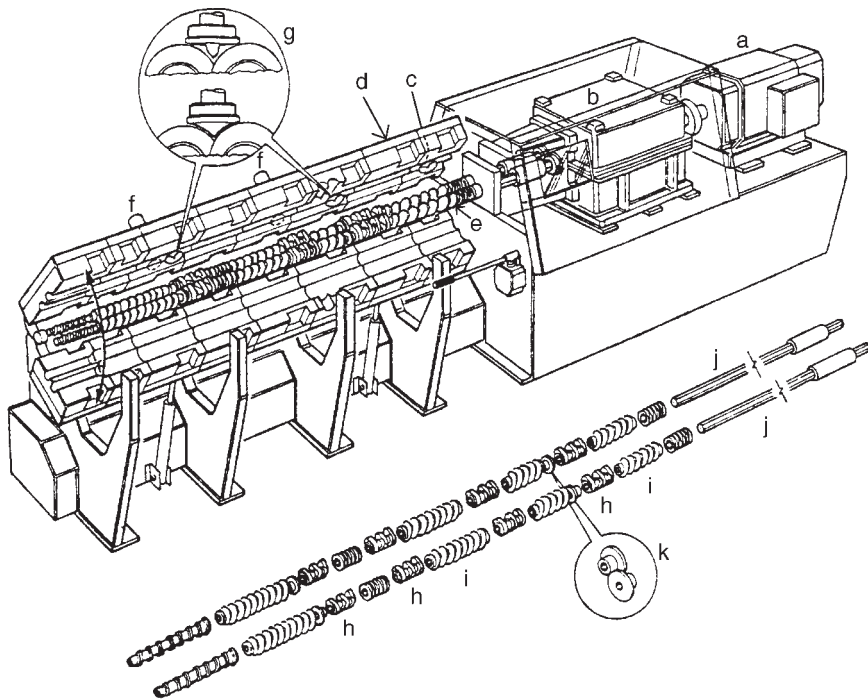
FIG. **18-50** Intermeshing corotating twin screw extruder: (a) drive motor; (b) gearbox; (c) feed port; (d) barrel; (e) assembled rotors; (f) vent; (g) barrel valve; (h) kneading paddles; (i) conveying screws; (j) splined shafts; (k) blister rings. (*APV Chemical Machinery, Inc.*)
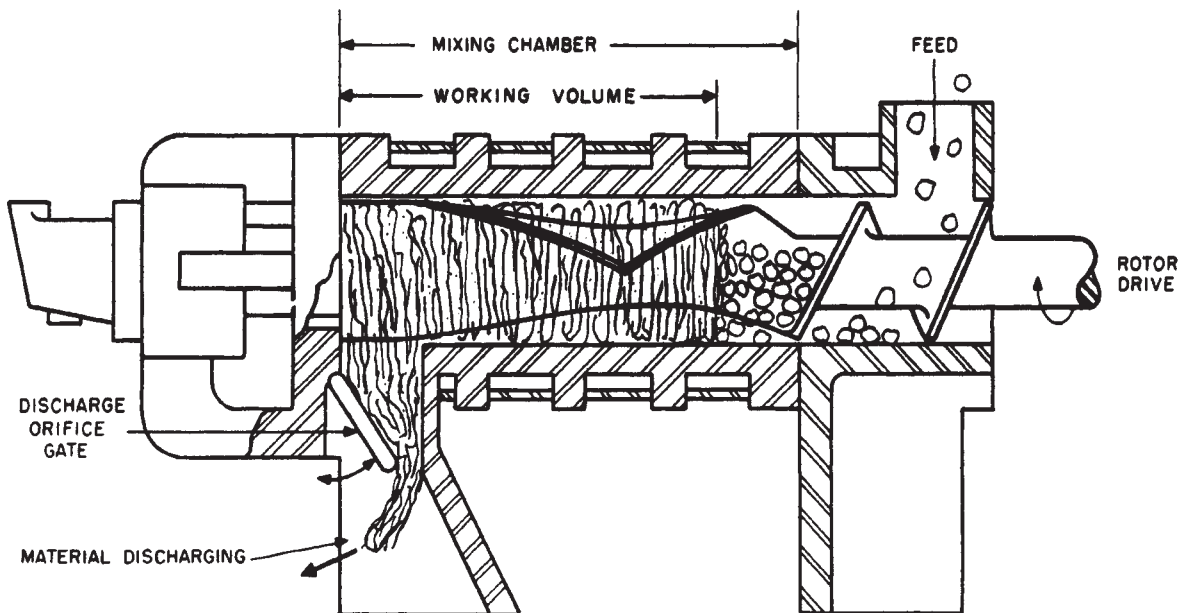
FIG. 18-51 Farrel continuous mixer. (*Farrel Co.*)

the product being handled goes through a sticky stage, which could plug the mixer or foul the heat-transfer surfaces.

Pug Mills A pug mill contains one or two shafts fitted with short, heavy paddles, mounted in a cylinder or trough which holds the material being processed. In two-shaft mills the shafts are parallel and may be horizontal or vertical. The paddles may or may not intermesh. Clearances are wide so that there is considerable mass mixing. Unmixed or partially mixed ingredients are fed at one end of the machine, which is usually totally enclosed. The paddles push the material forward as they cut through it, and carry the charge toward the discharge end as it is mixed. Product may discharge through one or two open ports or through one or more extrusion nozzles which give roughly shaped, continuous strips. Automatic cutters may be used to make blocks from the strips. Pug mills are most used for mixing mineral and clay products.

Kneadermaster This mixer (Patterson Industries, Inc.) is an adaptation of a sigma-blade mixer for continuous operation. Each two
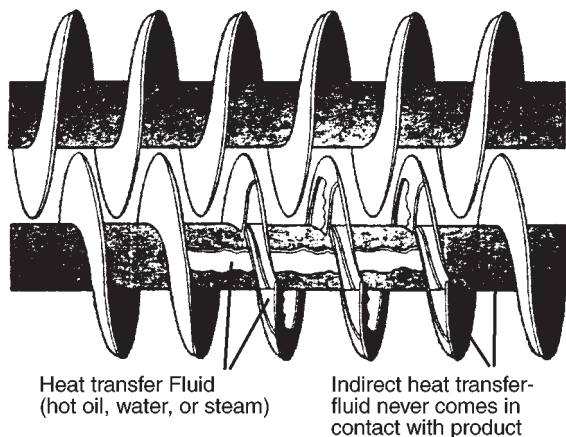
pairs of blades establish a mixing zone, the first pair pushing materials toward the discharge end of the trough and the second pair pushing them back. Forwarding to the next zone is by displacement with more feed material. Control of mixing intensity is by variation in rotor speed. Cored blades supplement the heat-transfer area of the jacketed trough.

Motionless Mixers An alternative to agitated equipment for continuous viscous mixing involves the use of stationary shaped diverters inside conduits which force the fluid media to mix themselves through a progression of divisions and recombinations, forming striations of ever-decreasing thickness until uniformity is achieved. Simple diverters, such as the **Kenics static mixer** (Chemineer, Inc.; Fig. 18-54), provide 2^n layerings per n diverters.

The power consumed by a motionless mixer in producing the mixing action is simply that delivered by a pump to the fluid which it moves against the resistance of the diverter conduit. For a given rate of pumping, it is substantially proportional to that resistance. When the diverter consists of several passageways, as in the **Sulzer static mixer** (Koch Engineering Co., Inc.) shown in Fig. 18-55, the number of layerings (hence, the rate of mixing) per diverter is increased, but at the expense of a higher pressure drop. The pressure drop, usually expressed as a multiple K of that of the empty duct, is strongly dependent upon the hydraulic radius of the divided flow passageway. The value of K, obtainable from the mixer supplier, can range from 6 to several hundred, depending on the Reynolds number and the geometry of the mixer.

Motionless mixers continuously interchange fluid elements between the walls and the center of the conduit, thereby providing enhanced heat transfer and relatively uniform residence times. Distributive mixing is usually excellent; however, dispersive mixing may be poor, especially when viscosity ratios are high.

PROCESS DESIGN CONSIDERATIONS

Scaling Up Mixing Performance

Scale-Up of Batch Mixers The prime basis of scale-up of batch mixers has been equal power per unit volume, although the most desirable practical criterion is equal blending per unit time. As size is increased, mechanical-design requirements may limit the larger mixer to lower agitator speeds; if so, blend times will be longer in the larger

Heat transfer Fluid
(hot oil, water, or steam)

Indirect heat transfer-
fluid never comes in
contact with product

FIG. 18-52 Holo-Flite Processor. (*Denver Sala.*)
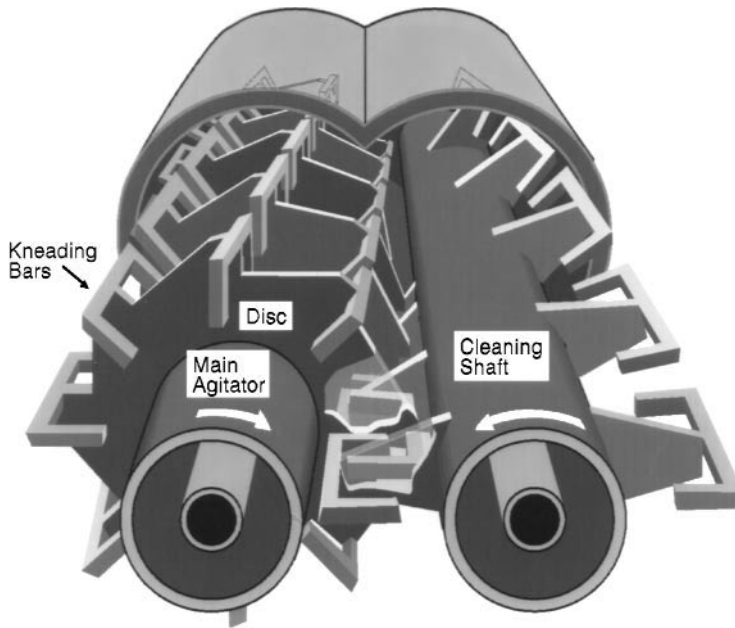
FIG. 18-53 AP Conti paste mixer. (*LIST.*)

mixer than in the smaller prototype. If the power is high, the lower surface-to-volume ratio as size is increased may make temperature buildup a limiting factor. Since the impeller in a paste mixer generally comes close to the vessel wall, it is not possible to add cooling coils. In some instances, the impeller blades can be cored for additional heat-transfer area.

Experience with double-arm mixers indicates that power is proportional to the product of blade radius, blade-wing depth, trough length, and average of the speeds of the two blades (Irving and Saxton, loc. cit.). The mixing time scales up inversely with blade speed. Goodness of mixing is dependent primarily on the number of revolutions that the blades have made. As indicated previously, the minimum possible mixing time may become dependent on heat-transfer rate.

Frequently, the physical properties of a paste vary considerably during the mixing cycle. Even if one knew exactly how power depended upon density and viscosity, it might be better to predict the requirements for a large paste mixer from the power-time curve observed in the prototype mixer rather than to try to calculate or measure all intermediate properties during the processing sequence (i.e., the prototype mixer may be the best instrument to use to measure the effective viscosity).

Scale-Up of Continuous Mixers   Although scaling up on the basis of constant power per unit feed rate [kWh/kg or (hp·h)/lb] is usually a good first estimate, several other factors may have to be considered. As the equipment scale is increased, geometric similarity being

at least approximated, there is a loss in surface-to-volume ratio. As size is increased, changing shear rate or length-to-diameter ratio may be required because of equipment-fabrication limitations. Furthermore, even if a reliable method of scaling up power exists, the determination of net power in small-scale test equipment is frequently difficult and inaccurate because of fairly large no-load power.

As a matter of fact, geometrical similarity usually cannot be maintained exactly as the size of the model is increased. In single-screw extruders, for example, channel depth in the flights cannot be increased in proportion to screw diameter because the distribution of heat generated by friction at the barrel wall requires more time as channel depth becomes greater. With constant retention time, therefore, nonhomogeneous product would be discharged from the scaled-up model. As the result of the departure from geometrical similarity, the throughput rate of single-screw extruders scales up with diameter

FIG. 18-54 Kenics static mixer. (*Chemineer, Inc.*)
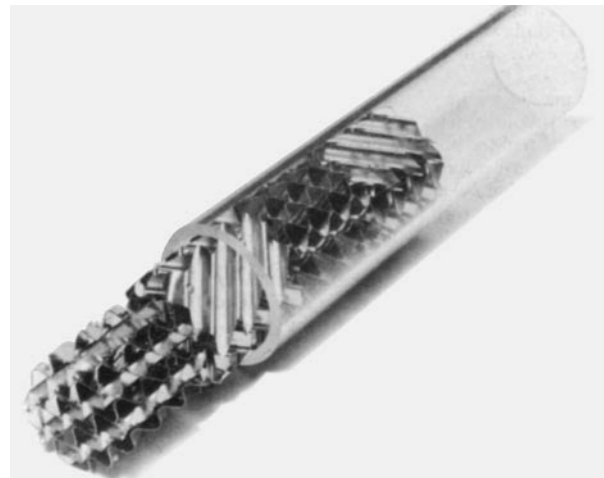
FIG. 18-55 Sulzer static mixer. (*Koch Engineering Co., Inc.*)

to the power 2.0 to 2.5 (instead of diameter cubed) at constant length-to-diameter ratio and screw speed.

The throughput rate of intermeshing twin-screw extruders (Fig. 18-56) and the Farrel continuous mixer (Fig. 18-51) is scaled up with diameter to about the 2.6 power.

If the process can be operated adiabatically, the production capacity is scaled up as the cube of diameter since geometry, shear rate, residence time, and power input per unit volume all can be held constant.

Residence-time distributions.   For flow through a conduit, the extent of axial dispersion can be characterized either by an axial-diffusion coefficient or by analogy to a number of well-mixed stages in series. Retention time can control the performance of a mixing system. As the number of apparent stages increases, there is greater assurance that all the material will have the required residence time. Under conditions requiring uniform retention time, it is imperative that the feed streams be fed in the correct ratio on a time scale much shorter than the average residence time of the mixer; otherwise, a perturbation in the feed will produce a comparable perturbation in the product. The mixing impellers in continuous mixers can be designed to cover the full range from minimum axial mixing (plug flow) to maximum (to damp out feed irregularities). Residence-time distributions and effective Peclet numbers have been determined for a wide variety of twin-screw configurations [Todd and Irving, *Chem. Eng. Prog.*, **65**(9), 84 (1969)]. Conventional single-screw extruder mixers have Peclet numbers about equal to the length-to-diameter ratio, or an equivalent number of stages equal to one-half of that.

HEATING AND COOLING MIXERS

Heat Transfer   Pastes are often heated or cooled by heat transfer through the walls of the container or hollow mixing arms. Good agitation, a large ratio of transfer surface to mixer volume, and frequent removal of material from the surface are essential for high rates of heat transfer. Sometimes evaporation of part of the mix is used for cooling.

In most mixers, the metal wall has a negligible thermal resistance. The paste film, however, usually has high resistance. It is important, therefore, while minimizing the resistance of the heating or cooling medium, to move the paste up to and away from the smooth wall surface as steadily and rapidly as possible. This is best achieved by having the paste flow so as to follow a close-fitting scraper which wipes the film from the wall with each rotation. Typical overall heat-transfer coefficients are between 25 and 200 J/(m²·s·K) [4 to 35 Btu/(h·ft²·°F)].

Heating Methods   The most economical heating method varies with plant location and available facilities. Direct firing is rarely used, since it does not permit good surface-temperature control and may cause scorching of the material on the vessel walls. Steam heating is the most widely used method. It is economical, safe, and easily controlled. With thin-wall mixers there must be automatic release of the vacuum that results when the pressure is reduced and the steam in the jacket condenses; otherwise, weak sections will collapse. Transfer-liquid heating using water, oil, special organic liquids, or molten inorganic salts permits good temperature control and provides insurance against overheating the processed material. Jackets for transfer-liquid heating usually must be baffled to provide good circulation. Higher temperatures can be achieved without requiring the heavy vessel construction otherwise required by steam.

Electrical heating is accomplished with resistance bands or ribbons which must be electrically insulated from the machine body but in good thermal contact with it. The heaters must be carefully spaced to avoid a succession of hot and cold areas. Sometimes they are mounted in aluminum blocks shaped to conform to the container walls. Their effective temperature range is 150 to 500°C (about 300 to 930°F). Temperature control is precise, maintenance and supervision costs are low, and conversion of electrical energy to useful heat is almost 100 percent. The cost of electrical energy is usually large, however, and may be prohibitive.

Frictional heat develops rapidly in some units such as a Banbury mixer. The first temperature rise may be beneficial in softening the materials and accelerating chemical reactions. High temperatures detrimental to the product may easily be reached, however, and pro-

vision for cooling or frequent stopping of the machine must be made. Frictional heating may be lessened by reducing the number of working elements, their area, and their speed. Cooling thus is facilitated, but at the expense of increased mixing time.

Cooling Methods   In air cooling, air may be blown over the machine surfaces, the area of which is best extended with fins. Air or cooled inert gas may also be blown over the exposed surface of the mix, provided contamination or oxidation of the charge does not result. Evaporation of excess water or solvent under vacuum or at atmospheric pressure provides good cooling. A small amount of evaporation produces a large amount of cooling. Removing too much solvent, however, may damage the charge. Direct addition of ice to the mixer provides rapid, convenient cooling, but the resulting dilution of the mix must be permissible. Addition of dry ice is more expensive but results in lower temperatures, the mix is not diluted, and the CO_2 gas evolved provides a good inert atmosphere. Many mixers are cooled by circulation of water or refrigerants through jackets or hollow agitators. In general, this is the least expensive method, but it is limited by the magnitude of heat-transfer coefficient obtainable.

Selection of Equipment   If a new product is being considered, the preliminary study must be highly detailed. Laboratory or pilot-plant work must be done to establish the controlling factors. The problem is then to select and install equipment which will operate for quantity production at minimum overall cost. Most equipment vendors have pilot equipment available on a rental basis or can conduct test runs in their own customer-demonstration facilities.

One approach to proper equipment specification is by analogy. What current product is most similar to the new one? How is this material produced? What difficulties are being experienced?

In other situations the following procedure is recommended:

1.   List carefully all materials to be handled at the processing point and describe their characteristics, such as:

a.   How received at the processing unit: in bags, barrels, or drums, in bulk, by pipe line, etc.?

b.   Must storage and/or weighing be done at the site?

c.   Physical form.

d.   Specific gravity and bulk characteristics.

e.   Particle size or size range.

f.   Viscosity.

g.   Melting or boiling point.

h.   Corrosive properties.

i.   Abrasive characteristics.

j.   Is material poisonous?

k.   Is material explosive?

l.   Is material an irritant to skin, eyes, or lungs?

m.   Is material sensitive to exposure of air, moisture, or heat?

2.   List pertinent data covering production:

a.   Quantity to be produced per 8-h shift.

b.   Formulation of finished product.

c.   What accuracy of analysis is required?

d.   Will changes in color, flavor, odor, or grade require frequent cleaning of equipment?

e.   Is this operation independent, or does it serve other process stages with which it must be synchronized?

f.   Is there a change in physical state during processing?

g.   Is there a chemical reaction? Is it endothermic or exothermic?

h.   What are the temperature requirements?

i.   What is the form of the finished product?

j.   How must the material be removed from the apparatus (by pumping, free flow through pipe or chute, dumping, etc.)?

3.   Describe in detail the controlling characteristics of the finished product:

a.   Permanence of the emulsion or dispersion.

b.   Degree of blending of aggregates or of ultimate particles.

c.   Ultimate color development required.

d.   Uniformity of the dispersion of active ingredients, as in a drug product.

e.   Degree of control of moisture content for pumping extrusion, and so on.

Preparation and Addition of Materials   To ensure maximum production of high-grade mixed material, the preliminary preparation

of the ingredients must be correct and they must be added in the proper order. There are equipment implications to these considerations.

Some finely powdered materials, such as carbon black, contain much air. If possible they should be compacted or wet out before being added to the mix. If a sufficient quantity of light solvent is a part of the formula, it may be used to wet the powder and drive out the air. If the powder cannot be wet, it may be possible to densify it somewhat by mechanical means. Removal of adsorbed gas under vacuum is sometimes necessary.

Not uncommonly, critical ingredients that are present in small proportion (e.g., vulcanizers, antioxidants, and antiacids) tend to form aggregates when dry. Before entering the mixer, they should be fluffed, either by screening if the aggregates are soft or by passage through a hammer mill, roll mill, or muller if they are hard. The mixing time is cut down and the product is more uniform if all ingredients are freed from aggregates before mixing.

If any solids present in small amounts are soluble in a liquid portion of the mix, it is well to add them as a solution, making provision to distribute the liquid uniformly throughout the mass. When a trace of solid material which is not soluble in any other ingredients is to be added, it may be expedient to add it as a solution in a neutral solvent, with provision to evaporate the solvent at the end of the mixing cycle.

It may be advisable to consider master batching, in which a low-proportion ingredient is separately mixed with part of some other ingredient of the mix, this premix then being added to the rest of the mix for final dispersion. Master batching is especially valuable in adding tinting colors, antioxidants, and the like. The master batch may be made up with laboratory accuracy, while at the mixing station weighing errors are minimized by the dilution of the important ingredient.

Considerations such as these may make it desirable to consider automatic weighing and batch accumulation, metering of liquid ingredients, and automatic control of various time cycles.

CRYSTALLIZATION FROM SOLUTION

GENERAL REFERENCES: *AIChE Testing Procedures: Crystallizers,* American Institute of Chemical Engineers, New York, 1970; *Evaporators,* 1961. Bennett, *Chem. Eng. Prog.,* **58**(9), 76 (1962). Buckley, *Crystal Growth,* Wiley, New York, 1951. Campbell and Smith, *Phase Rule,* Dover, New York, 1951. De Jong and Jancic (eds.), *Industrial Crystallization,* North-Holland Publishing Company, Amsterdam, 1979. "Crystallization from Solution: Factors Influencing Size Distribution," *Chem. Eng. Prog. Symp. Ser.,* **67**(110), (1971). Mullin (ed.), *Industrial Crystallization,* Plenum, New York, 1976. Newman and Bennett, *Chem. Eng. Prog.,* **55**(3), 65 (1959). Palermo and Larson (eds.), "Crystallization from Solutions and Melts," *Chem. Eng. Prog. Symp. Ser.,* **65**(95), (1969). Randolph (ed.), "Design, Control and Analysis of Crystallization Processes," *Am. Inst. Chem. Eng. Symp. Ser.,* **76**(193), (1980). Randolph and Larson, *Theory of Particulate Processes,* Academic, New York, 2d ed., 1988. Rousseau and Larson (eds.), "Analysis and Design of Crystallization Processes," *Am. Inst. Chem. Eng. Symp. Ser.,* **72**(153), (1976). Seidell, *Solubilities of Inorganic and Metal Organic Compounds,* American Chemical Society, Washington, 1965. Myerson (ed.), *Handbook of Industrial Crystallization,* Butterworth, 1993.

Crystallization is important as an industrial process because of the number of materials that are and can be marketed in the form of crystals. Its wide use is probably due to the highly purified and attractive form of a chemical solid which can be obtained from relatively impure solutions in a single processing step. In terms of energy requirements, crystallization requires much less energy for separation than do distillation and other commonly used methods of purification. In addition, it can be performed at relatively low temperatures and on a scale which varies from a few grams up to thousands of tons per day.

Crystallization may be carried out from a vapor, from a melt, or from a solution. Most of the industrial applications of the operation involve crystallization from solutions. Nevertheless, crystal solidification of metals is basically a crystallization process, and much theory has been developed in relation to metal crystallization. This topic is so specialized, however, that it is outside the scope of this subsection, which is limited to crystallization from solution.

PRINCIPLES OF CRYSTALLIZATION

Crystals A crystal may be defined as a solid composed of atoms arranged in an orderly, repetitive array. The interatomic distances in a crystal of any definite material are constant and are characteristic of that material. Because the pattern or arrangement of the atoms is repeated in all directions, there are definite restrictions on the kinds of symmetry that crystals can possess.

There are five main types of crystals, and these types have been arranged into seven crystallographic systems based on the crystal interfacial angles and the relative length of its axes. The treatment of the description and arrangement of the atomic structure of crystals is the science of **crystallography.** The material in this discussion will be limited to a treatment of the growth and production of crystals as a unit operation.

Solubility and Phase Diagrams Equilibrium relations for crystallization systems are expressed in the form of solubility data which are plotted as phase diagrams or solubility curves. Solubility data are ordinarily given as parts by weight of anhydrous material per 100 parts by weight of total solvent. In some cases these data are reported as parts by weight of anhydrous material per 100 parts of solution. If water of crystallization is present in the crystals, this is indicated as a separate phase. The concentration is normally plotted as a function of temperature and has no general shape or slope. It can also be reported as a function of pressure, but for most materials the change in solubility with change in pressure is very small. If there are two components in solution, it is common to plot the concentration of these two components on the X and Y axes and represent the solubility by isotherms. When three or more components are present, there are various techniques for depicting the solubility and phase relations in both three-dimension and two-dimension models. For a description of these techniques, refer to Campbell and Smith (loc. cit.). Shown in Fig. 18-56 is a phase diagram for magnesium sulfate in water. The line p–a represents the freezing points of ice (water) from solutions of magne-
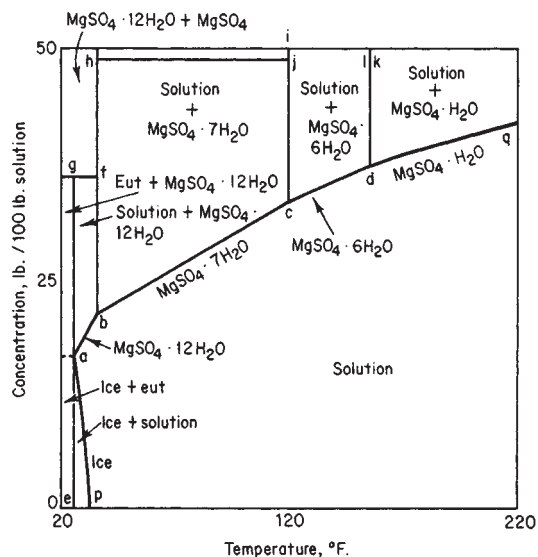

FIG. 18-56 Phase diagram. $MgSO_4 \cdot H_2O$. To convert pounds to kilograms, divide by 2.2; $K = (°F + 459.7)/1.8$.

sium sulfate. Point a is the eutectic, and the line $a–b–c–d–q$ is the solubility curve of the various hydrates. Line $a–b$ is the solubility curve for $MgSO_4\cdot12H_2O$, $b–c$ is the solubility curve for $MgSO_4\cdot7H_2O$, $c–d$ is the solubility curve for $MgSO_4\cdot6H_2O$, and $d–q$ is the portion of the solubility curve for $MgSO_4\cdot H_2O$.

As shown in Fig. 18-57, the mutual solubility of two salts can be plotted on the X and Y axes with temperatures as isotherm lines. In the example shown, all the solution compositions corresponding to 100°C with solid-phase sodium chloride present are shown on the line DE. All the solution compositions at equilibrium with solid-phase KCl at 100°C are shown by the line EF. If both solid-phase KCl and NaCl are present, the solution composition at equilibrium can only be represented by point E, which is the invariant point (at constant pressure). Connecting all the invariant points results in the mixed-salt line. The locus of this line is an important consideration in making phase separations.

There are numerous solubility data in the literature; the standard reference is by Seidell (loc. cit.). Valuable as they are, they nevertheless must be used with caution because the solubility of compounds is often influenced by pH and/or the presence of other soluble impurities which usually tend to depress the solubility of the major constituents. While exact values for any system are frequently best determined by actual composition measurements, the difficulty of reproducing these solubility diagrams should not be underestimated. To obtain data which are readily reproducible, elaborate pains must be taken to be sure the system sampled is at equilibrium, and often this means holding a sample at constant temperature for a period of from 1 to 100 h. While the published curves may not be exact for actual solutions of interest, they generally will be indicative of the shape of the solubility curve and will show the presence of hydrates or double salts.

Heat Effects in a Crystallization Process   The heat effects in a crystallization process can be computed by two methods: (1) a heat balance can be made in which individual heat effects such as sensible heats, latent heats, and the heat of crystallization can be combined into an equation for total heat effects; or (2) an enthalpy balance can be made in which the total enthalpy of all leaving streams minus the total enthalpy of all entering streams is equal to the heat absorbed from external sources by the process. In using the heat-balance method, it is necessary to make a corresponding mass balance, since the heat effects are related to the quantities of solids produced through the heat of crystallization. The advantage of the enthalpy-concentration-diagram method is that both heat and mass effects are taken into account simultaneously. This method has limited use because of the difficulty in obtaining enthalpy-concentration data. This information has been published for only a few systems.
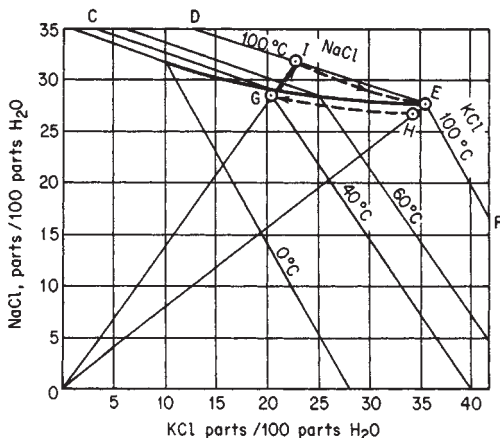
With compounds whose solubility increases with increasing temperature there is an absorption of heat when the compound dissolves. In compounds with decreasing solubility as the temperature increases, there is an evolution of heat when solution occurs. When there is no change in solubility with temperature, there is no heat effect. The solubility curve will be continuous as long as the solid substance of a given phase is in contact with the solution, and any sudden change in the slope of the curve will be accompanied by a change in the heat of solution and a change in the solid phase. Heats of solution are generally reported as the change in enthalpy associated with the dissolution of a large quantity of solute in an excess of pure solvent. Tables showing the heats of solution for various compounds are given in Sec. 2.

At equilibrium the heat of crystallization is equal and opposite in sign to the heat of solution. Using the heat of solution at infinite dilution as equal but opposite in sign to the heat of crystallization is equivalent to neglecting the heat of dilution. With many materials the heat of dilution is small in comparison with the heat of solution and the approximation is justified; however, there are exceptions. Relatively large heat effects are usually found in the crystallization of hydrated salts. In such cases the total heat released by this effect may be a substantial portion of the total heat effects in a cooling-type crystallizer. In evaporative-type crystallizers the heat of crystallization is usually negligible when compared with the heat of vaporizing the solvent.

Yield of a Crystallization Process   In most cases the process of crystallization is slow, and the final mother liquor is in contact with a sufficiently large crystal surface so that the concentration of the mother liquor is substantially that of a saturated solution at the final temperature in the process. In such cases it is normal to calculate the yield from the initial solution composition and the solubility of the material at the final temperature. If evaporative crystallization is involved, the solvent removed must be taken into account in determining the final yield. If the crystals removed from solution are hydrated, account must be taken of the water of crystallization in the crystals, since this water is not available for retaining the solute in solution. The yield is also influenced in most plants by the removal of some mother liquor with the crystals being separated from the process. Typically, with a product separated on a centrifuge or filter, the adhering mother liquor would be in the range of 2 to 10 percent of the weight of the crystals.

The actual yield may be obtained from algebraic calculations or trial-and-error calculations when the heat effects in the process and any resultant evaporation are used to correct the initial assumptions on calculated yield. When calculations are made by hand, it is generally preferable to use the trial-and-error system, since it permits easy adjustments for relatively small deviations found in practice, such as the addition of wash water, or instrument and purge water additions. The following calculations are typical of an evaporative crystallizer precipitating a hydrated salt. If SI units are desired, kilograms = pounds × 0.454; $K = (°F + 459.7)/1.8$.

Example 1: Yield from a Crystallization Process   A 10,000-lb batch of a 32.5 percent $MgSO_4$ solution at 120°F is cooled without appreciable evaporation to 70°F. What weight of $MgSO_4\cdot7H_2O$ crystals will be formed (if it is assumed that the mother liquor leaving is saturated)?

From the solubility diagram in Fig. 18-56 at 70°F the concentration of solids is 26.3 lb $MgSO_4$ per 100-lb solution.

The mole weight of $MgSO_4$ is 120.38.

The mole weight of $MgSO_4\cdot7H_2O$ is 246.49.

For calculations involving hydrated salts, it is convenient to make the calculations based on the hydrated solute and the "free water."

$$0.325 \text{ weight fraction} \times \frac{246.94}{120.38} = 0.6655 \; MgSO_4\cdot7H_2O \text{ in the feed solution}$$

$$0.263 \times \frac{246.94}{120.38} = 0.5385 \; MgSO_4\cdot7H_2O \text{ in the mother liquor}$$

Since the free water remains constant (except when there is evaporation), the final amount of soluble $MgSO_4\cdot7H_2O$ is calculated by the ratio of

$$\frac{0.538 \text{ lb } MgSO_4\cdot7H_2O}{(1 - 0.538) \text{ lb free water}}$$

FIG. 18-57   Phase diagram, $KCl – NaCl – H_2O$. $K = °C + 273.2$.

	Total	MgSO₄·7H₂O	Free water	MgSO₄·7H₂O / Free water

	Total	$MgSO_4 \cdot 7H_2O$	Free water	$\dfrac{MgSO_4 \cdot 7H_2O}{Free\ water}$
Feed	10,000	6655	3345	1.989
Mother liquor	7249	3904*	3345	1.167
Yield	2751	2751		

*$3345 \times (0.538/0.462) = 3904$

A formula method for calculation is sometimes used where

$$P = R\,\frac{100W_0 - S(H_0 - E)}{100 - S(R - 1)}$$

where P = weight of crystals in final magma, lb
   R = mole weight of hydrate/mole weight of anhydrous = 2.04759
   S = solubility at mother-liquor temperature (anhydrous basis) in lb per 100 lb solvent. $[0.263/(1 - 0.263)] \times 100 = 35.68521$
   W_0 = weight of anhydrous solute in the original batch. $10,000(0.325) = 3250$ lb
   H_0 = total weight of solvent at the beginning of the batch. $10,000 - 3250 = 6750$ lb
   E = evaporation = 0

$$P = 2.04\,\frac{(100)(3250) - 35.7(6750)}{100 - 35.7(2.04 - 1)} = 2751\ lb$$

Note that taking the difference between large numbers in this method can increase the chance for error.

Fractional Crystallization   When two or more solutes are dissolved in a solvent, it is often possible to (1) separate these into the pure components or (2) separate one and leave the other in the solution. Whether or not this can be done depends on the solubility and phase relations of the system under consideration. Normally alternative 2 is successful only when one of the components has a much more rapid change in solubility with temperature than does the other. A typical example which is practiced on a large scale is the separation of KCl and NaCl from water solution. A phase diagram for this system is shown in Fig. 18-57. In this case the solubility of NaCl is plotted on the Y axis in parts per 100 parts of water, and the solubility of KCl is plotted on the X axis. The isotherms show a marked decrease in solubility for each component as the amount of the other is increased. This is typical for most inorganic salts. As explained earlier, the mixed-salt line is CE, and to make a separation of the solutes into the pure components it is necessary to be on one side of this line or the other. Normally a 95 to 98 percent approach to this line is possible. When evaporation occurs during a cooling or concentration process, this can be represented by movement away from the origin on a straight line through the origin. Dilution by water is represented by movement in the opposite direction.

A typical separation might be represented as follows: Starting at E with a saturated brine at 100°C a small amount of water is added to dissolve any traces of solid phase present and to make sure the solids precipitated initially are KCl. Evaporative cooling along line HG results in the precipitation of KCl. During this evaporative cooling, part of the water evaporated must be added back to the solution to prevent the coprecipitation of NaCl. The final composition at G can be calculated by the NaCl/KCl/H₂O ratios and the known amount of NaCl in the incoming solution at E. The solution at point G may be concentrated by evaporation at 100°C. During this process the solution will increase in concentration with respect to both components until point I is reached. Then NaCl will precipitate, and the solution will become more concentrated in KCl, as indicated by the line IE, until the original point E is reached. If concentration is carried beyond point E, a mixture of KCl and NaCl will precipitate.

Example 2: Yield from Evaporative Cooling   Starting with 1000 lb of water in a solution at H on the solubility diagram in Fig. 18-57, calculate the yield on evaporative cooling and concentrate the solution back to point H so the cycle can be repeated, indicating the amount of NaCl precipitated and the evaporation and dilution required at the different steps in the process.

In solving problems of this type, it is convenient to list the material balance and the solubility ratios. The various points on the material balance are calculated by multiplying the quantity of the component which does not precipitate from solution during the transition from one point to another (normally the

NaCl in cooling or the KCl in the evaporative step) by the solubility ratio at the next step, illustrated as follows:
   Basis. 1000 lb of water at the initial conditions.

Solution component	KCl	NaCl	Water	Solubility ratios KCl	Solubility ratios NaCl	Solubility ratios Water

| | | | | Solubility ratios | | |
Solution component	KCl	NaCl	Water	KCl	NaCl	Water
H	343	270	1000	34.3	27.0	100
G(a)	194	270	950	20.4	28.4	100
KCl yield	149					
Net evaporation			50			
I(b)	194	270	860	22.6	31.4	100
E(c)	194	153	554	35.0	27.5	100
NaCl yield		117				
Evaporation			306			
Dilution			11			
H′	194	153	565	34.3	27.0	−100

The calculations for these steps are:

a. 270 lb NaCl (100 lb water/28.4 lb NaCl) = 950 lb water
   950 lb water (20.4 lb KCl/100 lb water) = 194 lb KCl
b. 270 lb NaCl (100 lb water/31.4 lb NaCl) = 860 lb water
   860 lb water (22.6 lb KCl/100 lb water) = 194 lb KCl
c. 194 lb KCl (100 lb water/35.0 lb KCl) = 554 lb water
   554 lb water (27.5 lb NaCl/100 lb water) = 153 lb NaCl

Note that during the cooling step the maximum amount of evaporation which is permitted by the material balance is 50 lb for the step shown. In an evaporative-cooling step, however, the actual evaporation which results from adiabatic cooling is more than this. Therefore, water must be added back to prevent the NaCl concentration from rising too high; otherwise, coprecipitation of NaCl will occur.

Inasmuch as only mass ratios are involved in these calculations, kilograms or any other unit of mass may be substituted for pounds without affecting the validity of the example.

Although the figures given are for a step-by-step process, it is obvious that the same techniques will apply to a continuous system if the fresh feed containing KCl and NaCl is added at an appropriate part of the cycle, such as between steps G and I for the case of dilute feed solutions.

Another method of fractional crystallization, in which advantage is taken of different crystallization rates, is sometimes used. Thus, a solution saturated with borax and potassium chloride will, in the absence of borax seed crystals, precipitate only potassium chloride on rapid cooling. The borax remains behind as a supersaturated solution, and the potassium chloride crystals can be removed before the slower borax crystallization starts.

Crystal Formation   There are obviously two steps involved in the preparation of crystal matter from a solution. The crystals must first form and then grow. The formation of a new solid phase either on an inert particle in the solution or in the solution itself is called **nucleation.** The increase in size of this nucleus with a layer-by-layer addition of solute is called **growth.** Both nucleation and crystal growth have supersaturation as a common driving force. Unless a solution is supersaturated, crystals can neither form nor grow. Supersaturation refers to the quantity of solute present in solution compared with the quantity which would be present if the solution were kept for a very long period of time with solid phase in contact with the solution. The latter value is the equilibrium solubility at the temperature and pressure under consideration. The supersaturation coefficient can be expressed

$$S = \frac{\text{parts solute/100 parts solvent}}{\text{parts solute at equilibrium/100 parts solvent}} \geqq 1.0 \quad (18\text{-}22)$$

Solutions vary greatly in their ability to sustain measurable amounts of supersaturation. With some materials, such as sucrose, it is possible to develop a supersaturation coefficient of 1.4 to 2.0 with little danger of nucleation. With some common inorganic solutions such as sodium chloride in water, the amount of supersaturation which can be generated stably is so small that it is difficult or impossible to measure.

Certain qualitative facts in connection with supersaturation, growth, and the yield in a crystallization process are readily apparent.

If the concentration of the initial solution and the final mother liquor are fixed, the total weight of the crystalline crop is also fixed if equilibrium is obtained. The particle-size distribution of this weight, however, will depend on the relationship between the two processes of nucleation and growth. Considering a given quantity of solution cooled through a fixed range, if there is considerable nucleation initially during the cooling process, the yield will consist of many small crystals. If only a few nuclei form at the start of the precipitation and the resulting yield occurs uniformly on these nuclei without secondary nucleation, a crop of large uniform crystals will result. Obviously, many intermediate cases of varying nucleation rates and growth rates can also occur, depending on the nature of the materials being handled, the rate of cooling, agitation, and other factors.

When a process is continuous, nucleation frequently occurs in the presence of a seeded solution by the combined effects of mechanical stimulus and nucleation caused by supersaturation (heterogeneous nucleation). If such a system is completely and uniformly mixed (i.e., the product stream represents the typical magma circulated within the system) and if the system is operating at steady state, the particle-size distribution has definite limits which can be predicted mathematically with a high degree of accuracy, as will be shown later in this section.

Geometry of Crystal Growth   Geometrically a crystal is a solid bounded by planes. The shape and size of such a solid are functions of the interfacial angles and of the linear dimension of the faces. As the result of the constancy of its interfacial angles, each face of a growing or dissolving crystal, as it moves away from or toward the center of the crystal, is always parallel to its original position. This concept is known as the "principle of the parallel displacement of faces." The rate at which a face moves in a direction perpendicular to its original position is called the translation velocity of that face or the rate of growth of that face.

From the industrial point of view, the term **crystal habit** or **crystal morphology** refers to the relative sizes of the faces of a crystal. The crystal habit is determined by the internal structure and external influences on the crystal such as the growth rate, solvent used, and impurities present during the crystallization growth period. The crystal habit of commercial products is of very great importance. Long, needlelike crystals tend to be easily broken during centrifugation and drying. Flat, platelike crystals are very difficult to wash during filtration or centrifugation and result in relatively low filtration rates. Complex or twinned crystals tend to be more easily broken in transport than chunky, compact crystal habits. Rounded or spherical crystals (caused generally by attrition during growth and handling) tend to give considerably less difficulty with caking than do cubical or other compact shapes.

Internal structure can be different in crystals that are chemically identical, even though they may be formed at different temperatures and have a different appearance. This is called **polymorphism** and can be determined only by X-ray diffraction. For the same internal structure, very small amounts of foreign substances will often completely change the crystal habit. The selective adsorption of dyes by different faces of a crystal or the change from an alkaline to an acidic environment will often produce pronounced changes in the crystal habit. The presence of other soluble anions and cations often has a similar influence. In the crystallization of ammonium sulfate, the reduction in soluble iron to below 50 ppm of ferric ion is sufficient to cause significant change in the habit of an ammonium sulfate crystal from a long, narrow form to a relatively chunky and compact form. Additional information is available in the patent literature and Table 18-4 lists some of the better-known additives and their influences.

Since the relative sizes of the individual faces of a crystal vary between wide limits, it follows that different faces must have different translational velocities. A geometric law of crystal growth known as the **overlapping principle** is based on those velocity differences: in growing a crystal, only those faces having the lowest translational velocities survive; and in dissolving a crystal, only those faces having the highest translational velocities survive.

For example, consider the cross sections of a growing crystal as in Fig. 18-58. The polygons shown in the figure represent varying stages in the growth of the crystal. The faces marked A are slow-growing faces (low translational velocities), and the faces marked B are fast-growing (high translational velocities). It is apparent from Fig. 18-58 that the faster B faces tend to disappear as they are overlapped by the slower A faces.

Hartman and Perdok (1955) predicted that crystal habit or crystal morphology was related to the internal structure based on energy considerations and speculated it should be possible to predict the growth shape of crystals from the slice energy of different flat faces. Later, Hartman was able to predict the calculated attachment energy for various crystal species. Recently computer programs have been developed that predict crystal morphology from attachment energies. These techniques are particularly useful in dealing with organic or molecular crystals and rapid progress in this area is being made by companies such as Molecular Simulations of Cambridge, England.

Purity of the Product   If a crystal is produced in a region of the phase diagram where a single-crystal composition precipitates, the crystal itself will normally be pure provided that it is grown at relatively low rates and constant conditions. With many products these purities approach a value of about 99.5 to 99.8 percent. The difference between this and a purity of 100 percent is generally the result of small pockets of mother liquor called occlusions trapped within the crystal. Although frequently large enough to be seen with an ordinary microscope, these occlusions can be submicroscopic and represent dislocations within the structure of the crystal. They can be caused by either attrition or breakage during the growth process or by slip planes within the crystal structure caused by interference between screw-type dislocations and the remainder of the crystal faces. To increase the purity of the crystal beyond the point where such occlusions are normally expected (about 0.1 to 0.5 percent by volume), it is generally necessary to reduce the impurities in the mother liquor itself to an acceptably low level so that the mother liquor contained within these occlusions will not contain sufficient impurities to cause an impure product to be formed. It is normally necessary to recrystallize material from a solution which is relatively pure to surmount this type of purity problem.

In addition to the impurities within the crystal structure itself, there is normally an adhering mother-liquid film left on the surface of the crystal after separation in a centrifuge or on a filter. Typically a centrifuge may leave about 2 to 10 percent of the weight of the crystals as adhering mother liquor on the surface. This varies greatly with the size and shape or habit of the crystals. Large, uniform crystals precipitated from low-viscosity mother liquors will retain a minimum of mother liquor, while nonuniform or small crystals precipitated from viscous solutions will retain a considerably larger proportion. Comparable statements apply to the filtration of crystals, although normally the amounts of mother liquor adhering to the crystals are considerably larger. It is common practice when precipitating materials from solutions which contain appreciable quantities of impurities to wash the crystals on the centrifuge or filter with either fresh solvent or feed solution. In principle, such washing can reduce the impurities quite substantially. It is also possible in many cases to reslurry the crystals in fresh solvent and recentrifuge the product in an effort to obtain a longer residence time during the washing operation and better mixing of the wash liquors with the crystals.

Coefficient of Variation   One of the problems confronting any user or designer of crystallization equipment is the expected particle-size distribution of the solids leaving the system and how this distribution may be adequately described. Most crystalline-product distributions plotted on arithmetic-probability paper will exhibit a straight line for a considerable portion of the plotted distribution. In this type of plot the particle diameter should be plotted as the ordinate and the cumulative percent on the log-probability scale as the abscissa.

It is common practice to use a parameter characterizing crystal-size distribution called the coefficient of variation. This is defined as follows:

$$CV = 100\,\frac{PD_{16\%} - PD_{84\%}}{2PD_{50\%}} \qquad (18\text{-}23)$$

where   CV = coefficient of variation, as a percentage
PD = particle diameter from intercept on ordinate axis at percent indicated

TABLE 18-4 Some Impurities Known to Be Habit Modifiers

Material crystallized	Additive(s)	Effect	Concentration	References
$Ba(NO_3)^2$	Mg, Te^{+4}	Helps growth	—	1
$CaSO_4 \cdot 2H_2O$	Citric, succinic, tartaric acids	Helps growth	Low	
	Sodium citrate	Forms prisms	—	5
$CuSO_4 \cdot 5H_2O$	H_2SO_4	Chunky crystals	0.3%	5
KCl	$K_4Fe(CN)_6$	Inhibits growth, dendrites	1000 ppm	4
	Pb, Bi, Sn^{+2}, Ti, Zr, Th, Cd, Fe, Hg, Mg	Helps growth	Low	1
$KClO_4$	Congo red (dye)	Modifies the 102 face	50 ppm	6
K_2CrO_4	Acid magenta (dye)	Modifies the 010 face	50 ppm	6
KH_2PO_4	$Na_2B_4O_7$	Aids growth	—	1
KNO_2	Fe	Helps growth	Low	1
KNO_3	Acid magenta (dye)	Tabular crystals		7
	Pb, Th, Bi	Helps growth	Low	1
K_2SO_4	Acid magenta (dye)	Forms plates	2000 ppm	6
	Cl, Mn, Mg, Bi, Cu, Al, Fe	Helps growth	Low	1
	Cl_3	Reduces growth rate	1000 ppm	4
	$(NH_4)_3Ce(NO_3)_6$	Reduces growth rate	1000 ppm	4
$LiCl \cdot H_2O$	Cr·Mn^{+2}, Sn^{+2}, Co, Ni, Fe^{+3}	Helps growth	Low	1
$MgSO_4 \cdot 7H_2O$	Borax	Aids growth	5%	1
$Na_2B_4O_7 \cdot 10H_2O$	Sodium oleate	Reduces growth & nuc.	5 ppm	
	Casein, gelatin	Promotes flat crystals	—	2, 5
	NaOH, Na_2CO_3	Promotes chunky crystals	—	
$Na_2CO_3 \cdot H_2O$	$SO_4^=$	Reduces L/D ratio	0.1–1.0%	Canadian Patent 812,685
	Ca^{+2} and Mg^{+2}	Increase bulk density	400 ppm	U.S. Patent 3,459,497
$NaCO_3 \cdot NaHCO_3 \cdot 2H_2O$	D-40 detergent	Aids growth	20 ppm	U.S. Patent 3,233,983
NaCl	$Na_4Fe(CN)_6$, CdBr	Forms dendrites	100 ppm	4
	Pb, Mn^{+2}, Bi, Sn^{+2}, Ti, Fe, Hg	Helps growth	Low	1
	Urea, formamide	Forms octahedra	Low	2
	Tetraalkyl ammon. salts	Helps growth & hardness	1–100 ppm	U.S. Patent 3,095,281
	Polyethylene-oxy compounds	Helps growth & hardness	—	U.S. Patent 3,000,708
$NaClO_3$	Na_2SO_4, $NaClO_4$	Tetrahedrons	—	3
$NaNO_3$	Acid green (dye)	Flattened rhombahedra		7
Na_2SO_4	NH_4SO_4 @ pH 6.5	Large single crystals	Low	
	$CdCl_2$	Inhibits growth	1000 ppm	4
	Alkyl aryl sulfonates	Aids growth	—	2
	Calgon	Aids growth	100 ppm	
NH_4Cl	Mn, Fe, Cu, Co, Ni, Cr	Aid growth	Low	1
	Urea	Forms octahedra		5
NH_4ClO_4	Azurine (dye)	Modifies the 102 face	22 ppm	6
NF_4F	Ca	Helps growth	Low	1
$(NH_4)NO_3$	Acid magenta (dye)	Forms 010 face plates	1%	6
$(NH_4)_2HPO_4$	H_2SO_4	Reduces L/D ratio	7%	
$NH_4H_2PO_4$	Fe^{+3}, Cr, Al, Sn	Helps growth	Traces	1
$(NH_4)_2SO_4$	Cr^{+3}, Fe^{+3}, Al^{+3}	Promotes needles	50 ppm	
	H_2SO_4	Promotes needles	2–6%	U.S. Patent 2,092,073
	Oxalic acid, citric acid	Promotes chunky crystals	1000 ppm	U.S. Patent 2,228,742
	H_3PO_4, SO_2	Promotes chunky crystals	1000 ppm	
$ZnSO_4 \cdot 7H_2O$	Borax	Aids growth	—	1
Adipic acid	Surfactant-SDBS	Aids growth	50–100 ppm	2
Fructose	Glucose, difructose	Affects growth		8
L-asparagine	L-glutamic acid	Affects growth		8
Naphthalene	Cyclohexane (solvent)	Forms needles	—	2
	Methanol (solvent)	Forms plates		
Pentaerythritol	Sucrose	Aids growth	—	1
	Acetone (solvent)	Forms plates	—	2
Sodium glutamate	Lysine, CaO	Affects growth		8
Sucrose	Raffinose, KCl, NaBr	Modify growth rate		
Urea	Biuret	Reduces L/D & aids growth	2–7%	
	NH_4Cl	Reduces L/D & aids growth	5–10%	

1. Gillman, *The Art and Science of Growing Crystals,* Wiley, New York, 1963.
2. Mullin, *Crystallization,* Butterworth, London, 1961.
3. Buckley, *Crystal Growth,* Wiley, New York, 1961.
4. Phoenix, L., *British Chemical Engineering,* vol. II, no. 1 (Jan. 1966), pp. 34–38.
5. Garrett, D. E., *British Chemical Engineering,* vol. I, no. 12 (Dec. 1959), pp. 673–677.
6. Buckley, *Crystal Growth,* (Faraday Soc.) Butterworths, 1949, p. 249.
7. Butchart and Whetstone, *Crystal Growth,* (Faraday Soc.) Butterworths, 1949, p. 259.
8. Nyvlt, J., *Industrial Crystallization,* Verlag Chemie Publishers, New York, 1978, pp. 26–31.

In order to be consistent with normal usage, the particle-size distribution when this parameter is used should be a straight line between approximately 10 percent cumulative weight and 90 percent cumulative weight. By giving the coefficient of variation and the mean particle diameter, a description of the particle-size distribution is obtained which is normally satisfactory for most industrial purposes. If the product is removed from a mixed-suspension crystallizer, this coeffi-cient of variation should have a value of approximately 50 percent (Randolph and Larson, op. cit., chap. 2).

Crystal Nucleation and Growth

Rate of Growth Crystal growth is a layer-by-layer process, and since growth can occur only at the face of the crystal, material must be transported to that face from the bulk of the solution. Diffusional
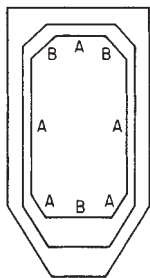
FIG. 18-58 Overlapping principle.

resistance to the movement of molecules (or ions) to the growing crystal face, as well as the resistance to integration of those molecules into the face, must be considered. As discussed earlier, different faces can have different rates of growth, and these can be selectively altered by the addition or elimination of impurities.

If L is a characteristic dimension of a crystal of selected material and shape, the rate of growth of a crystal face that is perpendicular to L is, by definition,

$$G \equiv \lim_{\Delta L \to O} \frac{\Delta L}{\Delta t} = \frac{dL}{dt} \qquad (18\text{-}24)$$

where G is the growth rate over time internal t. It is customary to measure G in the practical units of millimeters per hour. It should be noted that growth rates so measured are actually twice the facial growth rate.

The delta L *law.*   It has been shown by McCabe [*Ind. Eng. Chem.,* **21**, 30, 112 (1929)] that all geometrically similar crystals of the same material suspended in the same solution grow at the same rate if growth rate is defined as in Eq. (18-24). The rate is independent of crystal size, provided that all crystals in the suspension are treated alike. This generalization is known as the delta L law. Although there are some well-known exceptions, they usually occur when the crystals are very large or when movement of the crystals in the solution is so rapid that substantial changes occur in diffusion-limited growth of the faces.

It is emphasized that the delta L law does not apply when similar crystals are given preferential treatment based on size. It fails also when surface defects or dislocations significantly alter the growth rate of a crystal face. Nevertheless, it is a reasonably accurate generalization for a surprising number of industrial cases. When it is, it is important because it simplifies the mathematical treatment in modeling real crystallizers and is useful in predicting crystal-size distribution in many types of industrial crystallization equipment.

Important exceptions to McCabe's growth-rate model have been noted by Bramson, by Randolph, and by Abegg. These are discussed by Canning and Randolph, *Am. Inst. Chem. Eng. J.,* **13**, 5 (1967).

Nucleation   The mechanism of crystal nucleation from solution has been studied by many scientists, and recent work suggests that—in commercial crystallization equipment, at least—the nucleation rate is the sum of contributions by (1) homogeneous nucleation and (2) nucleation due to contact between crystals and (*a*) other crystals, (*b*) the walls of the container, and (*c*) the pump impeller. If B^0 is the net number of new crystals formed in a unit volume of solution per unit of time,

$$B^0 = B_{ss} + B_e + B_c \qquad (18\text{-}25)$$

where B_e is the rate of nucleation due to crystal-impeller contacts, B_c is that due to crystal-crystal contacts, and B_{ss} is the homogeneous nucleation rate due to the supersaturation driving force. The mechanism of the last-named is not precisely known, although it is obvious that molecules forming a nucleus not only have to coagulate, resisting the tendency to redissolve, but also must become oriented into a fixed lattice. The number of molecules required to form a stable crystal nucleus has been variously estimated at from 80 to 100 (with ice), and the probability that a stable nucleus will result from the simultaneous collision of that large number is extremely low unless the supersatura-

tion level is very high or the solution is supersaturated in the absence of agitation. In commercial crystallization equipment, in which supersaturation is low and agitation is employed to keep the growing crystals suspended, the predominant mechanism is contact nucleation or, in extreme cases, attrition.

In order to treat crystallization systems both dynamically and continuously, a mathematical model has been developed which can correlate the nucleation rate to the level of supersaturation and/or the growth rate. Because the growth rate is more easily determined and because nucleation is sharply nonlinear in the regions normally encountered in industrial crystallization, it has been common to assume

$$B^0 = ks^i \qquad (18\text{-}26)$$

where s, the supersaturation, is defined as $(C - C_s)$, C being the concentration of the solute and C_s its saturation concentration; and the exponent i and dimensional coefficient k are values characteristic of the material.

While Eq. (18-26) has been popular among those attempting correlations between nucleation rate and supersaturation, recently it has become commoner to use a derived relationship between nucleation rate and growth rate by assuming that

$$G = k's \qquad (18\text{-}27)$$

whence, in consideration of Eq. (18-26),

$$B^0 = k''G^i \qquad (18\text{-}28)$$

where the dimensional coefficient k' is characteristic of the material and the conditions of crystallization and $k'' = k/(k')^i$. Feeling that a model in which nucleation depends only on supersaturation or growth rate is simplistically deficient, some have proposed that contact nucleation rate is also a power function of slurry density and that

$$B^0 = k_n G^i M_T^j \qquad (18\text{-}29)$$

where M_T is the density of the crystal slurry, g/L.

Although Eqs. (18-28) and (18-29) have been adopted by many as a matter of convenience, they are oversimplifications of the very complex relationship that is suggested by Eq. (18-25); Eq. (18-29) implicitly and quite arbitrarily combines the effects of homogeneous nucleation and those due to contact nucleation. They should be used only with caution.

In work pioneered by Clontz and McCabe [*Chem. Eng. Prog. Symp. Ser.,* **67**(110), 6 (1971)] and subsequently extended by others, contact nucleation rate was found to be proportional to the input of energy of contact, as well as being a function of contact area and supersaturation. This observation is important to the scaling up of crystallizers: at laboratory or bench scale, contact energy level is relatively low and homogeneous nucleation can contribute significantly to the total rate of nucleation; in commercial equipment, on the other hand, contact energy input is intense and contact nucleation is the predominant mechanism. Scale-up modeling of a crystallizer, therefore, must include its mechanical characteristics as well as the physiochemical driving force.

Nucleation and Growth   From the preceding, it is clear that no analysis of a crystallizing system can be truly meaningful unless the simultaneous effects of nucleation rate, growth rate, heat balance, and material balance are considered. The most comprehensive treatment of this subject is by Randolph and Larson (op. cit), who developed a mathematical model for continuous crystallizers of the mixed-suspension or circulating-magma type [*Am. Inst. Chem. Eng. J.,* **8**, 639 (1962)] and subsequently examined variations of this model that include most of the aberrations found in commercial equipment. Randolph and Larson showed that when the total number of crystals in a given volume of suspension from a crystallizer is plotted as a function of the characteristic length as in Fig. 18-59, the slope of the line is usefully identified as the crystal population density, n:

$$n = \lim_{\Delta L \to O} \frac{\Delta N}{\Delta L} = \frac{dN}{dL} \qquad (18\text{-}30)$$

where N = total number of crystals up to size L per unit volume of magma. The population density thus defined is useful because it char-
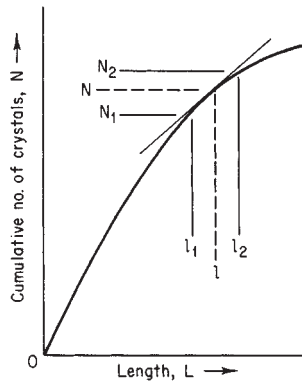
FIG. 18-59 Determination of the population density of crystals.

acterizes the nucleation-growth performance of a particular crystallization process or crystallizer.

The data for a plot like Fig. 18-60 are easily obtained from a screen analysis of the total crystal content of a known volume (e.g., a liter) of magma. The analysis is made with a closely spaced set of testing sieves, as discussed in Sec. 19, Table 19-6, the cumulative number of particles smaller than each sieve in the nest being plotted against the aperture dimension of that sieve. The fraction retained on each sieve is weighed, and the mass is converted to the equivalent number of particles by dividing by the calculated mass of a particle whose dimension is the arithmetic mean of the mesh sizes of the sieve on which it is retained and the sieve immediately above it.

In industrial practice, the size-distribution curve usually is not actually constructed. Instead, a mean value of the population density for any sieve fraction of interest (in essence, the population density of the particle of average dimension in that fraction) is determined directly as $\Delta N/\Delta L$, ΔN being the number of particles retained on the sieve and ΔL being the difference between the mesh sizes of the retaining sieve and its immediate predecessor. It is common to employ the units of $(mm \cdot L)^{-1}$ for n.

For a steady-state crystallizer receiving solids-free feed and containing a well-mixed suspension of crystals experiencing negligible breakage, a material-balance statement degenerates to a particle balance (the Randolph-Larson general-population balance); in turn, it simplifies to

$$\frac{dn}{dL} + \frac{n}{Gt} = 0 \qquad (18\text{-}31)$$

if the delta L law applies (i.e., G is independent of L) and the drawdown (or retention) time is assumed to be invariant and calculated as $t = V/Q$. Integrated between the limits n^0, the population density of nuclei (for which L is assumed to be zero), and n, that of any chosen crystal size L, Eq. (18-31) becomes

$$\int_{n^0}^{n} \frac{dn}{n} = -\int_{0}^{L} \frac{dL}{Gt} \qquad (18\text{-}32)$$

$$\ln n = \frac{-L}{Gt} + \ln n^0 \qquad (18\text{-}33a)$$

or

$$n = n^0 e^{-L/Gt} \qquad (18\text{-}33b)$$

A plot of $\ln n$ versus L is a straight line whose intercept is $\ln n^0$ and whose slope is $-1/Gt$. (For plots on base-10 log paper, the appropriate slope correction must be made.) Thus, from a given product sample of known slurry density and retention time it is possible to obtain the nucleation rate and growth rate for the conditions tested if the sample satisfies the assumptions of the derivation and yields a straight line. A number of derived relations which describe the nucleation rate, size distribution, and average properties are summarized in Table 18-5.

If a straight line does *not* result (Fig. 18-60), at least part of the explanation may be violation of the delta L law (Canning and Ran-

dolph, loc. cit.). The best current theory about what causes size-dependent growth suggests what has been called growth dispersion or "Bujacian behavior" [Mullen (ed.), op. cit., p. 23]. In the same environment different crystals of the same size can grow at different rates owing to differences in dislocations or other surface effects. The graphs of "slow" growers (Fig. 18-60, curve A) and "fast" growers (curve B) sum to a resultant line (curve C), concave upward, that is described by Eq. (18-34) (Randolph, in deJong and Jancic, op. cit., p. 295):

$$n = \sum \frac{B^0 i}{G_i} e^{(-L/G_i t)} \qquad (18\text{-}34)$$

Equation (18-31) contains no information about the crystallizer's influence on the nucleation rate. If the crystallizer is of a mixed-suspension, mixed-product-removal (MSMPR) type, satisfying the criteria for Eq. (18-31), and if the model of Clontz and McCabe is valid, the contribution to the nucleation rate by the circulating pump can be calculated [Bennett, Fiedelman, and Randolph, *Chem. Eng. Prog.*, **69**(7), 86 (1973)]:

$$B_e = K_e \left(\frac{I^2}{P}\right) \rho G \int_0^\infty nL^4 \, dL \qquad (18\text{-}35)$$

where I = tip speed of the propeller or impeller, m/s
ρ = crystal density, g/cm³
P = volume of crystallizer/circulation rate (turnover), m³/(m³/s) = s

Since the integral term is the fourth moment of the distribution (m_4), Eq. (18-35) becomes

$$B_e = K_e \rho G \left(\frac{I^2}{P}\right) m_4 \qquad (18\text{-}36)$$

Equation (18-36) is the general expression for impeller-induced nucleation. In a fixed-geometry system in which only the speed of the circulating pump is changed and in which the flow is roughly proportional to the pump speed, Eq. (18-36) may be satisfactorily replaced with

$$B_e = K_e'' \rho G (S_R)^3 m_4 \qquad (18\text{-}37)$$

where S_R = rotation rate of impeller, r/min. If the maximum crystal-impeller impact stress is a nonlinear function of the kinetic energy, shown to be the case in at least some systems, Eq. (18-37) no longer applies.

In the specific case of an MSMPR exponential distribution, the fourth moment of the distribution may be calculated as

$$m_4 = 4! n^0 (Gt)^5 \qquad (18\text{-}38)$$

Substitution of this expression into Eq. (18-36) gives

$$B_e = k n^0 G (S_R)^3 L_D^5 \qquad (18\text{-}39)$$

where $L_D = 3Gt$, the dominant crystal (mode) size.

Equation (18-39) displays the competing factors that stabilize secondary nucleation in an operating crystallizer when nucleation is due mostly to impeller-crystal contact. Any increase in particle size produces a fifth-power increase in nucleation rate, tending to counteract the direction of the change and thereby stabilizing the crystal-size distribution. From dimensional argument alone the size produced in a mixed crystallizer for a (fixed) nucleation rate varies as $(B^0)^{1/3}$. Thus, this fifth-order response of contact nucleation does not wildly upset the crystal size distribution but instead acts as a stabilizing feedback effect.

Nucleation due to crystal-to-crystal contact is greater for equal striking energies than crystal-to-metal contact. However, the viscous drag of the liquid on particle sizes normally encountered limits the velocity of impact to extremely low values. The assumption that only the largest crystal sizes contribute significantly to the nucleation rate by crystal-to-crystal contact permits a simple computation of the rate:

$$B_c = K_c \rho G m_j^2 \qquad (18\text{-}40)$$

where m_j = the fourth, fifth, sixth, or higher moments of the distribution.

A number of different crystallizing systems have been investigated by using the Randolph-Larson technique, and some of the published

TABLE 18-5 Common Equations for Population-Balance Calculations

Name	Symbol	Units	Systems without fines removal	Systems with fines removal — Fines stream	Systems with fines removal — Product stream	References
Drawdown time (retention time)	t	h	$t = V/Q$	$t_F = V_{\text{liquid}}/Q_F$	$t = V/Q$	
Growth rate	G	mm/h	$G = dL/dt$	$G = dL/dt$	$G = dL/dt$	
Volume coefficient	K_v	1/no. (crystals)	$K_v = \dfrac{\text{volume of one crystal}}{L^3}$	$K_v = \dfrac{\text{volume of one crystal}}{L^3}$	$K_v = \dfrac{\text{volume of one crystal}}{L^3}$	
Population density	n	No. (crystals)/mm	$n = dN/dL$	$n = dN/dL$	$n = dN/dL$	1
Nuclei population density	n^o	No. (crystals)/mm	$n^o = K_M M^j G^{i-1}$			2
Population density	n	No. (crystals)/mm	$n = n^o e^{-L/Gt}$	$n_F = n^o e^{-L/Gt_F}$	$n = n^{o - L_a/Gt_F} e^{-L/Gt}$	1, 3
Nucleation rate	B_0	No. (crystals)/h	$B_0 = Gn^o = K_M M^j G^i$	$B_0 = G^o_n$		4
Dimensionless length	x	None	$x = \dfrac{L}{Gt}$	$x_F = \dfrac{L}{Gt_F},\ L_0 \to L_f$	$x = \dfrac{L}{Gt},\ L_f \to L$	1
Mass/unit volume (slurry density)	M_T	g/L	$M_t = K_v \rho \displaystyle\int_0^\infty nL^3\, dL$ $M_t = K_v \rho 6\, n^o(Gt)^4$	$M_{T_F} = K_v \rho \displaystyle\int_0^{L_f} n^o e^{-L/Gt_F}\, L^3\, dL$	$M_T = K_v \rho \displaystyle\int_{L_f}^\infty n^o e^{-L/Gt_F} e^{-L/Gt}\, L^3\, dL$	1
Cumulative mass to x / Total mass	W_x	None	$W_x = 1 - e^{-x}\left(\dfrac{x^3}{6} + \dfrac{x^2}{2} + x + 1\right)$	$W_F = \dfrac{e^{-x}(x^3 + 3x^2 + 6x + 6) - 6}{e^{-x}c(x_c^3 + 3x_c^2 + 6x_c + 6) - 6}$	$W = \dfrac{6K_v \rho n^o e^{-L_a/Gt_F}(Gt)^4\left[1 - e^{-x}\left(\dfrac{x^3}{6} + \dfrac{x^2}{2} + x + 1\right)\right]}{\text{Slurry density } M,\ g/L}$ when $L_c \approx 0$, compared with L_a	5
Dominant particle	L_d	mm	$I_d = 3Gt$			
Average particle, weight	L_a	mm	$I_a = 3.67Gt$			6
Total number of crystals	N_T	No./L	$N_T = \displaystyle\int_0^\infty n\, dl$	$N_F = \displaystyle\int_0^{L_f} n_F\, dL$	$N_T = \displaystyle\int_{L_f}^\infty n\, dL$	1, 3

1. Randolph and Larson, *Am. Inst. Chem. Eng. J.*, **8,** 639 (1962).
2. Timm and Larson, *Am. Inst. Chem. Eng. J.*, **14,** 452 (1968).
3. Larson, private communication.
4. Larson, Timm, and Wolff, *Am. Inst. Chem. Eng. J.*, **14,** 448 (1968).
5. Larson and Randolph, *Chem. Eng. Prog. Symp. Ser.*, **65**(95), 1 (1969).
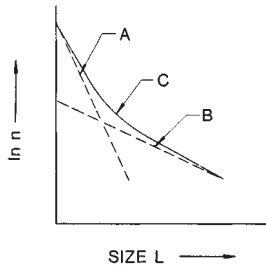6. Schoen, *Ind. Eng. Chem.*, **53,** 607 (1961).

FIG. 18-60   Population density of crystals resulting from Bujacian behavior.

growth rates and nucleation rates are included in Table 18-6. Although the usefulness of these data is limited to the conditions tested, the table gives a range of values which may be expected, and it permits resolution of the information gained from a simple screen analysis into the fundamental factors of growth rate and nucleation rate. Experiments may then be conducted to determine the independent effects of operation and equipment design on these parameters.

Although this procedure requires laborious calculations because of the number of samples normally needed, these computations and the determination of the best straight-line fit to the data are readily programmed for digital computers.

Example 3: Population, Density, Growth and Nucleation Rate
Calculate the population density, growth, and nucleation rates for a crystal sample of urea for which there is the following information. These data are from Bennett and Van Buren [*Chem. Eng. Prog. Symp. Ser.,* **65**(95), 44 (1969)].

Slurry density = 450 g/L
Crystal density = 1.335 g/cm^3
Drawdown time t = 3.38 h
Shape factor k_v = 1.00

Product size:

−14 mesh, +20 mesh	4.4 percent
−20 mesh, +28 mesh	14.4 percent
−28 mesh, +35 mesh	24.2 percent
−35 mesh, +48 mesh	31.6 percent
−48 mesh, +65 mesh	15.5 percent
−65 mesh, +100 mesh	7.4 percent
−100 mesh	2.5 percent

n = number of particles per liter of volume
14 mesh = 1.168 mm, 20 mesh = 0.833 mm, average opening 1.00 mm
Size span = 0.335 mm = ΔL

$$n_{20} = \frac{(450 \text{ g/L})(0.044)}{(1.335/1000) \text{ g/mm}^3 (1.00^3 \text{ mm}^3/\text{particle})(0.335 \text{ mm})(1.0)}$$

$$n_{20} = 44{,}270$$

$$\ln n_{20} = 10{,}698$$

Repeating for each screen increment:

Screen size	Weight, %	k_v	$\ln n$	L, average diameter, mm
100	7.4	1.0	18.099	0.178
65	15.5	1.0	17.452	0.251
48	31.6	1.0	16.778	0.356
35	24.2	1.0	15.131	0.503
28	14.4	1.0	13.224	0.711
20	4.4	1.0	10.698	1.000

Plotting $\ln n$ versus L as shown in Fig. 18-61, a straight line having an intercept at zero length of 19.781 and a slope of −9.127 results. As mentioned in discussing Eq. (18-24), the growth rate can then be found.

Slope = $-1/Gt$ or $-9.127 = -1/[G(3.38)]$

or

$G = 0.0324$ mm/h

and

$B_0 = Gn^0 = (0.0324)(e^{19.781}) = 12.65 \times 10^6 \dfrac{n^0}{L \cdot h}$

and

$L_a = 3.67(0.0324)(3.38) = 0.40$ mm

An additional check can be made of the accuracy of the data by the relation

$$M_T = 6k_v \rho n^0 (Gt)^4 = 450 \text{ g/L}$$

$$M_T = (6)(1.0)\frac{1.335 \text{ g/cm}^3}{1000 \text{ mm}^3/\text{cm}^3} e^{19.78}[(0.0324)(3.38)]^4$$

$$M_T = 455 \text{ g/L} \approx 450 \text{ g/L}$$

Had only the growth rate been known, the size distribution of the solids could have been calculated from the equation

$$W_f = 1 - e^{-x}\left(\frac{x^3}{6} + \frac{x^2}{2} + x + 1\right)$$

where W_f is the weight fraction *up to* size L and $x = L/Gt$.

$$x = \frac{L}{(0.0324)(3.38)} = \frac{L}{0.1095}$$

Screen size	L, mm	x	W_f*	Cumulative % retained 100 $(1 - W_f)$	Measured cumulative % retained
20	0.833	7.70	0.944	5.6	4.4
28	0.589	5.38	0.784	21.6	18.8
35	0.417	3.80	0.526	47.4	43.0
48	0.295	2.70	0.286	71.4	74.6
65	0.208	1.90	0.125	87.5	90.1
100	0.147	1.34	0.048	95.2	97.5

*Values of W_f as a function of x may be obtained from a table of Wick's functions.

Note that the calculated distribution shows some deviation from the measured values because of the small departure of the actual sample from the theoretical coefficient of variation (i.e., 47.5 versus 52 percent).

Here it can be seen that the nucleation rate is a decreasing function of growth rate (and supersaturation). The physical explanation is believed to be the mechanical influence of the crystallizer on the growing suspension and/or the effect of Bujacian behavior.

Had sufficient data indicating a change in n^0 for various values of M at constant G been available, a plot of $\ln n^0$ versus $\ln M$ at corresponding G's would permit determination of the power j.

Crystallizers with Fines Removal   In Example 3, the product was from a forced-circulation crystallizer of the MSMPR type. In many cases, the product produced by such machines is too small for commercial use; therefore, a separation baffle is added within the crystallizer to permit the removal of unwanted fine crystalline material from the magma, thereby controlling the population density in the machine so as to produce a coarser crystal product. When this is done, the product sample plots on a graph of $\ln n$ versus L as shown in line P, Fig. 18-62. The line of steepest slope, line F, represents the particle-size distribution of the fine material, and samples which show this distribution can be taken from the liquid leaving the fines-separation baffle. The product crystals have a slope of lower value, and typically there should be little or no material present smaller than L_f, the size which the baffle is designed to separate. The effective nucleation rate for the product material is the intersection of the extension of line P to zero size.

As long as the largest particle separated by the fines-destruction baffle is small compared with the mean particle size of the product, the seed for the product may be thought of as the particle-size distribution corresponding to the fine material which ranges in length from zero to L_f, the largest size separated by the baffle.

The product discharged from the crystallizer is characterized by the integral of the distribution from size L_f to infinity:

$$M_T = k_v \rho \int_{L_f}^{\infty} n^0 \exp(-L_f/Gt_f) \exp(L/GT) L^3 \, dL \qquad (18\text{-}41)$$

The integrated form of this equation is shown in Table 18-5.

For a given set of assumptions it is possible to calculate the characteristic curves for the product from the crystallizer when it is operated at various levels of fines removal as characterized by L_f. This has been done for an ammonium sulfate crystallizer in Fig. 18-63. Also shown in that figure is the actual size distribution obtained. In calculating theoretical size distributions in accordance with the Eq. (18-41), it is

TABLE 18-6 Growth Rates and Kinetic Equations for Some Industrial Crystallized Products

Material crystallized	G, m/s $\times 10^8$	Range t, h	Range M_T, g/L	Temp., °C	Scale[*]	Kinetic equation for B_0 no./(L·s)	References[†]
$(NH_4)_2SO_4$	1.67	3.83	150	70	P	$B_0 = 6.62 \times 10^{-25}\, G^{0.82} p^{-0.92} m_2^{2.05}$	Bennett and Wolf, *AIChE*, SFC, 1979.
$(NH_4)_2SO_4$	0.20	0.25	38	18	B	$B_0 = 2.94(10^{10})G^{1.03}$	Larsen and Mullen, *J. Crystal Growth* **20**: 183 (1973).
$(NH_4)_2SO_4$	—	0.20	—	34	B	$B_0 = 6.14(10^{-11})S_R^{7.84}M_T^{0.98}G^{1.22}$	Youngquist and Randolph, *AIChE J.* **18**: 421 (1972).
$MgSO_4 \cdot 7H_2O$	3.0–7.0	—	—	25	B	$B_0 = 9.65(10^{12})M_T^{0.67}G^{1.24}$	Sikdar and Randolph, *AIChE J.* **22**: 110 (1976).
$MgSO_4 \cdot 7H_2O$	—	—	Low	29	B	$B_0 = f(N, L^4, N^{4.2}, S^{2.5})$	Ness and White, *AIChE Symposium Series 153*, vol. 72, p. 64.
KCl	2–12	—	200	32	P	$B_0 = 7.12(10^{39})M_T^{0.14}G^{4.99}$	Randolph et al., *AIChE J.* **23**: 500 (1977).
KCl	3.3	1–2	100	37	B	$B_0 = 5.16(10^{22})M_T^{0.91}G^{2.77}$	Randolph et al., *Ind. Eng. Chem. Proc. Design Dev.* **20**: 496 (1981).
KCl	0.3–0.45	—	50–147	25–68	B	$B_0 = 5 \times 10^{-3}\, G^{2.78}(M_T TIP^2)^{1.2}$	Qian et al., *AIChE J.* **33**(10): 1690 (1987).
KCr_2O_7	1.2–9.1	0.25–1	14–42	—	B	$B_0 = 7.33(10^4)M_T^{0.6}G^{0.5}$	Desari et al., *AIChE J.* **20**: 43 (1974).
KCr_2O_7	2.6–10	0.15–0.5	20–100	26–40	B	$B_0 = 1.59(10^{-3})S_R^3 M_T G^{0.48}$	Janse, Ph.D. thesis, Delft Technical University, 1977.
KNO_3	8.13	0.25–0.050	10–40	20	B	$B_0 = 3.85(10^{16})M_T^{0.5}G^{2.06}$	Juraszek and Larson, *AIChE J.* **23**: 460 (1977).
K_2SO_4	—	0.03–0.17	1–7	30	B	$B_0 = 2.62(10^3)S_R^{2.5}M_T^{0.5}G^{0.54}$	Randolph and Sikdar, *Ind. Eng. Chem. Fund.* **15**: 64 (1976).
K_2SO_4	2–6	0.25–1	2–20	10–50	B	$B_0 = 4.09(10^6) \exp\left(\dfrac{10900}{RT}\right)M_T G^{0.5}$	Jones, Budz, and Mullin, *AIChE J.* **33**: 12 (1986).
K_2SO_4	0.8–1.6	—	—	—	B	$\dfrac{G}{G_0} = 1 + 2L^{2/3}$ (L in μm)	White, Bendig, and Larson, *AIChE Mtg.*, Washington, D.C., Dec. 1974.
NaCl	4–13	0.2–1	25–200	50	B	$B_0 = 1.92(10^{10})S_R^2 M_T G^2$	Asselbergs, Ph.D. thesis, Delft Technical University, 1978.
NaCl	—	0.6	35–70	55	P	$B_0 = 8 \times 10^{10}N^2 G^2 M_T$	Grootscholten et al., *Chem. Eng. Design* **62**: 179 (1984).
NaCl	0.5	1–2.5	70–190	72	P	$B_0 = 1.47(10^2)\left(\dfrac{I^2}{P}\right)m_4^{0.84}G^{0.98}$	Bennett et al., *Chem. Eng. Prog.* **69**(7): 86 (1973).
Citric acid	1.1–3.7	—	—	16–24	B	$B_0 = 1.09(10^{10})m_4^{0.084}G^{0.84}$	Sikdar and Randolph, *AIChE J.* **22**: 110 (1976).
Fructose	0.1–0.25	—	—	50	B	—	Shiau and Berglund, *AIChE J.* **33**: 6 (1987).
Sucrose	—	—	—	80	B	$B_0 = 5 \times 10^6\, N^{0.7}M_T^{0.3}G^{0.4}$	Berglund and deJong, *Separations Technology* **1**: 38 (1990).
Sugar	2.5–5	0.375	50	45	B	$B_0 = 4.38(10^6)M_T^{1.01}(\Delta C - 0.5)^{1.42}$	Hart et al., *AIChE Symposium Series 193*, vol. 76, 1980.
Urea	0.4–4.2	2.5–6.8	350–510	55	P	$B_0 = 5.48(10^{-1})M_T^{-3.87}G^{1.66}$	Bennett and Van Buren, *Chem. Eng. Prog. Symposium Series* **95**(7): 65 (1973).
Urea	—	—	—	3–16	B	$B_0 = 1.49(10^{-31})S_R^{2.3}M_T^{1.07}G^{-3.54}$	Lodaya et al., *Ind. Eng. Chem. Proc. Design Dev.* **16**: 294 (1977).

[*]B = bench scale; P = pilot plant.
[†]Additional data on many components are in Garside and Shah, *Ind. Eng. Chem. Proc. Design Dev.*, **19**, 509 (1980).

assumed that the growth rate is a constant, whereas in fact larger values of L_f will interact with the system driving force to raise the growth rate and the nucleation rate. Nevertheless, Fig. 18-63 illustrates clearly the empirical result of the operation of such equipment, demonstrating that the most significant variable in changing the particle-size distribution of the product is the size removed by the baffle. Conversely, changes in retention time for a given particle-removal size L_f make a relatively small change in the product-size distribution.

It is implicit that increasing the value of L_f will raise the supersaturation and growth rate to levels at which mass homogeneous nucleation can occur, thereby leading to periodic upsets of the system or cycling [Randolph, Beer, and Keener, *Am. Inst. Chem. Eng. J.*, **19**, 1140 (1973)]. That this could actually happen was demonstrated experimentally by Randolph, Beckman, and Kraljevich [*Am. Inst. Chem. Eng. J.*, **23**, 500 (1977)], and that it could be controlled dynamically by regulating the fines-destruction system was shown by Beckman and Randolph [ibid., (1977)]. Dynamic control of a crystallizer with a fines-destruction baffle and fine-particle-detection equipment employing a light-scattering (laser) particle-size-measurement instrument is described in U.S. Patent, 4,263,010 and 5,124,265.

CRYSTALLIZATION EQUIPMENT

Whether a vessel is called an evaporator or a crystallizer depends primarily on the criteria used in arriving at its sizing. In an evaporator of the salting-out type, sizing is done on the basis of vapor release. In a crystallizer, sizing is normally done on the basis of the volume required for crystallization or for special features required to obtain the proper product size. In external appearance, the vessels could be identical. Evaporators are discussed in Sec. 11.

In the discussion which follows, crystallization equipment has been classified according to the means of suspending the growing product. This technique reduces the number of major classifications and segregates those to which Eq. (18-31) applies.

Mixed-Suspension, Mixed-Product-Removal Crystallizers This type of equipment, sometimes called the circulating-magma
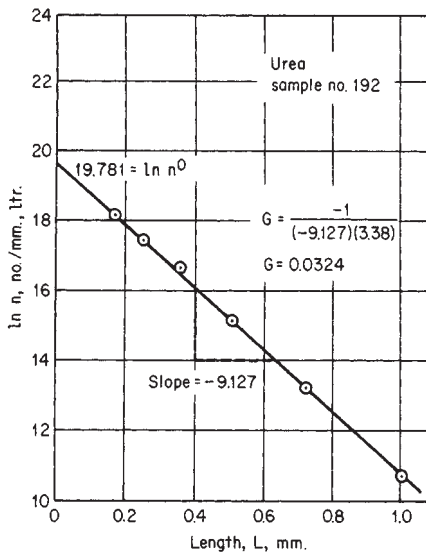
FIG. 18-61   Population density plot for Example 3.

FIG. 18-62   Plot of Log N against L for a crystallizer with fines removal.

crystallizer, is by far the most important in use today. In most commercial equipment of this type, the uniformity of suspension of product solids within the crystallizer body is sufficient for the theory [Eqs. (18-31) to (18-33b)] to apply. Although a number of different varieties and features are included within this classification, the equipment operating with the highest capacity is the kind in which the vaporization of a solvent, usually water, occurs.

Although surface-cooled types of MSMPR crystallizers are available, most users prefer crystallizers employing vaporization of solvents or of refrigerants. The primary reason for this preference is that heat transferred through the critical supersaturating step is through a boiling-liquid-gas surface, avoiding the troublesome solid deposits that can form on a metal heat-transfer surface.

Forced-Circulation Evaporator-Crystallizer   This crystallizer is shown in Fig. 18-64. Slurry leaving the body is pumped through a circulating pipe and through a tube-and-shell heat exchanger, where its temperature increases by about 2 to 6°C (3 to 10°F). Since this heating is done without vaporization, materials of normal solubility should produce no deposition on the tubes. The heated slurry, returned to the body by a recirculation line, mixes with the body slurry and raises its temperature locally near the point of entry, which causes boiling at the liquid surface. During the consequent cooling and

FIG. 18-63   Calculated product-size distribution for a crystallizer operation at different fine-crystal-separation sizes.

FIG. 18-64   Forced-circulation (evaporative) crystallizer. (*Swenson Process Equipment, Inc.*)

FIG. 18-65   Draft-tube-baffle (DTB) crystallizer. (*Swenson Process Equipment, Inc.*)

vaporization to achieve equilibrium between liquid and vapor, the supersaturation which is created causes deposits on the swirling body of suspended crystals until they again leave via the circulating pipe. The quantity and the velocity of the recirculation, the size of the body, and the type and speed of the circulating pump are critical design items if predictable results are to be achieved. A further discussion of the parameters affecting this type of equipment is given by Bennett, Newman, and Van Buren [*Chem. Eng. Prog.,* **55**(3), 65 (1959); *Chem. Eng. Prog. Symp. Ser.,* **65**(95), 34, 44 (1969)].

If the crystallizer is not of the evaporative type but relies only on *adiabatic evaporative cooling* to achieve the yield, the heating element is omitted. The feed is admitted into the circulating line after withdrawal of the slurry, at a point sufficiently below the free-liquid surface to prevent flashing during the mixing process.

Draft-Tube-Baffle (DTB) Evaporator-Crystallizer   Because mechanical circulation greatly influences the level of nucleation within the crystallizer, a number of designs have been developed that use circulators located within the body of the crystallizer, thereby reducing the head against which the circulator must pump. This technique reduces the power input and circulator tip speed and therefore the rate of nucleation. A typical example is the draft-tube-baffle (DTB) evaporator-crystalli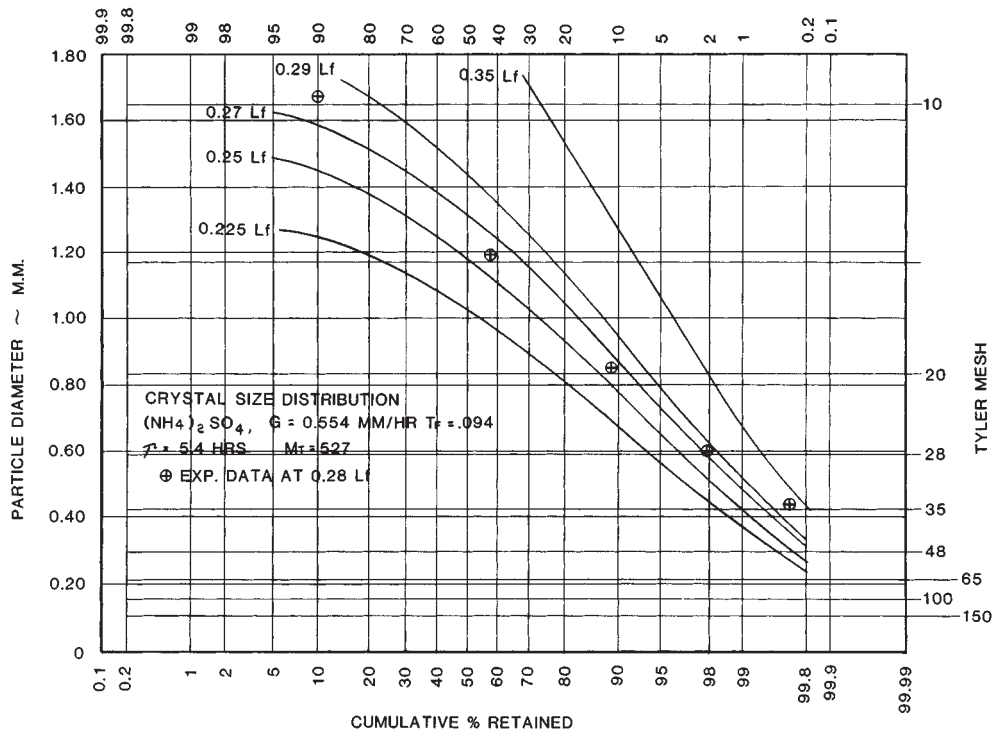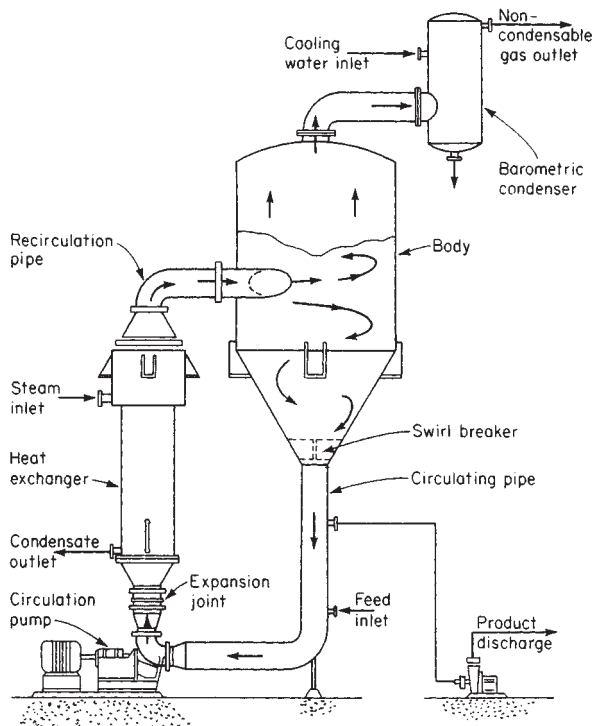zer (Swenson Process Equipment, Inc.) shown in Fig. 18-65. The suspension of product crystals is maintained by a large, slow-moving propeller surrounded by a draft tube within the body. The propeller directs the slurry to the liquid surface so as to prevent solids from short-circuiting the zone of the most intense supersaturation. Slurry which has been cooled is returned to the bottom of the vessel and recirculated through the propeller. At the propeller, heated solution is mixed with the recirculating slurry.

The design of Fig. 18-65 contains a fines-destruction feature comprising the settling zone surrounding the crystallizer body, the circulating pump, and the heating element. The heating element supplies sufficient heat to meet the evaporation requirements and to raise the temperature of the solution removed from the settler so as to destroy
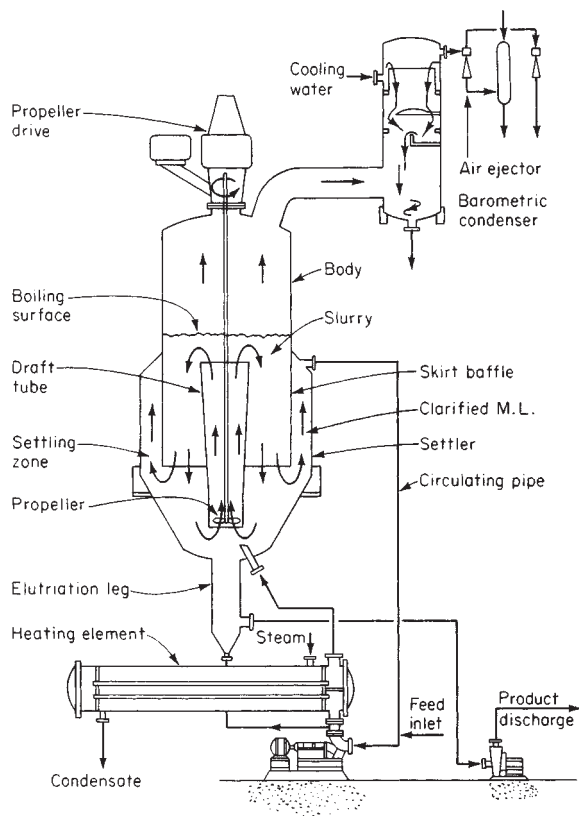
any small crystalline particles withdrawn. Coarse crystals are separated from the fines in the settling zone by gravitational sedimentation, and therefore this fines-destruction feature is applicable only to systems in which there is a substantial density difference between crystals and mother liquor.

This type of equipment can also be used for applications in which the only heat removed is that required for adiabatic cooling of the incoming feed solution. When this is done and the fines-destruction feature is to be employed, a stream of liquid must be withdrawn from the settling zone of the crystallizer and the fine crystals must be separated or destroyed by some means other than heat addition—for example, either dilution or thickening and physical separation.

In some crystallization applications it is desirable to increase the solids content of the slurry within the body above the natural consistency, which is that developed by equilibrium cooling of the incoming feed solution to the final temperature. This can be done by withdrawing a stream of mother liquor from the baffle zone, thereby thickening the slurry within the growing zone of the crystallizer. This mother liquor is also available for removal of fine crystals for size control of the product.

Draft-Tube (DT) Crystallizer   This crystallizer may be employed in systems in which fines destruction is not needed or wanted. In such cases the baffle is omitted, and the internal circulator is sized to have the minimum nucleating influence on the suspension.

In DTB and DT crystallizers the circulation rate achieved is generally much greater than that available in a similar forced-circulation crystallizer. The equipment therefore finds application when it is necessary to circulate large quantities of slurry to minimize supersaturation levels within the equipment. In general, this approach is required to obtain long operating cycles with material capable of growing on

the walls of the crystallizer. The draft-tube and draft-tube-baffle designs are commonly used in the production of granular materials such as ammonium sulfate, potassium chloride, photographic hypo, and other inorganic and organic crystals for which product in the range 8 to 30 mesh is required.

Surface-Cooled Crystallizer   For some materials, such as sodium chlorate, it is possible to use a forced-circulation tube-and-shell exchanger in direct combination with a draft-tube-crystallizer body, as shown in Fig. 18-66. Careful attention must be paid to the temperature difference between the cooling medium and the slurry circulated through the exchanger tubes. In addition, the path and rate of slurry flow within the crystallizer body must be such that the volume contained in the body is "active." That is to say, crystals must be so suspended within the body by the turbulence that they are effective in relieving supersaturation created by the reduction in temperature of the slurry as it passes through the exchanger. Obviously, the circulating pump is part of the crystallizing system, and careful attention must be paid to its type and its operating parameters to avoid undue nucleating influences.

The use of the internal baffle permits operation of the crystallizer at a slurry consistency other than that naturally obtained by the cooling of the feed from the initial temperature to the final mother-liquor temperature. The baffle also permits fines removal and destruction.

With most inorganic materials this type of equipment produces crystals in the range 30 to 100 mesh. The design is based on the allowable rates of heat exchange and the retention required to grow the product crystals.

Direct-Contact-Refrigeration Crystallizer   For some applications, such as the freezing of ice from seawater, it is necessary to go to such low temperatures that cooling by the use of refrigerants is the only economical solution. In such systems it is sometimes impractical to employ surface-cooled equipment because the allowable temperature difference is so small (under 3°C) that the heat-exchanger surface becomes excessive or because the viscosity is so high that the mechanical energy put in by the circulation system requires a heat-removal rate greater than can be obtained at reasonable temperature differences. In such systems, it is convenient to admix the refrigerant with the slurry being cooled in the crystallizer, as shown in Fig. 18-67, so that the heat of vaporization of the refrigerant cools the slurry by direct contact. The successful application of such systems requires that the refrigerant be relatively immiscible with the mother liquor and be capable of separation, compression, condensation, and subsequent recycle into the crystallizing system. The operating pressures and temperatures chosen have a large bearing on power consumption.

This technique has been very successful in reducing the problems associated with buildup of solids on a cooling surface. The use of direct-
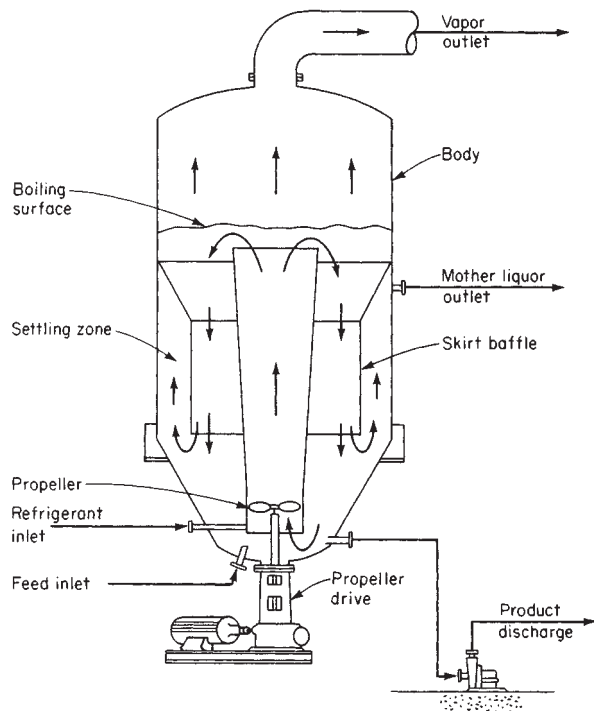
FIG. 18-67   Direct-contact-refrigeration crystallizer (DTB type). (*Swenson Process Equipment, Inc.*)

contact refrigeration also reduces overall process-energy requirements, since in a refrigeration process involving two fluids a greater temperature difference is required on an overall basis when the refrigerant must first cool some intermediate solution, such as calcium chloride brine, and that solution in turn cools the mother liquor in the crystallizer.

Equipment of this type has been successfully operated at temperatures as low as –59°C (–75°F).

Reaction-Type Crystallizers   In chemical reactions in which the end product is a solid-phase material such as a crystal or an amorphous solid the type of equipment described in the preceding subsections or shown in Fig. 18-68 may be used. By mixing the reactants in a large circulated stream of mother liquor containing suspended solids of the equilibrium phase, it is possible to minimize the driving force created during their reaction and remove the heat of reaction through the vaporization of a solvent, normally water. Depending on the final particle size required, it is possible to incorporate a fines-destruction baffle as shown in Fig. 18-68 and take advantage of the control over particle size afforded by this technique. In the case of ammonium sulfate crystallization from ammonia gas and concentrated sulfuric acid, it is necessary to vaporize water to remove the heat of reaction, and this water so removed can be reinjected after condensation into the fines-destruction stream to afford a very large amount of dissolving capability.

Other examples of this technique are where a solid material is to be decomposed by mixing it with a mother liquor of a different composition, as shown in Fig. 18-69. Carnallite ore ($KCl \cdot MgCl_2 \cdot 4H_2O$) can be added to a mother liquor into which water is also added so that decomposition of the ore into potassium chloride (KCl) crystals and magnesium chloride–rich mother liquor takes place. Circulated slurry in the draft tube suspends the product crystals as well as the incoming ore particles until the ore can decompose into potassium chloride crystals and mother liquor. By taking advantage of the fact that water must be added to the process, the fines-bearing mother liquor can be removed behind the baffle and then water added so that the finest particles are dissolved before being returned to the crystallizer body.
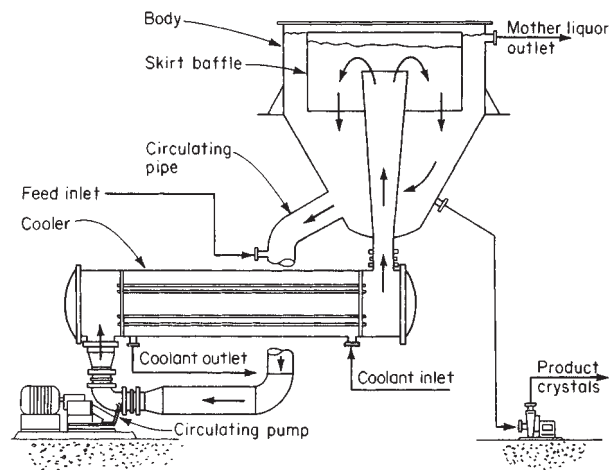
FIG. 18-66   Forced-circulation baffle surface-cooled crystallizer. (*Swenson Process Equipment, Inc.*)
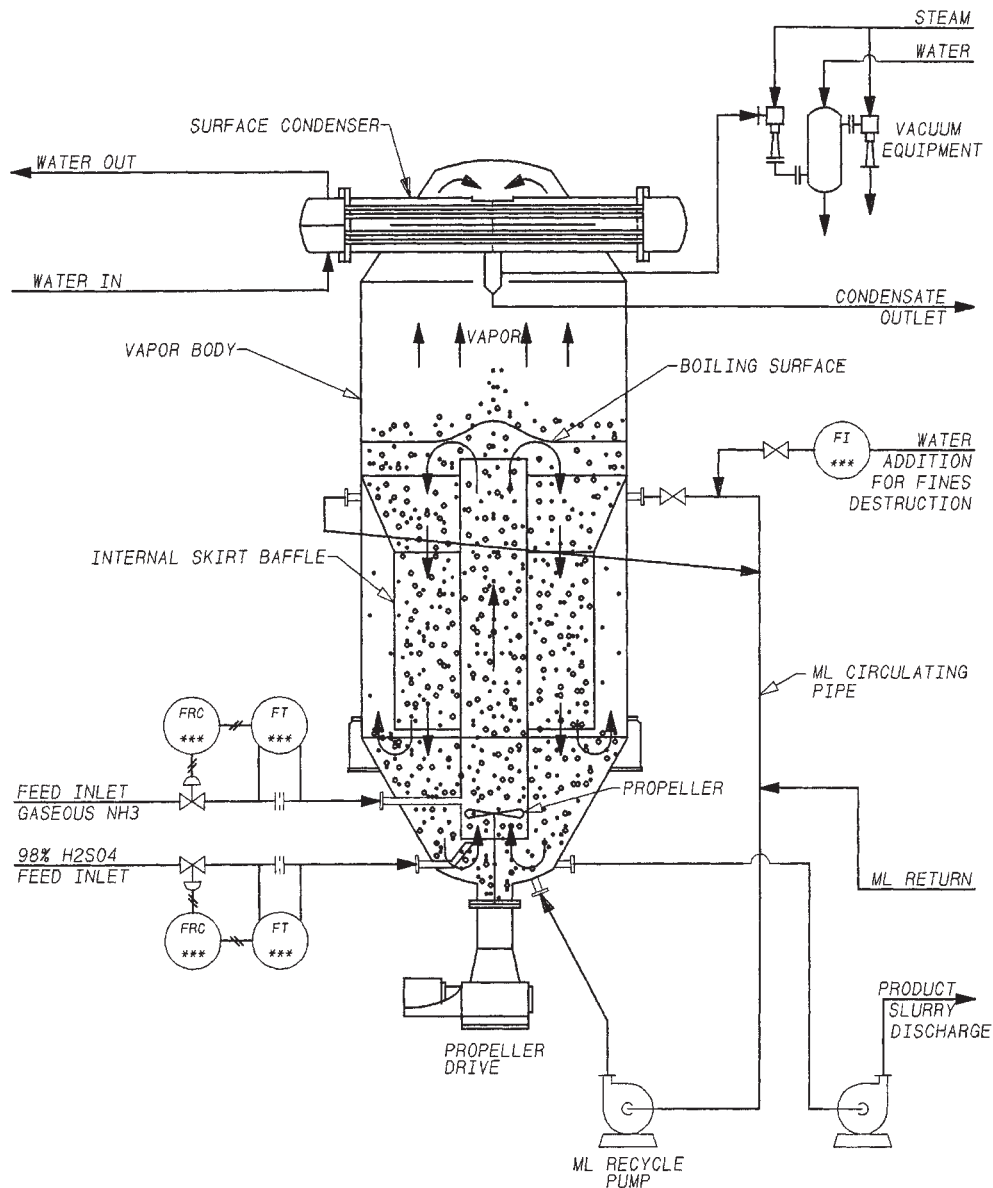
FIG. 18-68   Swenson reaction type DTB crystallizer. (*Swenson Process Equipment, Inc.*)

Other examples of this technique involve neutralization reactions such as the neutralization of sulfuric acid with calcium chloride to result in the precipitation of gypsum.

Mixed-Suspension, Classified-Product-Removal Crystallizers Many of the crystallizers just described can be designed for classified-product discharge. Classification of the product is normally done by means of an elutriation leg suspended beneath the crystallizing body as shown in Fig. 18-66. Introduction of clarified mother liquor to the lower portion of the leg fluidizes the particles prior to discharge and selectively returns the finest crystals to the body for further growth. A relatively wide distribution of material is usually produced unless the elutriation leg is extremely long. Inlet conditions at the leg are critical if good classifying action or washing action is to be achieved.

If an elutriation leg or other product-classifying device is added to a crystallizer of the MSMPR type, the plot of the population density versus L is distorted in the region of largest sizes. Also the incorporation of an elutriation leg destabilizes the crystal-size distribution and under some conditions can lead to cycling. The theoretical treatment of both the crystallizer model and the cycling relations is discussed by Randolph, Beer, and Keener (loc. cit.). Although such a feature can be included on many types of classified-suspension or mixed-suspension crystallizers, it is most common to use this feature with the forced-circulation evaporative-crystallizer and the DTB crystallizer.

Classified-Suspension Crystallizer This equipment is also known as the **growth** or **Oslo crystallizer** and is characterized by the production of supersaturation in a circulating stream of liquor. Supersaturation is developed in one part of the system by evaporative cooling or by cooling in a heat exchanger, and it is relieved by passing the liquor through a fluidized bed of crystals. The fluidized bed may be contained in a simple tank or in a more sophisticated vessel arranged
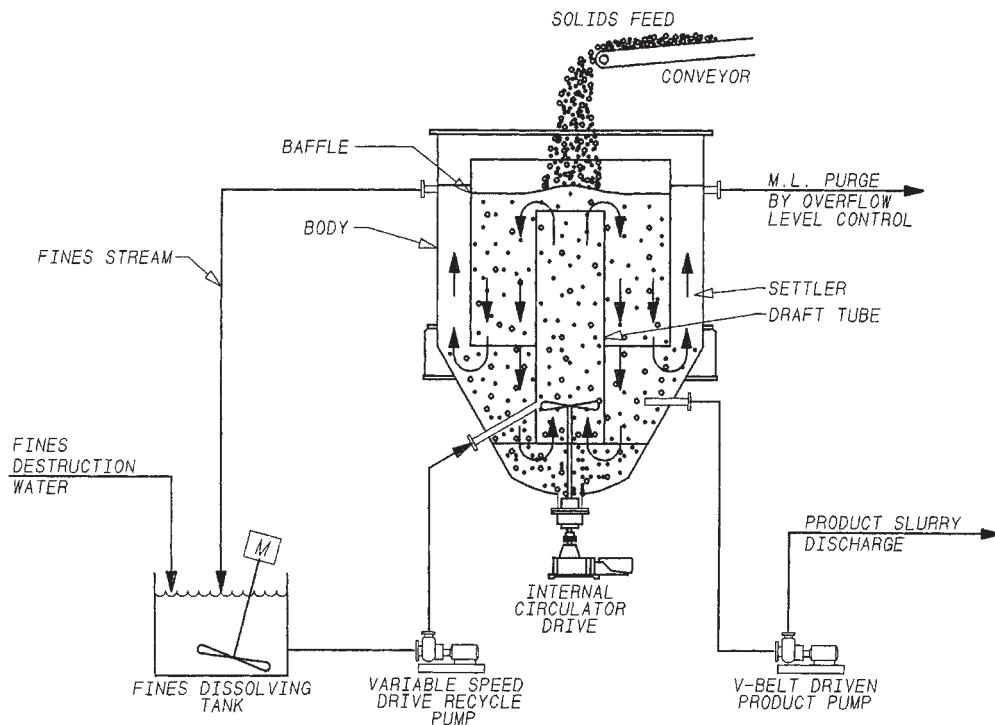
FIG. 18-69   Swenson atmospheric reaction–type DTB crystallizer. (*Swenson Process Equipment, Inc.*)

for a pronounced classification of the crystal sizes. Ideally this equipment operates within the metastable supersaturation field described by Miers and Isaac, *J. Chem. Soc.*, **1906,** 413.

In the **evaporative crystallizer** of Fig. 18-70, solution leaving the vaporization chamber at *B* is supersaturated slightly within the metastable zone so that new nuclei will not form. The liquor contacting the bed at *E* relieves its supersaturation on the growing crystals and leaves through the circulating pipe *F*. In a cooling-type crystallization hot feed is introduced at *G,* and the mixed liquor flashes when it reaches the vaporization chamber at *A*. If further evaporation is required to produce the driving force, a heat exchanger is installed between the circulating pump and the vaporization changer to supply the heat for the required rate of vaporization.

The transfer of supersaturated liquor from the vaporizer (point *B,* Fig. 18-69) often causes salt buildup in the piping and reduction of the operating cycle in equipment of this type. The rate of buildup can be reduced by circulating a thin suspension of solids through the vaporizing chamber; however, the presence of such small seed crystals tends to rob the supersaturation developed in the vaporizer, thereby lowering the efficiency of the recirculation system.

An **Oslo surface-cooled crystallizer** is illustrated in Fig. 18-71. Supersaturation is developed in the circulated liquor by chilling in the cooler *H*. This supersaturated liquor is contacted with the suspension of crystals in the suspension chamber at *E*. At the top of the suspension chamber a stream of mother liquor *D* can be removed to be used for fines removal and destruction. This feature can be added on either type of equipment. Fine crystals withdrawn from the top of the suspension are destroyed, thereby reducing the overall number of crystals in the system and increasing the particle size of the remaining product crystals.

Scraped-Surface Crystallizer   For relatively small-scale applications a number of crystallizer designs employing direct heat exchange between the slurry and a jacket or double wall containing a cooling medium have been developed. The heat-transfer surface is scraped or agitated in such a way that the deposits cannot build up.

The scraped-surface crystallizer provides an effective and inexpensive method of producing slurry in equipment which does not require expensive installation or supporting structures.

Double-Pipe Scraped-Surface Crystallizer   This type of equipment consists of a double-pipe heat exchanger with an internal agitator fitted with spring-loaded scrapers that wipe the wall of the inner pipe. The cooling liquid passes between the pipes, this annulus being dimensioned to permit reasonable shell-side velocities. The scrapers prevent the buildup of solids and maintain a good film coefficient of heat transfer. The equipment can be operated in a continuous or in a recirculating batch manner.

Such units are generally built in lengths to above 12 m (40 ft). They can be arranged in parallel or in series to give the necessary liquid velocities for various capacities. Heat-transfer coefficients have been reported in the range of 170 to 850 W/(m²·K) [30 to 150 Btu/(h·ft²·°F)] at temperature differentials of 17°C (30°F) and higher [Garrett and Rosenbaum, *Chem. Eng.,* **65**(16), 127 (1958)]. Equipment of this type is marketed as the **Votator** and the **Armstrong crystallizer.**

Batch Crystallization   Batch crystallization has been practiced longer than any other form of crystallization in both atmospheric tanks, which are either static or agitated, as well as in vacuum or pressure vessels. It is still widely practiced in the pharmaceutical and fine chemical industry or in those applications where the capacity is very small. The integrity of the batch with respect to composition and history can be maintained easily and the inventory management is more precise than with continuous processes. Batch crystallizers can be left unattended (overnight) if necessary and this is an important advantage for many small producers.

In any batch process the common mode of operation involves charging the crystallizer with concentrated or near-saturated solution, producing supersaturation by means of cooling the batch or evaporating solvent from the batch, seeding the batch by means of injecting seed crystals into the batch or by allowing homogeneous nucleation to occur, reaching the final mother-liquor temperature and concentration by some time-dependent means of control, and stopping the cycle
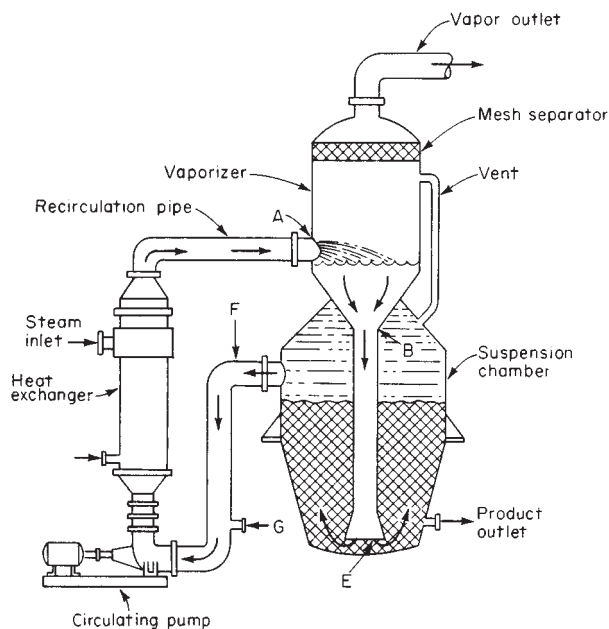
FIG. 18-70   OSLO evaporative crystallizer.

so that the batch may be dumped into a tank for processing by successive steps, which normally include centrifugation, filtration, and/or drying. In some cases, a small "heal" of slurry is left in the batch crystallizer to act as seed for the next batch.

Control of a batch crystallizer is almost always the most difficult part and very often is not practiced except to permit homogeneous nucleation to take place when the system becomes supersaturated. If control is practiced, it is necessary to have some means for determining when the initial solution is supersaturated so that seed of the appropriate size, quantity, and habit may be introduced into the batch. Following seeding, it is necessary to limit the cooling or evaporation in
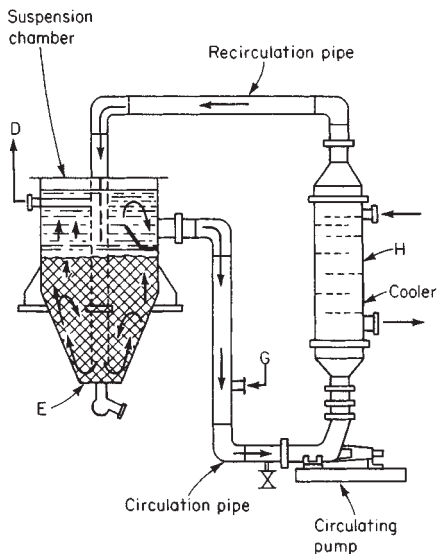

FIG. 18-71   OSLO surface-cooled crystallizer.

the batch to that which permits the generated supersaturation to be relieved on the seed crystals. This means that the first cooling or evaporation following seeding must be at a very slow rate, which is increased nonlinearly in order to achieve the optimum batch cycle. Frequently, such controls are operated by cycle timers or computers so as to achieve the required conditions. Sugar, many pharmaceutical products, and many fine chemicals are produced this way. Shown in Fig. 18-72 is a typical batch crystallizer comprising a jacketed closed tank with top-mounted agitator and feed connections. The tank is equipped with a short distillation column and surface condenser so that volatile materials may be retained in the tank and solvent recycled to maintain the batch integrity. Provisions are included so that the vessel may be heated with steam addition to the shell or cooling solution circulated through the jacket so as to control the temperature. Tanks of this type are intended to be operated with a wide variety of chemicals under both cooling and solvent evaporation conditions.

Recompression Evaporation-Crystallization   In all types of crystallization equipment wherein water or some other solvent is vaporized to produce supersaturation and/or cooling, attention should be given to the use of mechanical vapor recompression, which by its nature permits substitution of electrical energy for evaporation and solvent removal rather than requiring the direct utilization of heat energy in the form of steam or electricity. A typical recompression crystallizer flowsheet is shown in Fig. 18-73, which shows a single-stage evaporative crystallizer operating at approximately atmospheric pressure. The amount of heat energy necessary to remove 1 kg of water to produce the equivalent in crystal product is approximately 550 kilocalories. If the water evaporated is compressed by a mechanical compressor of high efficiency to a pressure where it can be condensed in the heat exchanger of the crystallizer, it can thereby supply the energy needed to sustain the process. Then the equivalent power for this compression is about 44 kilocalories (Bennett, *Chem. Eng. Progress,* 1978, pp. 67–70).

Although this technique is limited economically to those large-scale cases where the materials handled have a relatively low boiling point elevation and in those cases where a significant amount of heat is required to produce the evaporation for the crystallization step, it nevertheless offers an attractive technique for reducing the use of heat energy and substituting mechanical energy or electrical energy in those cases where there is a cost advantage for doing so. This technique finds many applications in the crystallization of sodium sulfate, sodium carbonate monohydrate, and sodium chloride. Shown in Fig. 18-74 is the amount of vapor compressed per kilowatt-hour for water vapor at 100°C and various ΔTs. The amount of water vapor compressed per horsepower decreases rapidly with increasing ΔT and, therefore, normal design considerations dictate that the recompression evaporators have a relatively large amount of heat-transfer surface so as to minimize the power cost. Often this technique is utilized only with the initial stages of evaporation where concentration of the solids is relatively low and, therefore, the boiling-point elevation is negligible. In order to maintain adequate tube velocity for heat transfer and suspension of crystals, the increased surface requires a large internal recirculation within the crystallizer body, which consequently lowers the supersaturation in the fluid pumped through the tubes. One benefit of this design is that with materials of flat or inverted solubility, the use of recompression complements the need to maintain low ΔTs to prevent fouling of the heat-transfer surface.

INFORMATION REQUIRED TO SPECIFY A CRYSTALLIZER

The following information regarding the product, properties of the feed solution, and required materials of construction must be available before a crystallizer application can be properly evaluated and the appropriate equipment options identified. Is the crystalline material being produced a hydrated or an anhydrous material? What is the solubility of the compound in water or in other solvents under consideration, and how does this change with temperature? Are other compounds in solution which coprecipitate with the product being crystallized, or do these remain in solution, increasing in concentration until some change in product phase occurs? What will be the influence of impurities in the solution on the crystal habit, growth, and
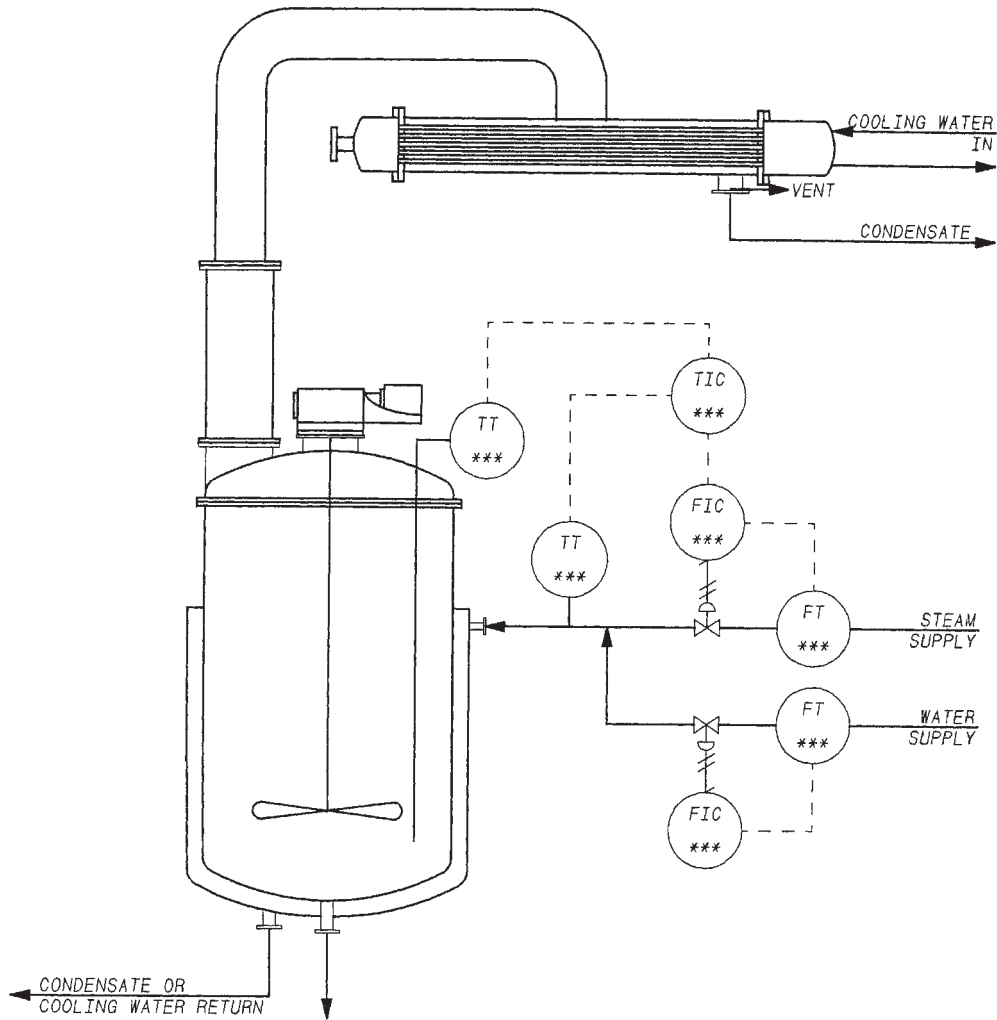
FIG. 18-72 Typical agitated batch crystallizer. (*Swenson Process Equipment, Inc.*)

nucleation rates? What are the physical properties of the solution and its tendency to foam? What is the heat of crystallization of the product crystal? What is the production rate, and what is the basis on which this production rate is computed? What is the tendency of the material to grow on the walls of the crystallizer? What materials of construction can be used in contact with the solution at various temperatures? What utilities will be available at the crystallizer location, and what are the costs associated with the use of these utilities? Is the final product to be blended or mixed with other crystalline materials or solids? What size of product and what shape of product are required to meet these requirements? How can the crystalline material be separated from the mother liquor and dried? Are there temperature requirements or wash requirements which must be met? How can these solids or mixtures of solids be handled and stored without undue breakage and caking?

Another basic consideration is whether crystallization is best carried out on a batch basis or on a continuous basis. The present tendency in most processing plants is to use continuous equipment whenever possible. Continuous equipment permits adjusting of the operating variables to a relatively fine degree in order to achieve the best results in terms of energy usage and product characteristics. It allows the use of a smaller labor force and results in a continuous util-

ity demand, which minimizes the size of boilers, cooling towers, and power-generation facilities. It also minimizes the capital investment required in the crystallizer and in the feed-storage and product-liquor-storage facilities.

Materials that have a tendency to grow readily on the walls of the crystallizer require periodic washout, and therefore an otherwise continuous operation would be interrupted once or even twice a week for the removal of these deposits. The impact that this contingency may have on the processing-equipment train ahead of the crystallizer must be considered.

The batch handling of wet or semidry crystalline materials is substantially more difficult than the storing and handling of dry crystalline materials. A batch operation has economic application only on a relatively small scale or when temperature or product characteristics require unusual precautions.

CRYSTALLIZER OPERATION

Crystal growth is a layer-by-layer process, and the retention time required in most commercial equipment to produce crystals of the size normally desired is on the order of 2 to 6 h. On the other hand, nucleation in a supersaturated solution can be generated in a fraction
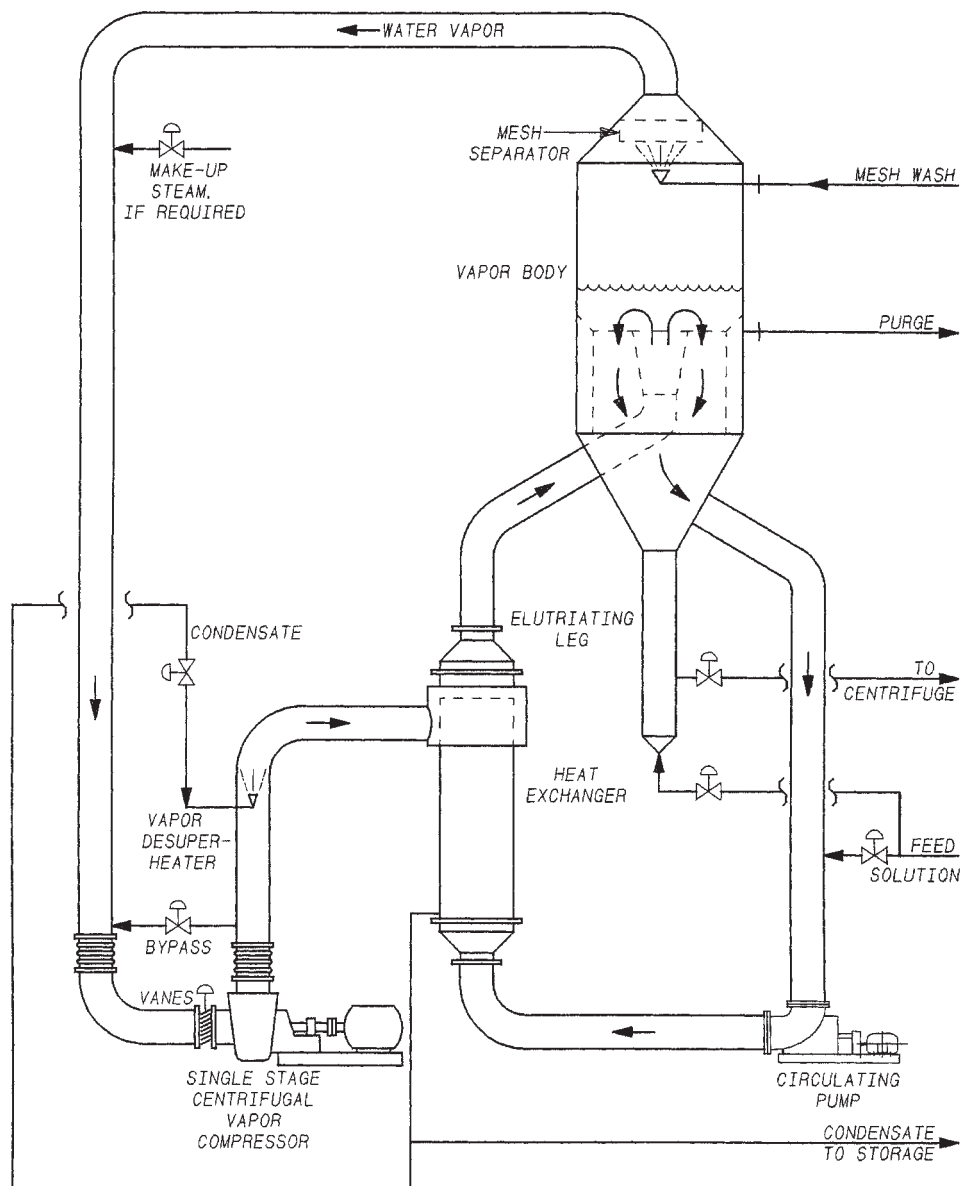
FIG. 18-73 Swenson single-stage recompression evaporator. (*Swenson Process Equipment, Inc.*)

of a second. The influence of any upsets in operating conditions, in terms of the excess nuclei produced, is very short-term in comparison with the total growth period of the product removed from the crystallizer. In a practical sense, this means that steadiness of operation is much more important in crystallization equipment than it is in many other types of process equipment.

It is to be expected that four to six retention periods will pass before the effects of an upset will be damped out. Thus, the recovery period may last from 8 to 36 h.

The **rate of nuclei formation** required to sustain a given product size decreases exponentially with increasing size of the product. Although when crystals in the range of 100 to 50 mesh are produced, the system may react quickly, the system response when generating large crystals in the 14-mesh size range is quite slow. This is because a single pound of 150-mesh seed crystals is sufficient to provide the total number of particles in a ton of 14-mesh product crystals. In any system producing relatively large crystals, nucleation must be carefully controlled with respect to all internal and external sources. Particular attention must be paid to preventing seed crystals from entering with the incoming feed stream or being returned to the crystallizer with recycle streams of mother liquor coming back from the filter or centrifuge.

Experience has shown that in any given body operating at a given production rate, control of the magma (slurry) density is important to the control of crystal size. Although in some systems a change in slurry density does not result in a change in the rate nucleation, the more general case is that an increase in the magma density increases the product size through reduction in nucleation and increased retention time of the crystals in the growing bed. The reduction in supersaturation at longer retention times together with the smaller distance

LB/HR OF VAPOR COMPRESSED PER BHP
VS TEMPERATURE DIFFERENCE
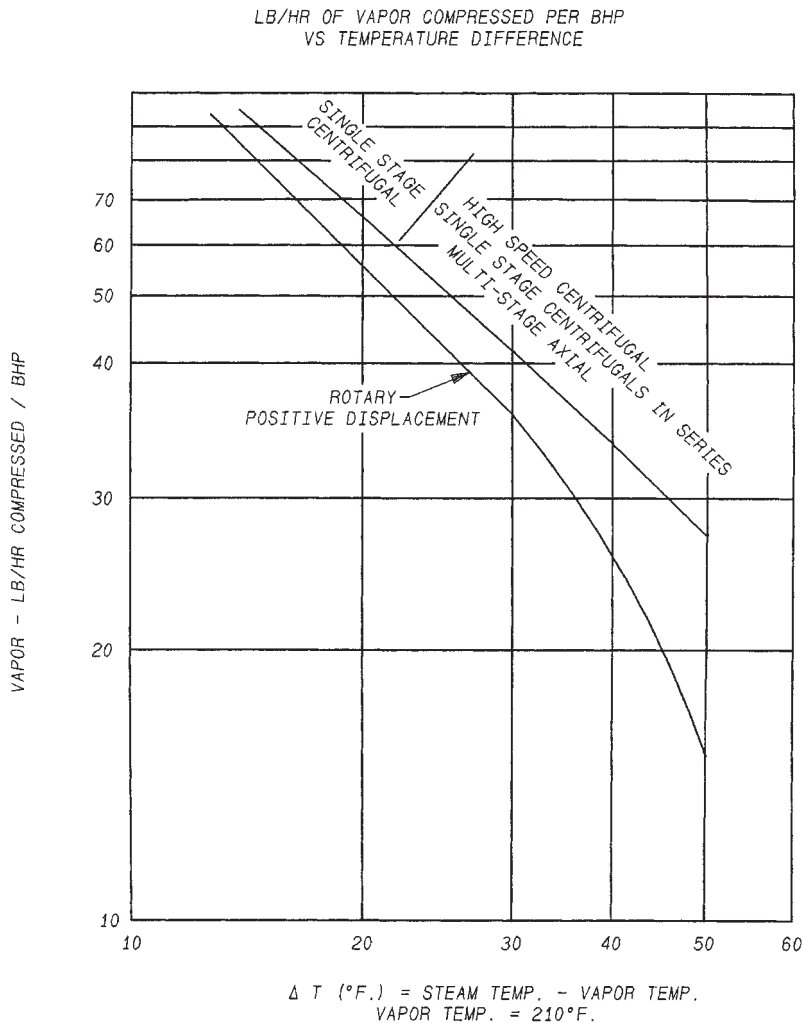
FIG. 18-74   Recompression evaporator horsepower as a function of overall ΔT.

between growing crystals, which lowers the driving force that is required to transport material from the liquid phase to the growing solids (**propinquity effect**), appears to be responsible for the larger product.

A reduction in the magma density will generally increase nucleation and decrease the particle size. This technique has the disadvantage that crystal formation on the equipment surfaces increases because lower slurry densities create higher levels of supersaturation within the equipment, particularly at the critical boiling surface in a vaporization-type crystallizer.

High levels of supersaturation at the liquid surface or at the tube walls in a surface-cooled crystallizer are the dominant cause of wall salting. Although some types of crystallizers can operate for several months continuously when crystallizing KCl or $(NH_4)_2SO_4$, most machines have much shorter operating cycles. Second only to control of particle size, the extension of operating cycles is the most difficult operating problem to be solved in most installations.

In the forced-circulation-type crystallizer (Fig. 19-43) primary control over particle size is exercised by the designer in selecting the circulating system and volume of the body. From the operating standpoint there is little that can be done to an existing unit other than supply external seed, classify the discharge crystals, or control the slurry density. Nevertheless, machines of this type are frequently carefully controlled by these techniques and produce a predictable and desirable product-size distribution.

When crystals cannot be grown sufficiently large in forced-circulation equipment to meet product-size requirements, it is common to employ one of the designs that allow some influence to be exercised over the population density of the finer crystals. In the DTB design (Fig. 18-69) this is done by regulating the flow in the circulating pipe so as to withdraw a portion of the fines in the body in the amount of about 0.05 to 0.5 percent by settled volume. The exact quantity of solids depends on the size of the product crystals and on the capacity of the fines-dissolving system. If the machine is not operating stably, this quantity of solids will appear and then disappear, indicating changes in the nucleation rate within the circuit. At steady-state operation, the quantity of solids overflowing will remain relatively constant, with some solids appearing at all times. Should the slurry density of product crystals circulated within the machine rise to a value higher than about 50 percent settled volume, large quantities of product crystals will appear in the overflow system, disabling the fines-destruction equipment. Too high a circulating rate through the fines trap will produce this same result. Too low a flow through the fines circuit will remove insufficient particles and result in a

smaller product-size crystal. To operate effectively, a crystallizer of the type employing fines-destruction techniques requires more sophisticated control than does operation of the simpler forced-circulation equipment.

The classifying crystallizer (Fig. 18-70) requires approximately the same control of the fines-removal stream and, in addition, requires control of the fluidizing flow circulated by the main pump. This flow must be adjusted to achieve the proper degree of fluidization in the suspension chamber, and this quantity of flow varies as the crystal size varies between start-up operation and normal operation. As with the draft-tube-baffle machine, a considerably higher degree of skill is required for operation of this equipment than of the forced-circulation type.

While most of the industrial designs in use today are built to reduce the problems due to excess nucleation, it is true that in some crystallizing systems a deficiency of seed crystals is produced and the prod-uct crystals are larger than are wanted or required. In such systems nucleation can be increased by increasing the mechanical stimulus created by the circulating devices or by seeding through the addition of fine crystals from some external source.

CRYSTALLIZER COSTS

Because crystallizers can come with such a wide variety of attachments, capacities, materials of construction, and designs, it is very difficult to present an accurate picture of the costs for any except certain specific types of equipment, crystallizing specific compounds. This is illustrated in Fig. 18-75, which shows the prices of equipment for crystallizing two different compounds at various production rates, one of the compounds being produced in two alternative crystallizer modes. Installed cost (including cost of equipment and accessories, foundations and supporting steel, utility piping,

(A), (B) Na2SO4 PRODUCTION FROM GLAUBERS
SALT. MELTING TANK INCLUDED

(C) REACTION OF NH3+H2SO4
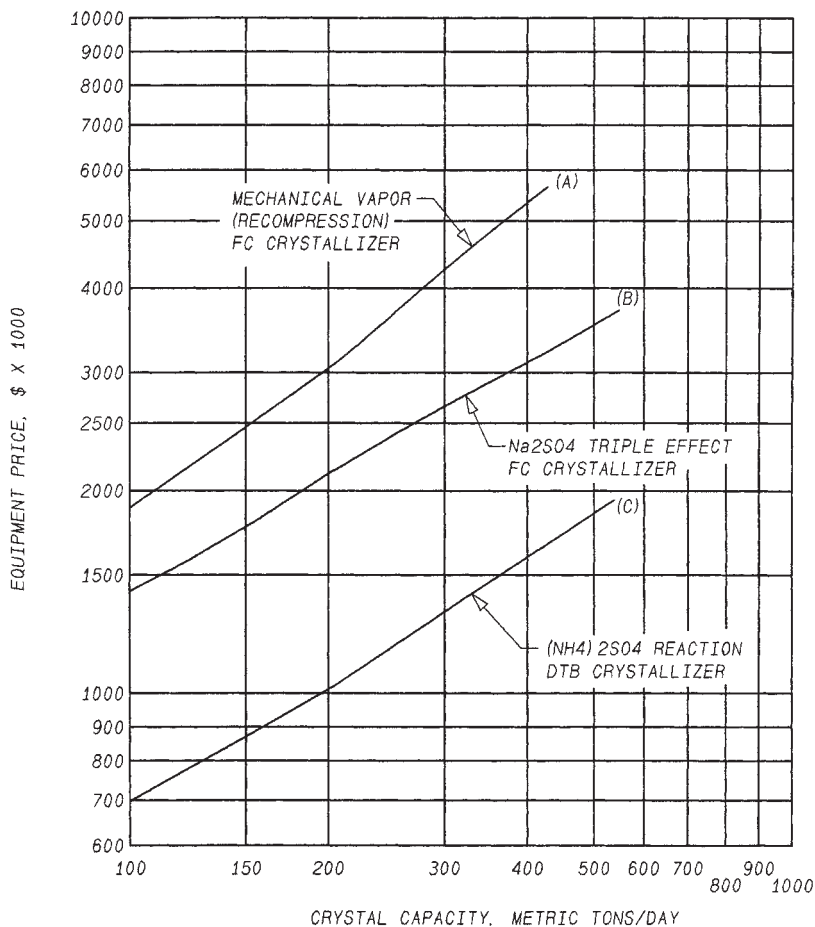TO MAKE (NH4)2SO4

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FIG. 18-75   Equipment prices, FOB point of fabrication, for typical crystallizer systems. Prices are for crystallizer plus accessories including vacuum equipment. (*Data supplied by Swenson Process Equipment, Inc., effective January, 1995.*)

process piping and pumps, electrical switchgear, instrumentation, and labor, but excluding cost of a building) will be approximately twice these price figures.

It should be ever present in the reader's mind that for every particular case the appropriate crystallizer manufacturers should be consulted for reliable price estimates. Most crystallization equipment is custom-designed, and costs for a particular application may vary greatly from those illustrated in Fig. 18-75. Realistic estimation of installation costs also requires reference to local labor rates, site-specific factors, and other case specifics.

LEACHING

GENERAL REFERENCES: Coulson and Richardson, *Chemical Engineering,* 4th ed., vol. 2, Pergamon Press, Oxford, 1991. Duby, "Hydrometallurgy," in *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed., vol. 16, Wiley, New York, 1995, p. 338. McCabe, Smith, and Harriott, *Unit Operations of Chemical Engineering,* 5th ed., McGraw-Hill, New York, 1993, chaps. 17 and 20. Prubhudesal, in Schweitzer, *Handbook of Separation Techniques for Chemical Engineers,* McGraw-Hill, New York, 1979, sec. 5.1. Rickles, *Chem. Eng.* **72**(6): 157 (1965). Schwartzberg (chap. 10, "Leaching—Organic Materials") and Wadsworth (chap. 9, "Leaching—Metals Applications") in Rousseau, *Handbook of Separation Process Technology,* Wiley, New York, 1987. Wakeman, "Extraction (Liquid-Solid)" in *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th ed., vol. 10, Wiley, New York, 1993, p. 186.

DEFINITION

Leaching is the removal of a soluble fraction, in the form of a solution, from an insoluble, permeable solid phase with which it is associated. The separation usually involves selective dissolution, with or without diffusion, but in the extreme case of simple washing it consists merely of the displacement (with some mixing) of one interstitial liquid by another with which it is miscible. The soluble constituent may be solid or liquid; and it may be incorporated within, chemically combined with, adsorbed upon, or held mechanically in the pore structure of the insoluble material. The insoluble solid may be massive and porous; more often it is particulate, and the particles may be openly porous, cellular with selectively permeable cell walls, or surface-activated.

It is common practice to exclude from consideration as leaching the elution of surface-adsorbed solute. This process is treated instead as a special case of the reverse operation, adsorption. Also usually excluded is the washing of filter cakes, whether in situ or by reslurrying and refiltration.

Because of its variety of applications and its importance to several ancient industries, leaching is known by a number of other names. Among those encountered in chemical engineering practice are extraction, solid-liquid extraction, lixiviation, percolation, infusion, washing, and decantation-settling. The stream of solids being leached and the accompanying liquid is known as the underflow; in hydrometallurgy practice it is called pulp. The solid content of the stream is sometimes called marc (particularly by oil seed processors). The stream of liquid containing the leached solute is the overflow. As it leaves the leaching process it has several optional names: extract, solution, lixiviate, leachate, or miscella.

Mechanism   The mechanism of leaching may involve simple physical solution or dissolution made possible by chemical reaction. The rate of transport of solvent into the mass to be leached, or of soluble fraction into the solvent, or of extract solution out of the insoluble material, or some combination of these rates may be significant. A membranous resistance may be involved. A chemical-reaction rate may also affect the rate of leaching.

Inasmuch as the overflow and underflow streams are not immiscible phases but streams based on the same solvent, the concept of equilibrium for leaching is not the one applied in other mass-transfer separations. If the solute is not adsorbed on the inert solid, true equilibrium is reached only when all the solute is dissolved and distributed uniformly throughout the solvent in both underflow and overflow (or when the solvent is uniformly saturated with the solute, a condition never encountered in a properly designed extractor). The practical interpretation of leaching equilibrium is the state in which the overflow and underflow liquids are of the same composition; on a *y-x* diagram, the equilibrium line will be a straight line through the origin with a slope of unity. It is customary to calculate the number of ideal (equilibrium) stages required for a given leaching task and to adjust the number by applying a stage efficiency factor, although local efficiencies, if known, can be applied stage by stage.

Usually, however, it is not feasible to establish a stage or overall efficiency or a leaching rate index (e.g., overall coefficient) without testing small-scale models of likely apparatus. In fact, the results of such tests may have to be scaled up empirically, without explicit evaluation of rate or quasi-equilibrium indices.

Methods of Operation   Leaching systems are distinguished by operating cycle (batch, continuous, or multibatch intermittent); by direction of streams (cocurrent, countercurrent, or hybrid flow); by staging (single-stage, multistage, or differential-stage); and by method of contacting (sprayed percolation, immersed percolation, or solids dispersion). In general, descriptors from all four categories must be assigned to stipulate a leaching system completely (e.g., the Bollman-type extractor is a continuous hybrid-flow multistage sprayed percolator).

Whatever the mechanism and the method of operation, it is clear that the leaching process will be favored by increased surface per unit volume of solids to be leached and by decreased radial distances that must be traversed within the solids, both of which are favored by decreased particle size. Fine solids, on the other hand, cause slow percolation rate, difficult solids separation, and possible poor quality of solid product. The basis for an optimum particle size is established by these characteristics.

LEACHING EQUIPMENT

It is classification by contacting method that provides the two principal categories into which leaching equipment is divided: (1) that in which the leaching is accomplished by percolation and (2) that in which particulate solids are dispersed into a liquid and subsequently separated from it. Each includes batch and continuous units. Materials which disintegrate during leaching are treated in equipment of the second class.

A few designs of continuous machines fall in neither of these major classes.

Percolation   In addition to being applied to ores and rock in place and by the simple technique of heap leaching (usually on very large scale; see Wadsworth, loc. cit.); percolation is carried out in batch tanks and in continuous or dump extractors (usually on smaller scale).

Batch Percolators   The **batch tank** is not unlike a big nutsche filter; it is a large circular or rectangular tank with a false bottom. The solids to be leached are dumped into the tank to a uniform depth. They are sprayed with solvent until their solute content is reduced to an economic minimum and are then excavated. Countercurrent flow of the solvent through a series of tanks is common, with fresh solvent entering the tank containing most nearly exhausted material. In a typical ore-dressing operation the tanks are 53 by 20 by 5.5 m (175 by 67 by 18 ft) and extract about 8200 Mg (9000 U.S. tons) of ore on a 13-day cycle. Some tanks operate under pressure, to contain volatile solvents or increase the percolation rate. A series of pressure tanks operating with countercurrent solvent flow is called a **diffusion battery.**

Continuous Percolators   Coarse solids are also leached by percolation in moving-bed equipment, including single-deck and multideck rake classifiers, bucket-elevator contactors, and horizontal-belt conveyors.

The Bollman-type extractor shown in Fig. 18-76 is a bucket-elevator unit designed to handle about 2000 to 20,000 kg/h (50 to 500 U.S. tons/day) of flaky solids (e.g., soybeans). Buckets with perforated
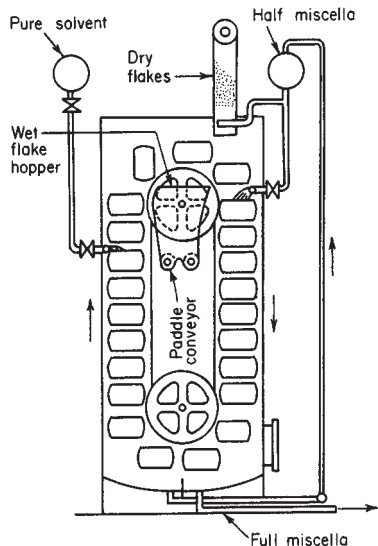
FIG. 18-76 Bollman-type extractor. (*McCabe, Smith, and Harriott,* Unit Operations of Chemical Engineering, *5th ed., p. 616. Copyright 1993 by McGraw-Hill, Inc., New York. Used with permission of McGraw-Hill Book Company.*)

bottoms are held on an endless moving belt. Dry flakes, fed into the descending buckets, are sprayed with partially enriched solvent ("half miscella") pumped from the bottom of the column of ascending buckets. As the buckets rise on the other side of the unit, the solids are sprayed with a countercurrent stream of pure solvent. Exhausted flakes are dumped from the buckets at the top of the unit into a paddle conveyor; enriched solvent, the "full miscella," is pumped from the bottom of the casing. Because the solids are unagitated and because the final miscella moves cocurrently, the Bollman extractor permits the use of thin flakes while producing extract of good clarity. It is only partially a countercurrent device, however, and it sometimes permits channeling and consequent low stage efficiency. Perhaps for

this reason, it is being displaced in the oil extraction industry by horizontal-basket, pan, or belt percolators (Schwartzberg, loc. cit.).

In the **horizontal-basket design,** illustrated by the **Rotocel extractor** (Fig. 18-77), walled compartments in the form of annular sectors with liquid-permeable floors revolve about a central axis. The compartments successively pass a feed point, a number of solvent sprays, a drainage section, and a discharge station (where the floor opens to discharge the extracted solids). The discharge station is circumferentially contiguous to the feed point. Countercurrent extraction is achieved by feeding fresh solvent only to the last compartment before dumping occurs and by washing the solids in each preceding compartment with the effluent from the succeeding one. The Rotocel is simple and inexpensive, and it requires little headroom. This type of equipment is made by a number of manufacturers. Horizontal table and tilting-pan vacuum filters, of which it is the gravity counterpart, are used as extractors for leaching processes involving difficult solution-residue separation.

The **endless-belt percolator** (Wakeman, loc. cit.) is similar in principle, but the successive feed, solvent spray, drainage, and dumping stations are linearly rather than circularly disposed. Examples are the **de Smet belt extractor** (uncompartmented) and the **Lurgi frame belt** (compartmented), the latter being a kind of linear equivalent of the Rotocel. Horizontal-belt vacuum filters, which resemble endless-belt extractors, are sometimes used for leaching.

The **Kennedy extractor** (Fig. 18-78), also requiring little headroom, operates substantially as a percolator that moves the bed of solids through the solvent rather than the conventional opposite. It comprises a nearly horizontal line of chambers through each of which in succession the solids being leached are moved by a slow impeller enclosed in that section. There is an opportunity for drainage between stages when the impeller lifts solids above the liquid level before dumping them into the next chamber. Solvent flows countercurrently from chamber to chamber. Because the solids are subjected to mechanical action somewhat more intense than in other types of continuous percolator, the Kennedy extractor is now little used for fragile materials such as flaked oil seeds.

Dispersed-Solids Leaching   Equipment for leaching fine solids by dispersion and separation includes batch tanks agitated by rotating impellers or by air and a variety of continuous devices.

Batch Stirred Tanks   Tanks agitated by coaxial impellers (turbines, paddles, or propellers) are commonly used for batch dissolution of solids in liquids and may be used for leaching fine solids. Insofar as the controlling rate in the mass transfer is the rate of transfer of mate-
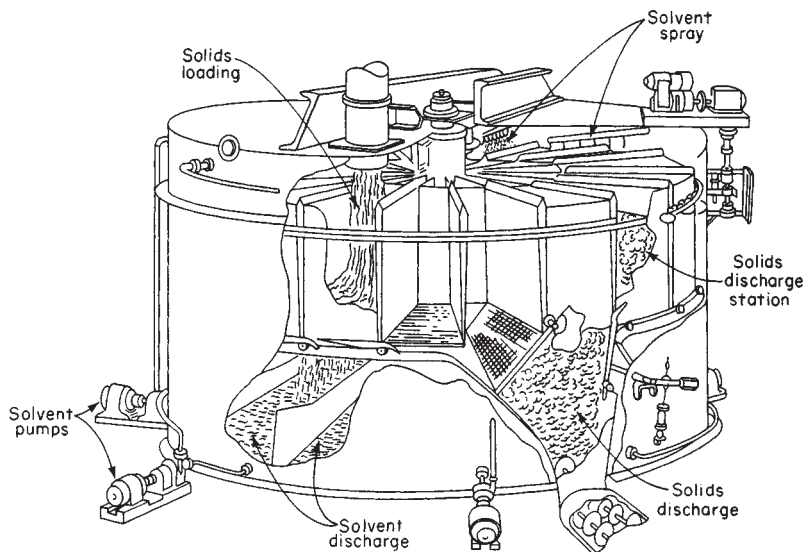

FIG. 18-77   Rotocel extractor. [*Rickles,* Chem. Eng. **72**(6): 164 (1965). Used with permission of McGraw-Hill, Inc.]
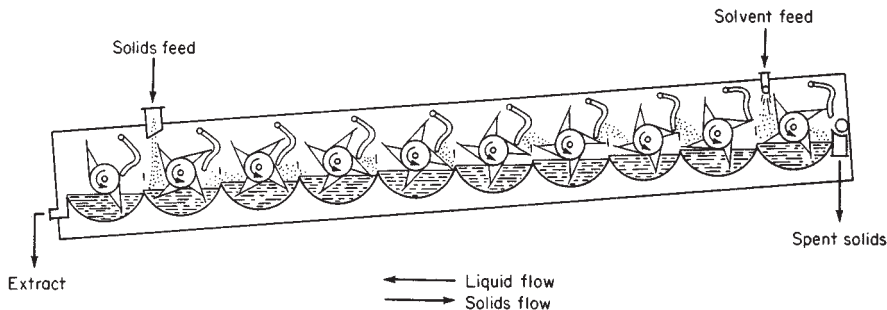
FIG. 18-78   Kennedy extractor. (*Vulcan Cincinnati, Inc.*)

rial into or from the interior of the solid particles rather than the rate of transfer to or from the surface of particles, the main function of the agitator is to supply unexhausted solvent to the particles while they reside in the tank long enough for the diffusive process to be completed. The agitator does this most efficiently if it just gently circulates the solids across the tank bottom or barely suspends them above the bottom.

The leached solids must be separated from the extract by settling and decantation or by external filters, centrifuges, or thickeners, all of which are treated elsewhere in Sec. 18. The difficulty of solids-extract separation and the fact that a batch stirred tank provides only a single equilibrium stage are its major disadvantages.

Pachuca Tanks   Ores of gold, uranium, and other metals are commonly batch-leached in large air-agitated vessels known as Pachuca tanks. A typical tank is a vertical cylinder with a conical bottom section usually with a 60° included angle, 7 m (23 ft) in diameter and 14 m (46 ft) in overall height. In some designs air is admitted from an open pipe in the bottom of the cone and rises freely through the tank; more commonly, however, it enters through a central vertical tube, characteristically about 46 cm (18 in) in diameter, that extends from the bottom of the tank to a level above the conical section—in some cases, almost to the liquid surface. Before it disengages at the liquid surface, the air induces in and above the axial tube substantial flow of pulp, which then finds its way down the outer part of the tank, eventually reentering the riser. The circulation rate in Pachuca tanks is discussed by Lamont [*Can. J. Chem. Eng.*, **36,** 153 (1958)].

Continuous Dispersed-Solids Leaching
Vertical-plate extractor.   Exemplified by the **Bonotto extractor** (Fig. 18-79), this consists of a column divided into cylindrical compartments by equispaced horizontal plates. Each plate has a radial opening staggered 180° from the openings of the plates immediately above and below it, and each is wiped by a rotating radial blade. Alternatively, the plates may be mounted on a coaxial shaft and rotated past stationary blades. The solids, fed to the top plate, thus are caused to fall to each lower plate in succession. The solids fall as a curtain into solvent which flows upward through the tower. They are discharged by a screw conveyor and compactor. Like the Bollman extractor, the Bonotto has been virtually displaced by horizontal belt or tray percolators for the extraction of oil seeds.

Gravity sedimentation tanks.   Operated as thickeners, these tanks can serve as continuous contacting and separating devices in which fine solids may be leached continuously. A series of such units properly connected permit true continuous countercurrent washing of fine solids. If appropriate, a mixing tank may be associated with each thickener to improve the contact between the solids and liquid being fed to that stage. Gravity sedimentation thickeners are described under "Gravity Sedimentation Operations." Of all continuous leaching equipment, gravity thickeners require the most area, and they are limited to relatively fine solids.

The Dorr agitator (Coulson and Richardson, loc. cit.) consolidates in one unit the principles of the thickener and the Pachuca tank. Resembling a rake-equipped thickener, it differs in that the rake is driven by a hollow shaft through which the solids-liquid suspension is lifted and circulated by an air stream. The rake moves the pulp to the center, where it can be entrained by the air stream. The unit may be operated batchwise or continuously.

Impeller-agitated tanks.   These can be operated as continuous leaching tanks, singly or in a series. If the solids feed is a mixture of particles of different settling velocities and if it is desirable that all particles reside in the leaching tank the same lengths of time, design of a continuous stirred leach tank is difficult and uncertain.

Screw-Conveyor Extractors   One type of continuous leaching equipment, employing the screw-conveyor principle, is strictly speaking neither a percolator nor a dispersed-solids extractor. Although it is often classed with percolators, there can be sufficient agitation of the solids during their conveyance by the screw that the action differs from an orthodox percolation.

The **Hildebrandt total-immersion extractor** is shown schematically in Fig. 18-80. The helix surface is perforated so that solvent can pass through countercurrently. The screws are so designed to compact
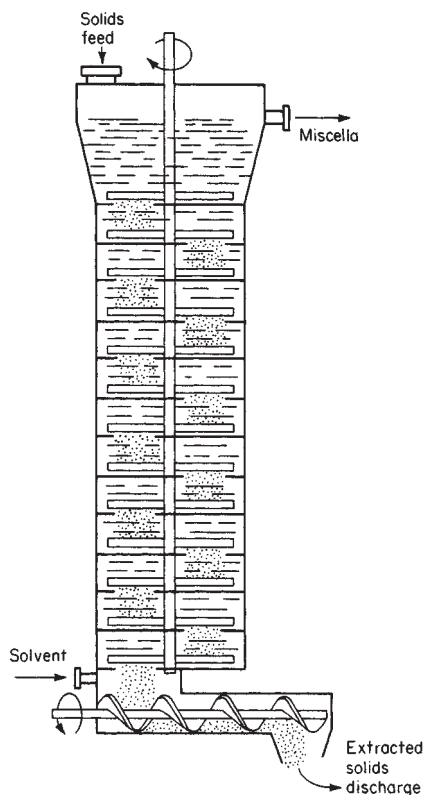

FIG. 18-79   Bonotto extractor. [*Rickles,* Chem. Eng. **72**(6): 163 (1965); copyright 1965 by McGraw-Hill, Inc., New York. Excerpted with special permission of McGraw-Hill.]

the solids during their passage through the unit. The design offers the obvious advantages of countercurrent action and continuous solids compaction, but there are possibilities of some solvent loss and feed overflow, and successful operation is limited to light, permeable solids.

A somewhat similar but simpler design uses a horizontal screw section for leaching and a second screw in an inclined section for washing, draining, and discharging the extracted solids.

In the **De Danske Sukkerfabriker,** the axis of the extractor is tilted to about 10° from the horizontal, eliminating the necessity of two screws at different angles of inclination.

Sugar-beet cossettes are successfully extracted while being transported upward in a vertical tower by an arrangement of inclined plates or wings attached to an axial shaft. The action is assisted by staggered guide plates on the tower wall. The shell is filled with water that passes downward as the beets travel upward. This configuration is employed in the **BMA diffusion tower** (Wakeman, loc. cit.).

Schwartzberg (loc. cit.) reports that screw-conveyor extractors, once widely employed to extract flaked oil seeds, have fallen into disuse for this application because of their destructive action on the fragile seed flakes.

Tray Classifier A hybrid like the screw-conveyor classifier, the tray classifier rakes pulp up the sloping bottom of a tank while solvent flows in the opposite direction. The solvent is forced by a baffle to the bottom of the tank at the lower end before it overflows. The solids must be rugged enough to stand the stress of raking.

SELECTION OR DESIGN OF A LEACHING PROCESS*

At the heart of a leaching plant design at any level—conceptual, preliminary, firm engineering, or whatever—is unit-operations and process design of the extraction unit or line. The major aspects that are particular for the leaching operation are the selection of process and operating conditions and the sizing of the extraction equipment.

Process and Operating Conditions The major parameters that must be fixed or identified are the solvent to be used, the temperature, the terminal stream compositions and quantities, leaching cycle (batch or continuous), contact method, and specific extractor choice.

Choice of Solvent The solvent selected will offer the best balance of a number of desirable characteristics: high saturation limit and selectivity for the solute to be extracted, capability to produce

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* Portions of this subsection are adaptations from the still-pertinent article by Rickles (loc. cit.).

FIG. 18-80 Hildebrandt extractor. (*McCabe, Smith, and Harriott,* Unit Operations of Chemical Engineering, *5th ed., p. 616. Copyright 1993 by McGraw-Hill, Inc., New York. Used with permission by McGraw-Hill Book Company.*)

extracted material of quality unimpaired by the solvent, chemical stability under process conditions, low viscosity, low vapor pressure, low toxicity and flammability, low density, low surface tension, ease and economy of recovery from the extract stream, and price. These factors are listed in an approximate order of decreasing importance, but the specifics of each application determine their interaction and relative significance, and any one can control the decision under the right combination of process conditions.

Temperature The temperature of the extraction should be chosen for the best balance of solubility, solvent-vapor pressure, solute diffusivity, solvent selectivity, and sensitivity of product. In some cases, temperature sensitivity of materials of construction to corrosion or erosion attack may be significant.

Terminal Stream Compositions and Quantities These are basically linked to an arbitrary given: the production capacity of the leaching plant (rate of extract production or rate of raw-material purification by extraction). When options are permitted, the degree of solute removal and the concentration of the extract stream chosen are those that maximize process economy while sustaining conformance to regulatory standards.

Leaching Cycle and Contact Method As is true generally, the choice between continuous and intermittent operation is largely a matter of the size and nature of the process of which the extraction is a part. The choice of a percolation or solids-dispersion technique depends principally on the amenability of the extraction to effective, sufficiently rapid percolation.

Type of Reactor The specific type of reactor that is most compatible (or least incompatible) with the chosen combination of the preceding parameters seldom is clearly and unequivocally perceived without difficulty, if at all. In the end, however, that remains the objective. As is always true, the ultimate criteria are reliability and profitability.

Extractor-Sizing Calculations For any given throughput rate (which fixes the cross-sectional area and/or the number of extractors), the size of the units boils down to the number of stages required, actual or equivalent. In calculation, this resolves into determination of the number of ideal stages required and application of appropriate stage efficiencies. The methods of calculation resemble those for other mass-transfer operations (see Secs. 13, 14, and 15), involving equilibrium data and contact conditions, and based on material balances. They are discussed briefly here with reference to countercurrent contacting.

Composition Diagrams In its elemental form, a leaching system consists of three components: inert, insoluble solids; a single nonadsorbed solute, which may be liquid or solid; and a single solvent.* Thus, it is a ternary system, albeit an unusual one, as already mentioned, by virtue of the total mutual "insolubility" of two of the phases and the simple nature of equilibrium.

The composition of a typical system is satisfactorily presented in the form of a diagram. Those diagrams most frequently employed are a right-triangular plot of mass fraction of solvent against mass fraction of solute (Fig. 18-81a) and a plot suggestive of a Ponchon-Savarit diagram, with inerts taking the place of enthalpy (Fig. 18-81b). A third diagram, less frequently used, is a modified McCabe-Thiele plot in which the overflow solution (inerts-free) and the underflow solution (traveling out of a stage with the inerts) are treated as pseudo phases, the mass fraction of solute in overflow, y, being plotted against the mass fraction of solute in underflow, x. (An additional representation, the equilateral-triangular diagram frequently employed for liquid-liquid ternary systems, is seldom used because the field of leaching data is confined to a small portion of the triangle.)

With reference to Fig. 18-81 (both graphs), EF represents the locus of overflow compositions for the case in which the overflow stream contains no inert solids. $E'F'$ represents the overflow streams containing some inert solids, either by entrainment or by partial solubility in the overflow solution. Lines GF, GL, and GM represent the loci of underflow compositions for the three different conditions indicated on the diagram. In Fig. 18-81a, the constant underflow line GM is parallel to EF, the hypotenuse of the triangle, whereas GF passes through
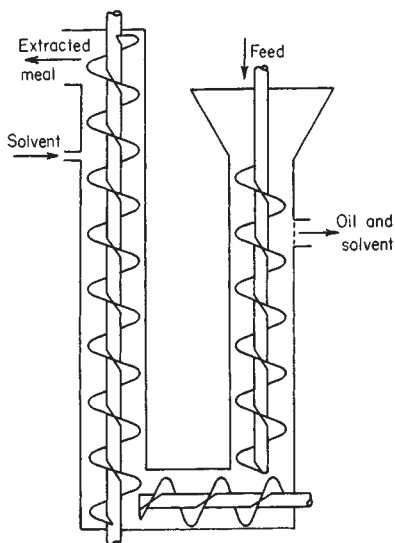
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* The solubility of the inert, adsorption of solute on the inert, and complexity of solvent and extracted material can be taken into account if necessary. Their consideration is beyond the scope of this treatment.
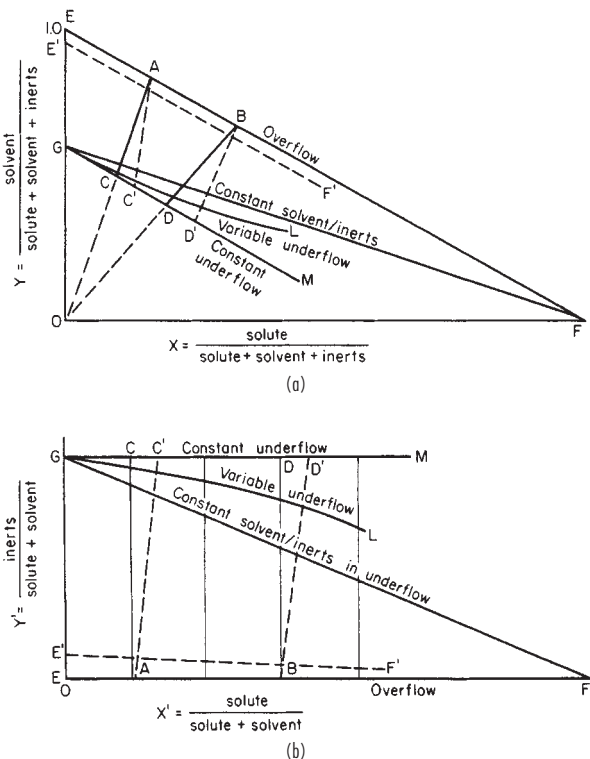
FIG. 18-81 Composition diagrams for leaching calculations: (a) right-triangular diagram; (b) modified Ponchon-Savarit diagram.

the right-hand vertex representing 100 percent solute. In Fig. 18-81b, underflow line GM is parallel to the abscissa, and GF passes through the point on the abscissa representing the composition of the clear solution adhering to the inert solids.

Compositions of overflow and underflow streams leaving the same stage are represented by the intersection of the composition lines for those streams with a tie line (AC, AC′, BD, BD′). Equilibrium tie lines (AC, BD) pass through the origin (representing 100 percent inerts) in Fig. 18-81a, and are vertical (representing the same inert-free solution composition in both streams) in Fig. 18-81b. For nonequilibrium conditions with or without adsorption or for equilibrium conditions with selective adsorption, the tie lines are displaced, such as AC′ and BD′. Point C′ is to the right of C if the solute concentration in the overflow solution is less than that in the underflow solution adhering to the solids. Unequal concentrations in the two solutions indicate insufficient contact time and/or preferential adsorption of one of the components on the inert solids. Tie lines such as AC′ may be considered as "practical tie lines" (i.e., they represent actual rather than ideal stages) if data on underflow and overflow composition have been

obtained experimentally under conditions simulating actual operation, particularly with respect to contact time, agitation, and particle size of solids.

The illustrative construction lines of Fig. 18-81 have been made with the assumption of constant underflow. In the more realistic case of variable underflow, the points C, C′, D, D′ would lie along line GL. Like the practical tie lines, GL is a representation of experimental data.

Algebraic Computation   This method starts with calculation of the quantities and compositions of all the terminal streams, using a convenient quantity of one of the streams as the basis of calculation. Material balance and stream compositions are then computed for a terminal ideal stage at either end of an extraction battery (i.e., at Point A or Point B in Fig. 18-81), using equilibrium and solution-retention data. Calculations are repeated for each successive ideal stage from one end of the system to the other until an ideal stage which corresponds to the desired conditions is obtained. Any solid-liquid extraction problem can be solved by this method.

For certain simplified cases it is possible to calculate directly the number of stages required to attain a desired product composition for a given set of feed conditions. For example, if equilibrium is attained in all stages and if the underflow mass rate is constant, both the equilibrium and operating lines on a modified McCabe-Thiele diagram are straight, and it is possible to calculate directly the number of ideal stages required to accommodate any rational set of terminal flows and compositions (McCabe, Smith, and Harriott, op. cit.):

$$N = \frac{\log\left[(y_b - x_b)/(y_a - x_a)\right]}{\log\left[(y_b - y_a)/(x_b - x_a)\right]} \tag{18-42}$$

Even when the conditions of equilibrium in each stage and constant underflow obtain, Eq. (18-42) normally is not valid for the first stage because the unextracted solids entering that stage usually are not premixed with solution to produce the underflow mass that will leave. This is easily rectified by calculating the exit streams for the first stage and using those values in Eq. (18-42) to calculate the number of stages required after stage 1.

Graphical Method   This method of calculation is simply a diagrammatic representation of all the possible compositions in a leaching system, including equilibrium values, on which material balances across ideal (or, in some cases, nonideal) stages can be evaluated in the graphical equivalent of the stage-by-stage algebraic computation. It normally is simpler than the hand calculation of the algebraic solution, and it is viewed by many as helpful because it permits visualization of the process variables and their effect on the operation. Any of the four types of composition diagrams described above can be used, but modified Ponchon-Savarit or right-triangular plots (Fig. 18-81) are most convenient for leaching calculations.

The techniques of graphical solution, in fact, are not unlike those for distillation and absorption (binary) problems using McCabe-Thiele, Ponchon-Savarit, and right-triangular diagrams and are similar to those described in Sec. 15 for solvent-extraction (ternary) systems. More detailed explanations of the application of the several graphical conventions to leaching are presented by: Coulson and Richardson, right triangle; Rickles, modified Ponchon-Savarit; McCabe, Smith, and Harriott, modified McCabe-Thiele; and Schwartzberg, equilateral ternary diagram; all in the publications cited as general references. (See also Treybal, *Mass Transfer Operations*, 3d ed., McGraw-Hill, New York, 1980.)

GRAVITY SEDIMENTATION OPERATIONS

GENERAL REFERENCES: Albertson, *Fluid/Particle Separation Journal*, **7**(1), 18 (1994). Coe and Clevenger, *Trans. Am. Inst. Min. Eng.*, **55**, 356 (1916). Comings, Pruiss, and DeBord, *Ind. Eng. Chem.*, **46**, 1164 (1954). Counselmann, *Trans. Am. Inst. Min. Eng.*, **187**, 223 (1950). Fitch, *Ind. Eng. Chem.*, **58**(10), 18 (1966). *Trans. Soc. Min. Eng. AIME*, **223**, 129 (1962). Kynch, *Trans. Faraday Soc.*, **48**, 166 (1952). Pearse, *Gravity Thickening Theories: A Review*, Warren Spring Laboratory, Hertfordshire, 1977. Purchas, *Solid/Liquid Separation Equipment Scale-Up*, Uplands Press, Croydon, England, 1977. Sankey and Payne, *Chemical Reagents in the Mineral Processing Industry*, **245**, SME (1985). Talmage and Fitch, *Ind. Eng. Chem.*, **47**, 38 (1955). Wilhelm and Naide, *Min. Eng. (Littleton, Colo.)*, **33**, 1710 (1981).

Sedimentation is the partial separation or concentration of suspended solid particles from a liquid by gravity settling. This field may be divided into the functional operations of thickening and clarification. The primary purpose of thickening is to increase the concentration of suspended solids in a feed stream, while that of clarification is to

remove a relatively small quantity of suspended particles and produce a clear effluent. These two functions are similar and occur simultaneously, and the terminology merely makes a distinction between the primary process results desired. Generally, thickener mechanisms are designed for the heavier-duty requirements imposed by a large quantity of relatively concentrated pulp, while clarifiers usually will include features that ensure essentially complete suspended-solids removal, such as greater depth, special provision for coagulation or flocculation of the feed suspension, and greater overflow-weir length.

CLASSIFICATION OF SETTLEABLE SOLIDS; SEDIMENTATION TESTS

The types of sedimentation encountered in process technology will be greatly affected not only by the obvious factors—particle size, liquid viscosity, solid and solution densities—but also by the characteristics of the particles within the slurry. These properties, as well as the process requirements, will help determine both the type of equipment which will achieve the desired ends most effectively and the testing methods to be used to select the equipment.

Figure 18-82 illustrates the relationship between solids concentration, interparticle cohesiveness, and the type of sedimentation that may exist. "Totally discrete" particles include many mineral particles (usually greater in diameter than 20 μm), salt crystals, and similar substances that have little tendency to cohere. "Flocculent" particles generally will include those smaller than 20 μm (unless present in a dispersed state owing to surface charges), metal hydroxides, many chemical precipitates, and most organic substances other than true colloids.

At low concentrations, the type of sedimentation encountered is called particulate settling. Regardless of their nature, particles are sufficiently far apart to settle freely. Faster-settling particles may collide with slower-settling ones and, if they do not cohere, continue downward at their own specific rate. Those that do cohere will form floccules of a larger diameter that will settle at a rate greater than that of the individual particles.

There is a gradual transition from particulate settling into the zone-settling regime, where the particles are constrained to settle as a mass. The principal characteristic of this zone is that the settling rate of the mass, as observed in batch tests, will be a function of its solids concentration (for any particular condition of flocculation, particle density, etc.).

The solids concentration ultimately will reach a level at which particle descent is restrained not only by hydrodynamic forces but also partially by mechanical support from the particles below; therefore,
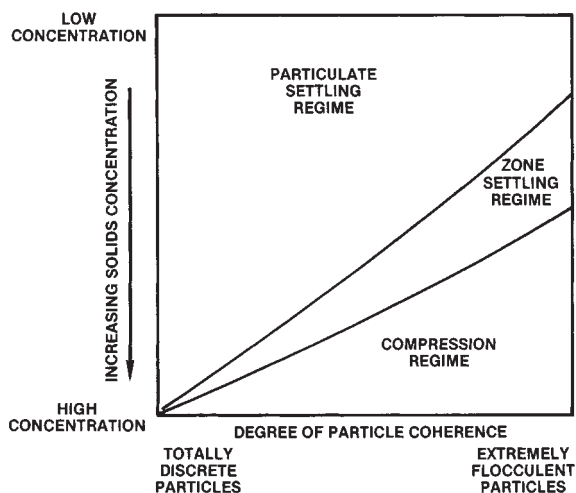
the weight of particles in mutual contact can influence the rate of sedimentation of those at lower levels. This compression, as it is termed, will result in further solids concentration because of compaction of the individual floccules and partial filling of the interfloc voids by the deformed floccules. Accordingly, the rate of sedimentation in the compression regime is a function of both the solids concentration and the depth of pulp in this particular zone. As indicated in Fig. 18-82, granular, nonflocculent particles may reach their ultimate solids concentration without passing through this regime.

As an illustration, coarse-size (45 μm) the aluminum oxide trihydrate particles produced in the Bayer process would be located near the extreme left of Fig. 18-82. These solids settle in a particulate manner, passing through a zone-settling regime only briefly, and reach a terminal density or ultimate solids concentration without any significant compressive effects. At this point, the solids concentration may be as much as 80 percent by weight. The same compound, but of the gelatinous nature it has when precipitated in water treatment as aluminum hydroxide, would be on the extreme right-hand side of the figure. This flocculent material enters into a zone-settling regime at a low concentration (relative to the ultimate concentration it can reach) and gradually thickens. With sufficient pulp depth present, preferably aided by gentle stirring or vibration, the compression-zone effect will occur; this is essential for the sludge to attain its maximum solids concentration, around 10 percent. Certain fine-size (1- to 2-μm) precipitates of this compound will possess characteristics intermediate between the two extremes.

A feed stream to be clarified or thickened can exist at any state represented within this diagram. As it becomes concentrated owing to sedimentation, it may pass through all the regimes, and the settling rate in any one may be the size-determining factor for the required equipment.

Sedimentation-Test Procedures

Determination of Clarification-Zone Requirements   In the treatment of solids suspensions which are in the particulate-settling regime, the usual objective will be the production of a clear effluent and test methods limited to this type of settling will be the normal sizing procedure, although the area demand for thickening should be verified. With particulate or slightly flocculent matter, any method that measures the rate of particle subsidence will be suitable, and either long-tube or short-tube procedures (described later) may be used. If the solids are strongly flocculent and particles cohere easily during sedimentation, the long tube test will yield erratic data, with better clarities being observed in samples taken from the lower taps (i.e., clarity appears to improve at higher settling rates). In these instances, time alone usually is the principal variable in clarification, and a simple detention test is recommended.

Long-Tube Method   A transparent tube 2 to 4 m long and at least 100 mm in diameter (preferably larger), fitted with sampling taps every 200 to 300 mm, is used in this test. The tube is mounted vertically and filled with a representative sample of feed suspension. At timed intervals approximately 100-mL samples are withdrawn from successive taps, beginning with the uppermost one. The time intervals will be determined largely by the settling rate of the particles and should be chosen so that a series of at least four time intervals will produce samples that bracket the desired solids-removal target. Also, this procedure will indicate whether or not detention time is a factor in the rate of clarification. Typically, intervals may be 30 min long, the last series of samples representing the results obtainable with 2-h detention. The samples are analyzed for suspended-solids concentration by any suitable means, such as filtration through membranes or centrifugation with calibrated tubes.

A plot is made of the suspended-solids concentration in each of the samples as a function of the nominal settling velocity of the sample, which is determined from the corresponding sample-tap depth divided by the elapsed time between the start of the test and the time of sampling. For each sampling series after the first, the depth will have changed because of the removal of the preceding samples, and this must be taken into account. With particulate solids having little or no tendency to cohere, the data points generally will fall on one line irrespective of the detention time. This indicates that the settling area

FIG. 18-82   Combined effect of particle coherence and solids concentration on the settling characteristics of a suspension.

available in the basin will determine the degree of solids removal, and the depth will have little bearing on the results, except as it may affect clarification efficiency.

Since the solids concentration in the 100-mL samples withdrawn at different depths does not correspond to the average concentration in the fluid above the sample point (which would be equivalent to the overflow from the clarifier at that particular design rate), an adjustment must be made in calculating the required area. Accordingly, an approximate average of the solids concentration throughout the column of liquid above a given tap can be obtained by summing the values obtained from all the higher taps and the one which is being sampled and dividing by the total number of taps sampled. This value is then used in a plot of overflow suspended-solids concentration versus nominal settling velocity.

Areal efficiencies for properly designed clarifiers in which detention time is not a significant factor range from 65 to 80 percent, and the surface area should be increased accordingly to reduce the overflow rate for scale-up.

Should the particles have a tendency to cohere slightly during sedimentation, each sampling time, representing a different nominal detention time in the clarifier, will produce different suspended-solids concentrations at similar rates. These data can be plotted as sets of curves of concentration versus settling rate for each detention time by the means just described. Scale-up will be similar, except that detention time will be a factor, and both depth and area of the clarifier will influence the results. In most cases, more than one combination of diameter and depth will be capable of producing the same clarification result.

These data may be evaluated by selecting different nominal overflow rates (equivalent to settling rates) for each of the detention-time values, and then plotting the suspended-solids concentrations for each nominal overflow rate (as a parameter) against the detention time. For a specified suspended-solids concentration in the effluent, a curve of overflow rate versus detention time can be prepared from this plot and used for optimizing the design of the equipment.

Short-Tube Method   This test is suitable in cases in which detention time does not change the degree of particle flocculation and hence has no significant influence on particle-settling rates. It is also useful for hydroseparator tests where the sedimentation device is to be used for classification (see Sec. 19). A tube 50 to 75 mm in diameter and 300 to 500 mm long is employed. A sample placed in the tube is mixed to ensure uniformity, and settling is allowed to occur for a measured interval. At the end of this time, the supernatant liquid is siphoned off quickly down to a chosen level, and the collected sample is analyzed for suspended-solids concentration. The level selected usually is based on the relative expected volumes of overflow and underflow. The suspended-solids concentration measured in the siphoned sample will be equivalent to the "averaged" values obtained in the long-tube test, at a corresponding settling rate.

In hydroseparator tests, it is necessary to measure solids concentrations and size distributions of both the supernatant sample withdrawn and the fraction remaining in the cylinder. The volume of the latter sample should be such as to produce a solids concentration that would be typical of a readily pumped underflow slurry.

Detention Test   This test utilizes a 1- to 4-L beaker or similar vessel. The sample is placed in the container, flocculated by suitable means if required, and allowed to settle. Small samples for suspended-solids analysis are withdrawn from a point approximately midway between liquid surface and settled solids interface, taken with sufficient care that settled solids are not resuspended. Sampling times may be at consecutively longer intervals, such as 5, 10, 20, 40, and 80 min.

The suspended-solids concentration can be plotted on log-log paper as a function of the sampling (detention) time. A straight line usually will result, and the required static detention time t to achieve a certain suspended-solids concentration C in the overflow of an ideal basin can be taken directly from the graph. If the plot is a straight line, the data are described by the equation

$$C = Kt^m \qquad (18-43)$$

where the coefficient K and exponent m are characteristic of the particular suspension.

Should the suspension contain a fraction of solids which can be considered "unsettleable," the data are more easily represented by using the so-called second-order procedure. This depends on the data being reasonably represented by the equation

$$Kt = \frac{1}{C - C_\infty} - \frac{1}{C_0 - C_\infty} \qquad (18-44)$$

where C_∞ is the unsettleable-solids concentration and C_0 is the concentration of suspended solids in the unsettled (feed) sample. The residual-solids concentration remaining in suspension after a sufficiently long detention time (C_∞) must be determined first, and the data then plotted on linear paper as the reciprocal concentration function $1/(C - C_\infty)$ versus time.

Bulk-settling test.   In cases involving detention time only, the overflow rate must be considered by other means. This is done by carrying out a settling test in which the solids are first concentrated to a level at which zone settling just begins. This is usually marked by a very diffuse interface during initial settling. Its rate of descent is measured with a graduated cylinder of suitable size, preferably at least 1 L, and the initial straight-line portion of the settling curve is used for specifying a bulk-settling rate. The design overflow rate generally should not exceed half of the bulk-settling rate.

Detention efficiency.   Conversion from the ideal basin sized by detention-time procedures to an actual clarifier requires the inclusion of an efficiency factor to account for the effects of turbulence and nonuniform flow. Efficiencies vary greatly, being dependent not only on the relative dimensions of the clarifier and the means of feeding but also on the characteristics of the particles. The curve shown in Fig. 18-83 can be used to scale up laboratory data in sizing circular clarifiers. The static detention time determined from a test to produce a specific effluent solids concentration is divided by the efficiency (expressed as a fraction) to determine the nominal detention time, which represents the volume of the clarifier above the settled pulp interface divided by the overflow rate. Different diameter-depth combinations are considered by using the corresponding efficiency factor. In most cases, area may be determined by factors other than the bulk-settling rate, such as practical tank-depth limitations.

Thickener-Basin Area   The area requirements for thickeners frequently are based on the solids flux rates measured in the zone-settling regime. Theory holds that, for any specific sedimentation condition, a critical concentration which will limit the solids throughput rate will exist in the thickener. This critical concentration will be evidenced as a pulp bed of variable depth in which the solids concentration is fairly uniform from top to bottom. Since the underflow concentration usually will be higher than this, gradually increasing concentrations will be found with progressing depth in the region beneath this constant-concentration zone. As the concentration within this critical zone represents a steady-state condition, its vertical extent may vary continually, responding to minor changes in the feed rate, underflow withdrawal rate, or flocculant dosage. In thickeners operating at relatively high underflow concentrations, with long
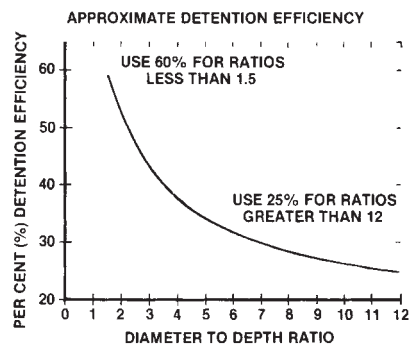

FIG. 18-83   Efficiency curve for scale-up of batch clarification data to determine nominal detention time in a continuous clarifier.

solids-detention times and lower throughput, this zone generally will not be present.

Many batch-test methods which are based on determining the solids flux rate at this critical concentration have been developed. Most methods recognize that as the solids enter compression, thickening behavior is no longer a function only of solids concentration. Hence, these methods attempt to utilize the "critical" point dividing these two zones and size the area on the basis of the settling rate of a layer of pulp at this concentration. The difficulty lies in discerning where this point is located on the settling curve.

Many procedures have been developed, but two in particular have been more widely used: the Coe and Clevenger approach and the Kynch method as defined by Talmage and Fitch (op. cit.).

The former requires measurement of the initial settling rate of a pulp at different solids concentrations varying from feed to final underflow value. The area requirement for each solids concentration tested is calculated by equating the net overflow rate to the corresponding interfacial settling rate, as represented by the following equation for the unit area:

$$\text{Unit area} = \frac{1/C_i - 1/C_u}{v_i} \qquad (18\text{-}45)$$

where C_i is the solids concentration at the interfacial settling velocity v_i and C_u is the underflow concentration, both concentrations being expressed in terms of mass of solids per unit volume of slurry. Using kg/L for the concentrations and m/day for the settling velocity yields a unit area value in $m^2/(ton/day)$.

These unit area values, plotted as a function of the feed concentration, will describe a maximum value that can be used to specify the thickener design unit area for the particular underflow concentration C_u employed in Eq. (18-45).

The method is applicable for *unflocculated* pulps or those in which the ionic characteristics of the solution produce a flocculent structure. If polymeric flocculants are used, the floccule size will be highly dependent on the feed concentration, and an approach based on the Kynch theory is preferred. In this method, the test is carried out at the expected feed solids concentration and is continued until underflow concentration is achieved in the cylinder. To determine the unit area, Talmage and Fitch (op. cit.) proposed an equation derived from a relationship equivalent to that shown in Eq. (18-45):

$$\text{Unit area} = \frac{t_u}{C_0 H_0} \qquad (18\text{-}46)$$

where t_u is the time, days; C_0 is the initial solids concentration in the feed, t/m^3; and H_0 is the initial height of the slurry in the test cylinder, m. The term t_u is taken from the intersection of a tangent to the curve at the critical point and a horizontal line representing the depth of pulp at underflow concentration. There are various means for selecting this critical point, all of them empirical, and the unit area value determined cannot be considered precise. The review by Pearse (op. cit.) presents many of the different procedures used in applying this approach to laboratory settling test data.

Because this method in itself does not adequately address the effect of different underflow concentrations on the unit area, a thickener sized using this approach could be too small in a case where a relatively concentrated underflow is desired.

Two other approaches avoid using the critical point by computing the area requirements from the settling conditions existing at the underflow concentration. The Wilhelm and Naide procedure (op. cit.) applies zone-settling theory (Kynch) to the entire thickening regime. Tangents drawn to the settling curve are used to calculate the settling velocity at all concentrations obtained in the test. This permits construction of a plot (Figure 18-84) showing unit area as a function of underflow concentration.

A second, "direct" approach which yields a similar result, since it also takes compression into account, utilizes the value of settling time t_x taken from the settling curve at a particular underflow concentration. This value is used to solve the Talmage and Fitch equation (18-46) for unit area.

Compression bed depth will have a significant effect on the overall settling rate (increasing compression zone depth reduces unit area).
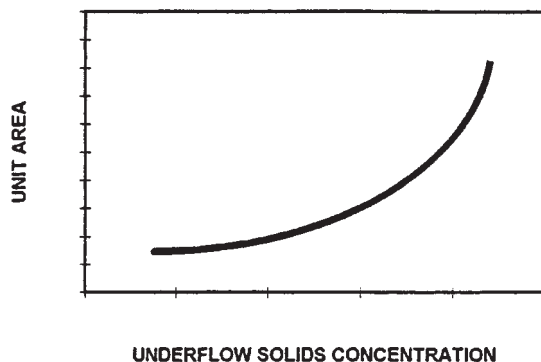
FIG. 18-84 Characteristic relationship between thickener unit area and underflow solids concentration (fixed flocculant dosage and pulp depth).

Therefore, in applying either of these two procedures it is necessary to run the test in a vessel having an average bed depth close to that expected in a full-scale thickener. This requires a very large sample, and it is more convenient to carry out the test in a cylinder having a volume of 1 to 4 liters. The calculated unit area value from this test can be extrapolated to full-scale depth by carrying out similar tests at different depths to determine the effect on unit area. Alternatively, an empirical relationship can be used which is effective in applying a depth correction to laboratory cylinder data over normal operating ranges. The unit area calculated by either the Wilhelm and Naide approach or the direct method is multiplied by a factor equal to $(h/H)^n$, where h is the average depth of the pulp in the cylinder, H is the expected full-scale compression zone depth, usually taken as 1 m, and n is the exponent calculated from Fig. 18-85. For conservative design purposes, the minimum value of this factor that should be used is 0.25.

It is essential to use a slow-speed (approximately 0.1 r/min) picket rake in all cylinder tests to prevent particle bridging and allow the sample to attain the underflow density which is obtainable in a full-scale thickener.

Continuously operated, small-scale or pilot-plant thickeners, ranging from 75 mm diameter by 400 mm depth to several meters in diameter, are also effectively used for sizing full-scale equipment. This approach requires a significantly greater volume of sample, such as
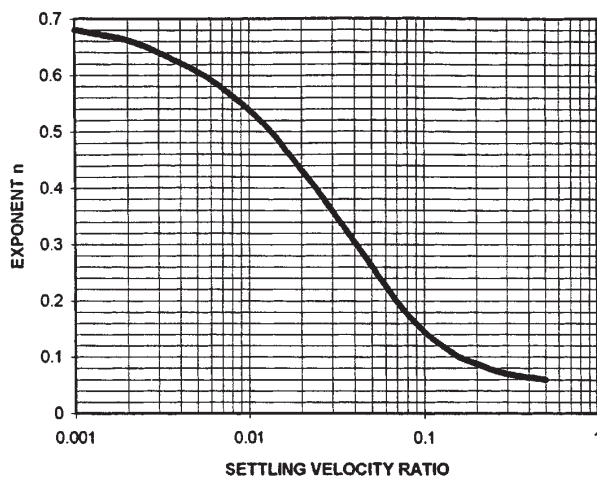
FIG. 18-85 Depth correction factor to be applied to unit areas determined with Wilhelm-Naide and "direct" methods. Velocity ratio calculated using tangents to settling curve at a particular settled solids concentration and at start of test.

would be available in an operating installation or a pilot plant. Continuous units and batch cylinders will produce equivalent results if proper procedures are followed with either system.

Thickener-Basin Depth   The pulp depth required in the thickener will be greatly affected by the role that compression plays in determining the rate of sedimentation. If the zone-settling conditions define the area needed, then depth of pulp will be unimportant and can be largely ignored, as the "normal" depth found in the thickener will be sufficient. On the other hand, with the compression zone controlling, depth of pulp will be significant, and it is essential to measure the sedimentation rate under these conditions.

To determine the compression-zone requirement in a thickener, a test should be run in a deep cylinder in which the average settling pulp depth approximates the depth anticipated in the full-scale basin. The average density of the pulp in compression is calculated and used in Eq. (18-47) to determine the required compression-zone volume:

$$V = \frac{\theta_c(\rho_s - \rho_l)}{\rho_s(\rho_{sl} - \rho_l)} \tag{18-47}$$

where V is the volume, m^3, required per ton of solids per day; θ_c is the compression time, days, required in the test to reach underflow concentration; and ρ_s, ρ_l, ρ_{sl}, are the densities of the solids, liquid, and slurry (average), respectively, ton/m^3. This value divided by the average depth of the pulp during the period represents the unit area defined by compression requirements. If it exceeds the value determined from the zone-settling tests, it is the quantity to be used.

The side depth of the thickener is determined as the sum of the depths needed for the compression zone and for the clear zone. Normally, 1.5 to 2 m of clear liquid depth above the expected pulp level in a thickener will be sufficient for stable, effective operation. When the location of the pulp level cannot be predicted in advance or it is expected to be relatively low, a thickener sidewall depth of 2 to 3 m is usually safe. Greater depth may be used in order to provide better clarity, although in most thickener applications the improvement obtained by this means will be marginal.

Scale-up Factors   Factors used in thickening will vary, but, typically, a 1.2 to 1.3 multiplier applied to the unit area calculated from laboratory data is sufficient if proper testing procedures have been followed and the samples are representative.

Flocculation   Flocculants are commonly used because of the considerable reduction in equipment size and capital cost that can be effected with very nominal reagent dosages. Selection of the reagents usually involves simple bench-scale comparison tests on small samples of pulp for rough screening, followed by larger-scale tests in cylinders or in continuous pilot-plant thickeners. Determination of the optimum dosage is complicated; it involves a number of economic factors such as reagent and capital costs, cost of a shutdown or loss in availability due to failure in the flocculation system, and consideration of possible future increases in plant capacity.

Polymeric flocculants are available in various chemical compositions and molecular weight ranges, and they may be nonionic in character or may have predominantly cationic or anionic charges. The range of application varies; but, in general, nonionics are well suited to acidic suspensions, anionic flocculants work well in neutral or alkaline environments, and cationics are most effective on organic material and colloidal matter.

Colloidal solids (e.g., as encountered in waste treatment) may require initial treatment with a chemical having strong ionic properties, such as acid, lime, alum, or ferric sulfate. The latter two will precipitate at neutral pH and produce a gelatinous, flocculent structure which further helps collect extremely small particles. Some cationic polymers also may be effective in flocculation of particles of this type. (This action is commonly termed *coagulation*.) Prolonged, gentle agitation improves the degree and rate of flocculation under these conditions. If the solids concentration is relatively low, e.g., <500 mg/L, results can usually be improved by recirculation of settled material to the flocculation zone to produce an optimum concentration for floc growth.

With polymer flocculation of slurries, however, extended agitation after the addition of the polymer may be detrimental. The reagent should be added to the slurry under conditions which promote rapid dispersion and uniform, complete mixing with a minimum of shear. In cylinder tests, this can be accomplished by simultaneously injecting and mixing flocculant with the slurry, using an apparatus consisting of a syringe, a tube, and an inverted rubber stopper. The stopper, with a diameter approximately three-fourths of that of the cylinder, provides sufficient turbulence as it is moved gently up and down through the sample to cause good blending of reagent and pulp.

Flocculant solution preparation and use should take into account specific properties of these reagents. During mixing and distribution, excessive shear should be avoided since it can reduce reagent effectiveness and result in higher consumption. Flocculant solution should be prepared at as high a concentration—generally, 0.25 to 1%—as can be handled by the metering pump and agitator, and added to the pulp at the maximum dilution possible. Dry polymers require sufficient aging time after initial mixing with water in order to develop their full effectiveness. Liquid polymers—emulsions and dispersions—contain additives such as carriers, activators, and other components which can have an effect on the process and other equipment, and this should be investigated before their use. Care should be taken that the water employed for dissolving as well as for dilution will not affect reagent activity, as this could increase consumption. Prior to design of the system, laboratory tests should be conducted with both plant and tap water to determine if there is a detrimental effect using process water.

Torque Requirements   Sufficient torque must be available in the raking mechanism of a full-scale thickener to allow it to move through the slurry and assist solids movement to the underflow outlet. Granular, particulate solids that settle rapidly and reach a terminal solids concentration without going through any apparent compression or zone-settling region require a maximum raking capability, as they must be moved to the outlet solely by the mechanism. At the other end of the spectrum, extremely fine materials, such as clays and precipitates, require a minimum of raking, for most of the solids may reach the underflow outlet hydrodynamically. The rakes prevent a gradual buildup of some solids on the bottom, however, and the gentle stirring action from the rake arm often aids the thickening process. As the underflow concentration approaches its ultimate limit, the consistency will increase greatly, resulting in a higher raking requirement and an increase in torque.

For most materials, the particle size lies somewhere between these two extremes, and the torques required in two properly designed thickeners of the same size but in distinct applications can differ greatly. Unfortunately, test methods to specify torque from small-scale tests are of questionable value, since it is difficult to duplicate actual conditions. Manufacturers of sedimentation equipment select torque ratings from experience with similar substances and will recommend a torque capability on this basis. Definitions of *operating torque* vary with the manufacturer, and the user should ask the supplier to specify the *B-10 life* for bearings and to reference appropriate mechanical standards for continuous operation of the selected gear set at specific torque levels. This will provide guidelines for plant operators and help avoid premature failure of the mechanism. Abnormal conditions above the normal operating torque are inevitable, and a thickener should be provided with sufficient torque capability for short-term operation at higher levels in order to ensure continuous performance.

Underflow Pump Requirements   Many suspensions will thicken to a concentration higher than that which can be handled by conventional slurry pumps. Thickening tests should be performed with this in mind, for, in general, the unit area to produce the maximum concentration that can be pumped is the usual design basis. Determination of this ultimate pumpable concentration is largely a judgmental decision requiring some experience with slurry pumping; however, the behavior of the thickened suspension can be used as an approximate guide to pumpability. The supernatant should be decanted following a test and the settled solids repulped in the cylinder to a uniform consistency. Repulping is done easily with a rubber stopper fastened to the end of a rigid rod. If the bulk of the repulped slurry can be poured from the cylinder when it is tilted 10 to 30° above the horizontal, the corresponding thickener underflow can be handled by most types of slurry pumps. But if the slurry requires cylinder shaking or other mechanical means for its removal, it should be diluted to a more fluid condition, if conventional pump systems are to be employed.

THICKENERS

The primary function of a continuous thickener is to concentrate suspended solids by gravity settling so that a steady-state material balance is achieved, solids being withdrawn continuously in the underflow at the rate they are supplied in the feed. Normally, an inventory of pulp is maintained in order to achieve the desired concentration. This volume will vary somewhat as operating conditions change; on occasion, this inventory can be used for storage of solids when feed and underflow rates are reduced or temporarily suspended.

A thickener has several basic components: a tank to contain the slurry, feed piping and a feedwell to allow the feed stream to enter the tank, a rake mechanism to assist in moving the concentrated solids to the withdrawal points, an underflow solids-withdrawal system, and an overflow launder. The basic design of a bridge-supported thickener mechanism is illustrated in Fig. 18-86.

High-Rate Thickeners   Flocculants are commonly used in thickeners, and this practice has resulted in thickener classification as either *conventional* or *high-rate*. These designations can be confusing in that they imply that there is a sharp distinction between the two,

which *is not* the case. The greater capacity expected from a high-rate thickener is due solely to the effective use of flocculant to maximize throughput, as shown in Fig. 18-87. In most applications, there is a threshold dosage at which a noticeable increase in capacity begins to occur. This effect will continue up to a limit, at which point the capacity will be a maximum unless a lower underflow concentration is accepted, as illustrated in Fig. 18-84. Since flocculant is usually added to a thickener either in the feed line or the feedwell, there are a number of proprietary feedwell designs which are used in high-rate thickeners in order to help optimize flocculation. De-aeration systems may be included in some cases to avoid air entrainment in the flocculated slurry. The other components of these units are not materially different from those of a conventional thickener.

High-Density Thickeners   Thickeners can be designed to produce underflows having a very high apparent viscosity, permitting disposal of waste slurries at a concentration that avoids segregation of fines and coarse particles or formation of a free-liquid pond on the surface of the deposit. This practice is applied in *dry-stacking* systems and underground *paste-fill* operations for disposal of mine tailings and similar materials. The thickener mechanism generally will require a special
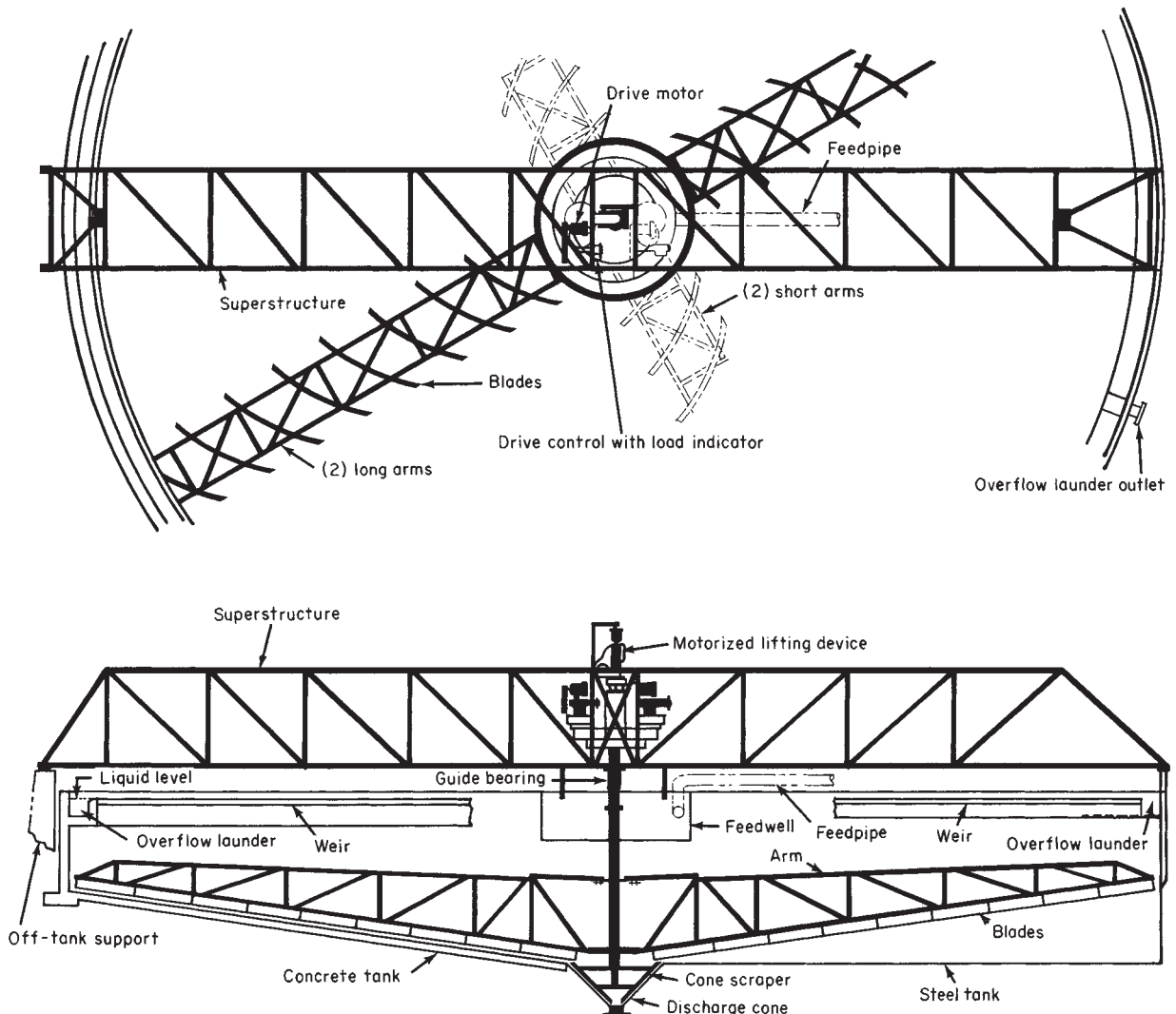

FIG. 18-86   Unit thickener with bridge-supported mechanism. (*EIMCO Process Equipment Co.*)
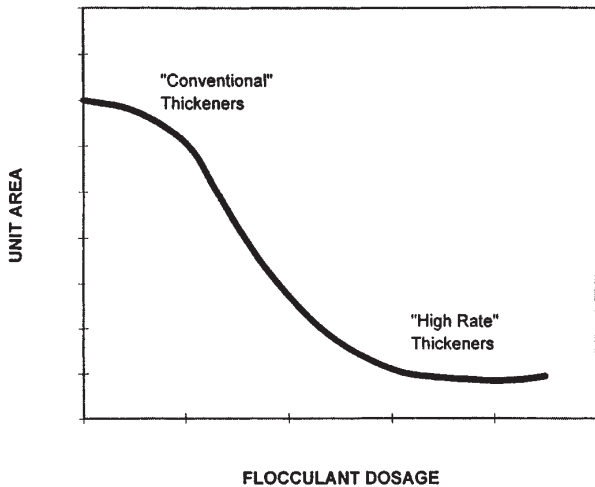
FIG. 18-87   Unit area vs. flocculant dose, illustrating the relationship between conventional and high-rate thickeners.

rake design and have a torque capability 3 to 4 times, or more, the normal for that particular diameter. Underflow slurries usually will be at a solids concentration 5 to 10% lower than that of a vacuum filter cake formed from the same material. Special pumping requirements are necessary if the slurry is to be transferred a significant distance, with line pressure drop typically in the range of 3 to 4 kPa/m of pipeline.

Design Features   There are three classes of thickeners, each differentiated by its drive mechanism: (1) bridge-supported, (2) center-column supported, and (3) traction drives. The diameter of the tank will range from 2 to 150 m (6.5 to 492 ft), and the support structure often is related to the size required. These classes are described in detail in the subsection "Components and Accessories for Sedimentation Units."

Operation   When operated correctly, thickeners require a minimum of attention and, if the feed characteristics do not change radically, can be expected to maintain design performance consistently. In this regard, it is usually desirable to monitor feed and underflow rates and solids concentrations, flocculant dosage rate, and pulp interface level, preferably with dependable instrumentation systems. Process variations are then easily handled by changing the principal operating controls—underflow rate and flocculant dose—to maintain stability.

Starting up a thickener is usually the most difficult part of the operation, and there is more potential for mechanical damage to the mechanism at this stage than at any other time. In general, two conditions require special attention at this point: underflow pumping and mechanism torque. If possible, the underflow pump should be in operation as soon as feed enters the system, recirculating underflow slurry at a reduced rate if the material is relatively fine or advancing it to the next process step (or disposal) if the feed contains a considerable quantity of coarse solids, e.g., more than 20 percent + 75 μm particles. At this stage of the operation, coarse solids separate from the pulp and produce a difficult raking and pumping situation. Torque can rise rapidly if this material accumulates faster than it is removed. If the torque reaches a point where the automatic control system raises the rakes, it is usually preferable to reduce or cut off the feed completely until the torque drops and the rakes are returned to the lowest position. As the fine fraction of the feed slurry begins to thicken and accumulate in the basin, providing both buoyancy and fluidity, torque will drop and normal feeding can be continued. This applies whether the thickener tank is empty at start-up or filled with liquid. The latter approach contributes to coarse-solids raking problems but at the same time provides conditions more suited to good flocculation, with the result that the thickener will reach stable operation much sooner.

As the solids inventory in the thickener reaches a normal level—usually about 0.5 to 1.0 m below the feedwell outlet—with underflow

slurry at the desired concentration, the torque will reach a normal operating range. Special note should be made of the torque reading at this time. Subsequent higher torque levels while operating conditions remain unchanged can almost always be attributed to island formation, and corrective action can be taken early, before serious problems develop. *Island* is the name given to a mass of semisolidified solids that have accumulated on or in front of the rakes, often as a result of excessive flocculant use. This mass usually will continue to grow in size, eventually producing a torque spike that can shut down the thickener and often resulting in lower underflow densities than would otherwise be achievable.

An island is easily detected, usually by the higher-than-normal, gradually increasing torque reading. Probing the rake arms near the thickener center with a rigid rod will confirm this condition—the mass is easily distinguished by its cohesive, claylike consistency. At an early stage, the island is readily removed by raising the rakes until the torque drops to a minimum value. The rakes are then lowered gradually, a few centimeters at a time, so as to shave off the mass of solids and discharge this gelled material through the underflow. This operation can take several hours, and if island formation is a frequent occurrence, the procedure should be carried out on a regular basis, typically once a day, preferably with an automatic system to control the entire operation.

Stable thickener performance can be maintained by carefully monitoring operating conditions, particularly the pulp interface level and the underflow rate and concentration. As process changes occur, the pulp level can vary; regulation of the underflow pumping rate will keep the level within the desired range. If the underflow varies in concentration, this can be corrected by adjusting the flocculant dosage. Response will not be immediate, of course, and care should be taken to make only small step changes at any one time. Procedures for use of automatic control are described in the section on instrumentation.

CLARIFIERS

Continuous clarifiers generally are employed with dilute suspensions, principally industrial process streams and domestic municipal wastes, and their primary purpose is to produce a relatively clear overflow. They are basically identical to thickeners in design and layout except that they employ a mechanism of lighter construction and a drive head with a lower torque capability. These differences are permitted in clarification applications because the thickened pulp produced is smaller in volume and appreciably lower in suspended solids concentration, owing in part to the large percentage of relatively fine (smaller than 10 μm) solids. The installed cost of a clarifier, therefore, is approximately 5 to 10 percent less than that of a thickener of equal tank size, as given in Fig. 18-94.

Rectangular Clarifiers   Rectangular clarifiers are employed primarily in municipal water and waste treatment plants, as well as in certain industrial plants, also for waste streams. The raking mechanism employed in many designs consists of a chaintype drag, although suction systems are used for light-duty applications. The drag moves the deposited pulp to a sludge hopper located on one end by means of scrapers fixed to endless chains. During their return to the sludge raking position, the flights may travel near the water level and thus act as skimming devices for removal of surface scum. Rectangular clarifiers are available in widths of 2 to 10 m (6 to 33 ft). The length is generally 3 to 5 times the width. The larger widths have multiple raking mechanisms, each with a separate drive.

This type of clarifier is used in applications such as preliminary oil-water separations in refineries and clarification of waste streams in steel mills. When multiple units are employed, common walls are possible, reducing construction costs and saving on floor space. Overflow clarities, however, generally are not as good as with circular clarifiers, due primarily to reduced overflow weir length for equivalent areas.

Circular Clarifiers   Circular units are available in the same three basic types as single-compartment thickeners: bridge, center-column, and peripheral-traction. Because of economic considerations, the bridge-supported type is limited generally to tanks less than 20 m in diameter.

A circular clarifier often is equipped with a surface-skimming device, which includes a rotating skimmer, scum baffle, and scum-box assembly. In sewage and organic-waste applications, squeegees normally are provided for the rake-arm blades, as it is desirable that the bottom be scraped clean to preclude accumulation of organic solids, with resultant septicity and flotation of decomposing material.

Center-drive mechanisms are also installed in square tanks. This mechanism differs from the standard circular mechanism in that a hinged corner blade is provided to sweep the corners which lie outside the path of the main mechanism.

Clarifier-Thickener Clarifiers can serve as thickeners, achieving additional densification in a deep sludge sump adjacent to the center that extends a short distance radially and provides adequate retention time and pulp depth to compact the solids to a high density. Drive mechanisms on this type of clarifier usually must have higher torque capability than would be supplied on a standard clarifier.

Industrial Waste Secondary Clarifiers Many plants which formerly discharged organic wastes to the sewer have turned to using their own treatment facilities in order to reduce municipal treatment plant charges. For organic wastes, the waste-activated sludge process is a preferred approach, using an aeration basin for the bio-oxidation step and a secondary clarifier to produce a clear effluent and to concentrate the biomass for recycling to the basin. To produce an acceptable effluent and achieve sufficient concentration of the low-density solids that make up the biomass, certain design criteria must be followed. If pilot-plant data are unavailable, the design procedures proposed by Albertson (op. cit.) can be used to specify tank diameter, depth, feedwell dimensions, feed inlet configuration, and rake-blade design for a unit which will meet the specifications for many waste-activated sludge plants. Typical design parameters recommended by Albertson include the following:

Feed pipe velocity: ≤1.2 m/s.
Energy-dissipating feed entry velocity (tangential): ≤0.5 m/s.
Downward velocity from feedwell: ≤0.5–0.75 (peak) m/min.
Feedwell depth: Entry port depth +1 m.
Radial velocity below feedwell: ≤90% of downward velocity.
Tank depth: Clear water zone above dense sludge blanket is determined largely by clarification requirements; typically 3–5 m.
Tank diameter: Largely a function of clear water depth; the maximum overflow rate in m/h = 0.278 × clear water depth. Resulting underflow design settling velocity should be less than 1.0 m/h for 1% solids and 120 mL/g SVI.

Tilted-Plate Clarifiers Lamella or tilted-plate separators have achieved increased use for clarification. They contain a multiplicity of plates inclined at 45 to 60° from the horizontal. Various feed methods are employed so that the influent passes into each inclined channel at about one-third of the vertical height from the bottom. This results in the solids having to settle only a short distance in each channel before sliding down the base to the collection zone beneath the plates. The clarified liquid passes in the opposite direction beneath the ceiling of each channel to the overflow connection.

The area that is theoretically available for separation is equal to the sum of the projected areas or all channels on the horizontal plane. Figure 18-88 shows the horizontally projected area A, of a single channel in a clarifier of unit width. If X is the uniform distance between plates (measured perpendicularly to the plate surface), the clarifier will contain $\sin \alpha / X$ channels per unit length and an effective collection area per unit clarifier length of A, $\sin \alpha / X$, where α is the angle of inclination of the plates to the horizontal. It follows that the total horizontally projected plate area per unit volume of sludge in the clarifier A_s is

$$A_s = \cos \alpha / X \qquad (18\text{-}48)$$

As α and X are decreased, A_s is increased. However, α must be larger than the angle of repose of the sludge so that it will slide down the plate, and the most common range is 55 to 60°. Plate spacing must be large enough to accommodate the opposite flows of liquid and sludge while reducing interference and preventing plugging and to provide enough residence time for the solids to settle to the bottom plate. Usual X values are 50 to 75 mm (2 to 3 in).
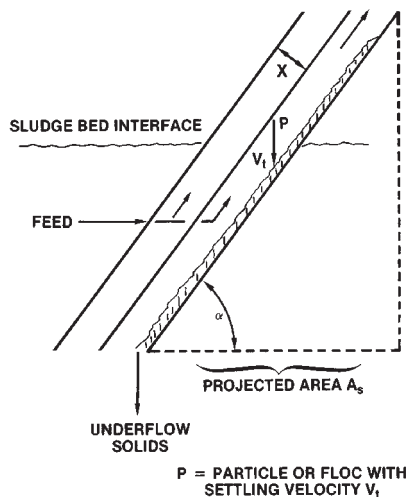

FIG. 18-88 Basic concept of the Lamella-type clarifier.

Many different designs are available, the major difference among them being in feed-distribution methods and plate configurations. Operating capacities range from 1 to 3 m^3 of feed/h/m^2 of projected horizontal area [0.4 to 1.2 gal/(min·ft)].

The principal advantage of the tilted-plate clarifier is the increased capacity per unit of plane area. Major disadvantages are an underflow solids concentration that generally is lower than in other gravity clarifiers and difficulty of cleaning when scaling or deposition occurs. The lower underflow composition is due primarily to the reduced compression-zone volume relative to the large settling area. When flocculants are employed, flocculating equipment and tankage preceding the separator are required, as the design does not permit internal flocculation.

Solids-Contact Clarifiers When desirable, mixing, flocculation, and sedimentation all may be accomplished in a single tank. Of the various designs available, those employing mechanically assisted mixing in the reaction zone are the most efficient. They generally permit the highest overflow rate at a minimum chemical dosage while producing the best effluent quality. The unit illustrated in Fig. 18-89 consists of a combination dual drive which moves the rake mechanism at a very slow speed as it rotates a high-pumping-rate, low-shear turbine located in the top portion of a center reaction well at a very much higher speed. The influent, dosed with chemicals as it enters, is contacted with previously settled solids in a recirculation draft tube within the reaction well by means of the pumping action of the turbine, resulting in a thorough mixing of these streams. Owing to the higher concentration of solids being recirculated, all chemical reactions are more rapid and more nearly complete, and flocculation is improved. The mixture passes out of the contacting and reaction well into the clarification area, where the flocculated particles settle out. They are raked to the center to be used again in the recirculation process, with a small amount being discharged through the sludge pump. When floccules are too heavy to be circulated up through the draft tube (as in the case of metallurgical pulps), a modified design using external recirculation of a portion of the thickened underflow is chosen. These units employ a special mixing impeller in a large feed well with a small-diameter central outlet.

Solids-contact clarifiers are advantageous for clarifying turbid waters or slurries that require coagulation and flocculation for the removal of bacteria, suspended solids, or color. Applications include softening water by lime addition; clarifying industrial-process streams, sewage, and industrial wastewaters; tertiary treatment for removal of phosphates, BOD_5, and turbidity; and silica removal from geothermal brines or from surface water for cooling-tower makeup.
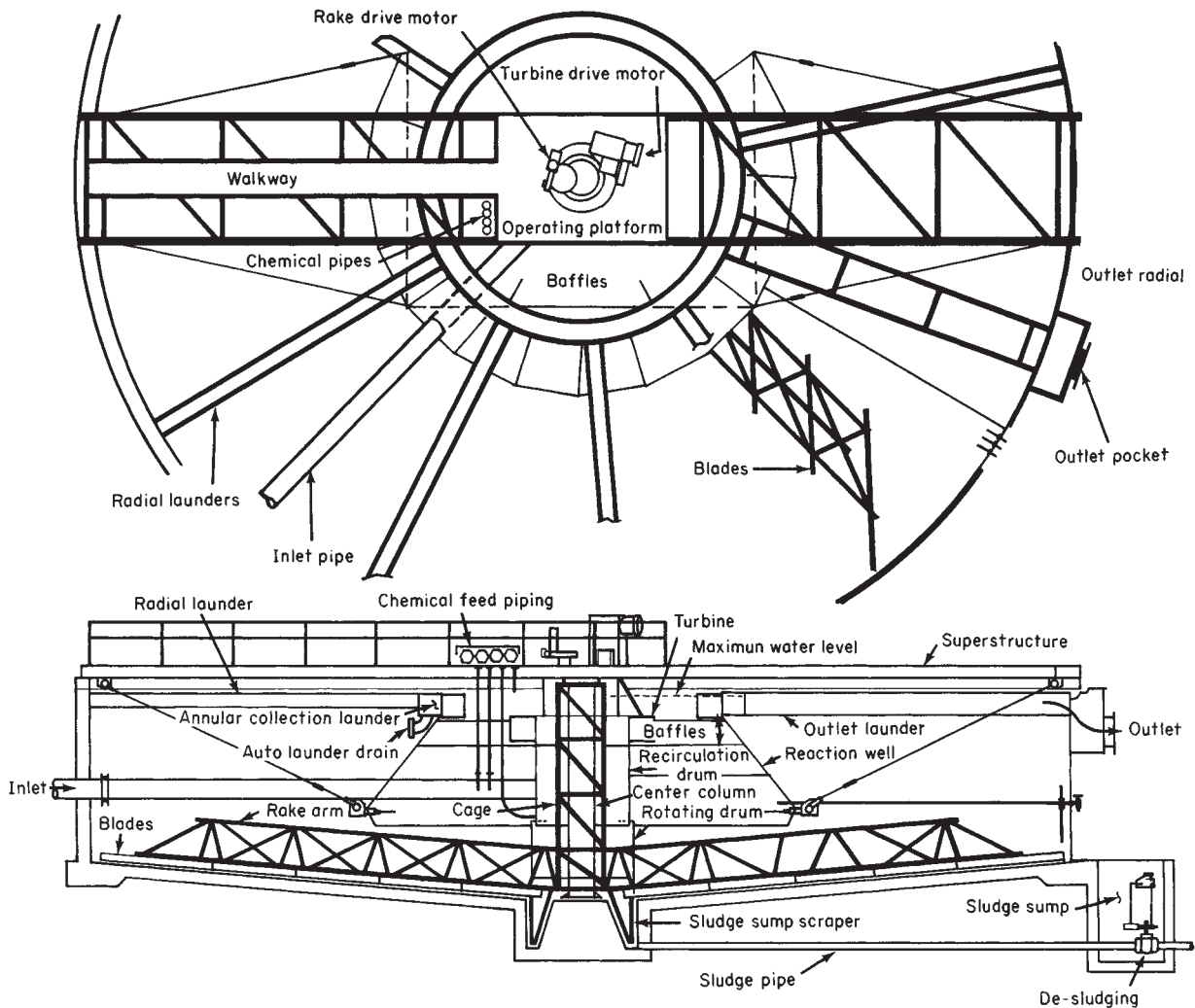
FIG. 18-89 Reactor-clarifier of the high-rate solids-contact type. (*EIMCO Process Equipment Co.*)

COMPONENTS AND ACCESSORIES FOR SEDIMENTATION UNITS

Sedimentation systems consist of a collection of components, each of which can be supplied in a number of variations. The basic components are the same, whether the system is for thickening or clarifying: tank, drive-support structure, drive unit and lifting device, rake structure, feedwell, overflow arrangement, underflow arrangement, instrumentation, and flocculation facilities.

Tanks Tanks or basins are constructed of such materials as steel, concrete, wood, compacted earth, plastic sheeting, and soil cement. The selection of the materials of construction is based on cost, availability, topography, water table, ground conditions, climate, operating temperature, and chemical-corrosion resistance. Typically, industrial tanks up to 30 m (100 ft) in diameter are made of steel. Concrete generally is used in municipal applications and in larger industrial applications. Extremely large units employing earthen basins with impermeable liners have proved to be economical.

Drive-Support Structures There are three basic drive mechanisms. These are (1) the bridge-supported mechanism, (2) the center-column-supported mechanism, and (3) the traction-drive thickener containing a center-column-supported mechanism with the driving arm attached to a motorized carriage at the tank periphery.

Bridge-Supported Thickeners These thickeners (Fig. 18-86) are common in diameters up to 30 m, the maximum being about 45 m (150 ft). They offer the following advantages over a center-column-supported design: (1) ability to transfer loads to the tank periphery; (2) ability to give a denser and more consistent underflow concentration with the single draw-off point; (3) a less complicated lifting device; (4) fewer structural members subject to mud accumulation; (5) access to the drive from both ends of the bridge; and (6) lower cost for units smaller than 30 m in diameter.

Center-Column-Supported Thickeners These thickeners are usually 20 m (65 ft) or more in diameter. The mechanism is supported by a stationary steel or concrete center column, and the raking arms are attached to a driving cage which rotates around the center column.

Traction Thickeners These thickeners are most adaptable to tanks larger than 60 m (200 ft) in diameter. Maintenance generally is less difficult than with other types of thickeners, which is an advantage

in remote locations. The installed cost of the traction thickener may be more than that of a center-driven unit primarily because of the cost of constructing the heavy concrete wall required to support the drive carriage. Disadvantages of the traction thickener are that (1) no practical lifting device can be used, (2) operation may be difficult in climates where snow and ice are common, and (3) the driving-torque effort must be transmitted from the tank periphery to the center, where the heaviest raking conditions occur.

Drive Assemblies The drive assembly is the key component of a sedimentation unit. The drive assembly provides (1) the force to move the rakes through the thickened pulp and to move settled solids to the point of discharge, (2) the support for the mechanism which permits it to rotate, (3) adequate reserve capacity to withstand upsets and temporary overloads, and (4) a reliable control which protects the mechanism from damage when a major overload occurs.

Drives usually have steel or iron main spur gears mounted on bearings, alloy-steel pinions, and either a bronze or a malleable iron worm gear driven by a hardened-steel worm or a planetary gear system. Direct-drive hydraulic systems are also employed. The gearing components preferably are enclosed for maximum service life. The drive typically includes a torque-measuring system with torque indicated on the mechanism and often transmitted to a remote indicator. If the torque becomes excessive, it can automatically activate such safeguards against structural damage as sounding an alarm, raising the rakes, and stopping the drive.

Rake-Lifting Mechanisms These should be provided when abnormal thickener operation is probable. Abnormal thickener operation or excessive torque may result from insufficient underflow pumping, surges in the solids feed rate, excessive amounts of large particles, sloughing of solids accumulated between the rakes and the bottom of the tank or on structural members of the rake mechanism, or miscellaneous obstructions falling into the thickener. The lifting mechanism may be set to raise the rakes automatically when a specific torque level (e.g., 40 percent of design) is encountered, continuing to lift until the torque returns to normal or until the maximum lift height is reached. Generally, corrective action must be taken to eliminate the cause of the upset. Once the torque returns to normal, the rake mechanism is lowered slowly to "plow" gradually through the excess accumulated solids until these are removed from the tank.

Rake-lifting devices can be manual for small-diameter thickeners or motorized for larger ones. Manual rake-lifting devices consist of a handwheel and a worm to raise or lower the rake mechanism by a distance usually ranging from 30 to 60 cm (1 to 2 ft). Motorized rake-lifting devices typically are designed to allow for a vertical lift of the rake mechanism of up to 90 cm (3 ft). A platform-type lifting device lifts the entire drive and rake mechanism up to 2.5 m (8 ft) and is used for applications in which excessive torque is most probable or when storage of solids in the thickener is desired.

Figure 18-90 illustrates the cable-arm design. This design uses cables attached to a truss above or near the liquid surface to move the rake arms, which are hinged to the drive structure, allowing the rakes to be raised when excessive torque is encountered. A major advantage of this design is the relatively small surface area of the raking mechanism, which reduces the solids accumulation and downtime in applications in which scaling or island formation can occur.

One disadvantage of this or any hinged-arm or other self-lifting design is that there is very little lift at the center, where the overload usually occurs. A further disadvantage is the difficulty of returning the rakes to the lowered position in settlers containing solids that compact firmly.
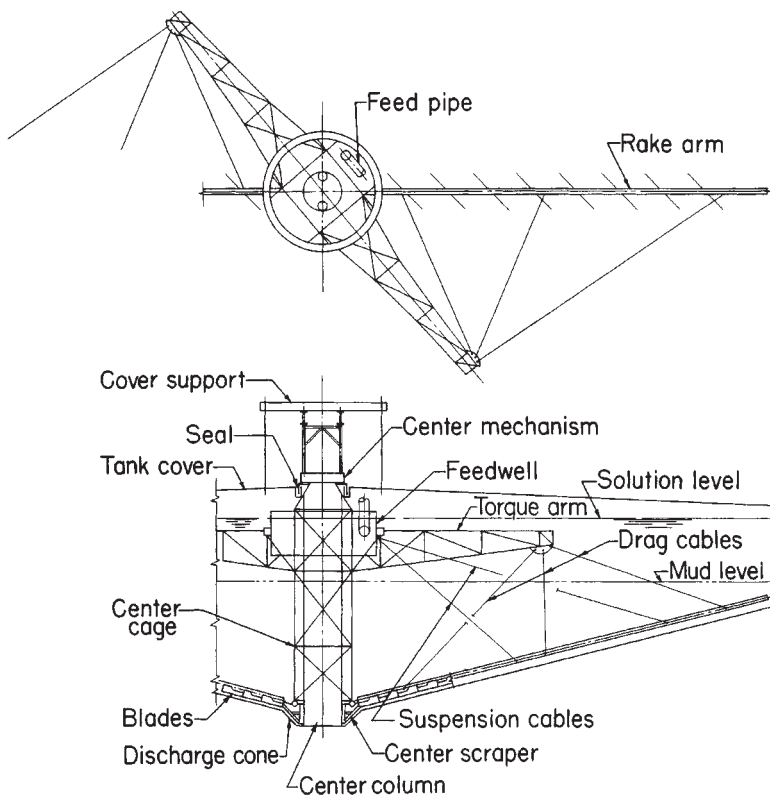

FIG. 18-90 Cable-arm design. (*Dorr-Oliver, Inc.*)

Rake Mechanism   The rake mechanism assists in moving the settled solids to the point of discharge. It also aids in thickening the pulp by disrupting bridged floccules, permitting trapped fluid to escape and allowing the floccules to become more consolidated. Rake mechanisms are designed for specific applications, usually having two long rake arms with an option for two short rake arms for bridge-supported and center-column-supported units. Traction units usually have one long arm and three short arms.

Figure 18-91 illustrates three types of rake-arm designs. The conventional design typically is used in bridge-supported units, while the dual-slope design is used for units of larger diameter. The "thixo post" design employs rake blades on vertical posts extending below the truss to keep the truss out of the thickest pulp and thereby prevent the collection of solids that might cause an "island" to form.

Rake blades can have attached spikes or serrated bottoms to cut into solids that have a tendency to compact. Lifting devices typically are used with these applications.

Rake-speed requirements depend on the type of solids entering the thickener. Peripheral speed ranges used are, for slow-settling solids, 3 to 8 m/min (10 to 25 ft/min); for fast-settling solids, 8 to 12 m/min (25 to 40 ft/min); and for coarse solids or crystalline materials, 12 to 30 m/min (40 to 100 ft/min).

Feedwell   The feedwell is designed to allow the feed to enter the thickener with minimum turbulence and uniform distribution while dissipating most of its kinetic energy. Feed slurry enters the feedwell, which is usually located in the center of the thickener, through a pipe or launder suspended from the bridge. To avoid excess velocity, an open launder normally has a slope no greater than 1 to 2 percent. Pulp should enter the launder at a velocity that prevents sanding at the inlet. With nonsanding pulps, the feed may also enter upward through the center column from a pipeline installed beneath the tank.

The standard feedwell for a thickener is designed for a maximum vertical outlet velocity of about 1.5 m/min (5 ft/min). High turbidity

Conventional design (raking inward)

Design used for sloping bottoms

Arms used for thixotropic slimes to prevent "donut" formations and attain maximum underflow densities

FIG. 18-91   Rake-mechanism designs employed for specific duties. (*EIMCO Process Equipment Co.*)

caused by short-circuiting the feed to the overflow can be reduced by increasing the depth of the feedwell. When overflow clarity is important or the solids specific gravity is close to the liquid specific gravity, deep feedwells of large diameter are used, and measures are taken to reduce the velocity of the entering feed slurry.

Shallow feedwells may be used when overflow clarity is not important, the overflow rate is low, and/or solids density is appreciably greater than that of water. Some special feedwell designs used to dissipate entrance velocity and create quiescent settling conditions split the feed stream and allow it to enter the feedwell tangentially on opposite sides. The two streams shear or collide with one another to dissipate kinetic energy.

When flocculants are used, often it will be found that the optimum solids concentration for flocculation is considerably less than the normal concentration, and significant savings in reagent cost will be made possible by dilution of the feed prior to flocculation. This can be achieved by recycling overflow or more efficiently by feedwell modifications, including openings in the feedwell rim. These will allow supernatant to enter the feedwell, and flocculant can be added at this point or injected below the surface of the pulp in the feedwell. Another effective means of achieving this dilution prior to flocculant addition is illustrated in Fig. 18-92. This approach utilizes the energy available in the incoming feed stream to achieve the dilution by momentum transfer and requires no additional energy expenditure to dilute this slurry by as much as three to four times.

Overflow Arrangements   Clarified effluent typically is removed in a peripheral launder located inside or outside the tank. The effluent enters the launder by overflowing a V-notch or level flat weir, or through submerged orifices in the bottom of the launder. Uneven overflow rates caused by wind blowing across the liquid surface in large thickeners can be better controlled when submerged orifices or V-notch weirs are used. Radial launders are used when uniform upward liquid flow is desired in order to improve clarifier detention efficiency. This arrangement provides an additional benefit in reducing the effect of wind, which can seriously impair clarity in applications that employ basins of large diameter.

The hydraulic capacity of a launder must be sufficient to prevent flooding, which can cause short-circuiting of the feed and deterioration of overflow clarity. Standards are occasionally imposed on weir overflow rates for clarifiers used in municipal applications; typical rates are 3.5 to 15 m³/(h·m) [7000 to 30,000 gal/(day·ft)], and they are highly dependent on clarifier side-water depth. Industrial clarifiers may have higher overflow rates, depending on the application and the desired overflow clarity. Launders can be arranged in a variety of configurations to achieve the desired overflow rate. Several alternatives to improve clarity include an annular launder inside the tank (the liquid overflows both sides), radial launders connected to the peripheral launder (providing the very long weir that may be needed when abnormally high overflow rates are encountered and overflow clarity is important), and Stamford baffles, which are located below the launder to direct flow currents back toward the center of the clarifier.

In many thickener applications, on the other hand, complete peripheral launders are not required, and no difference in either overflow clarity or underflow concentration will result through the use of launders extending over only a fraction (e.g., one-fifth) of the perimeter. For design purposes, a weir-loading rate in the range of 7.5 to 30.0 m³/(h·m) [10 to 40 gpm/ft] can be used, the higher values being employed with well-flocculated, rapidly settling slurries. The overflow launder required may occupy only a single section of the perimeter rather than consisting of multiple, shorter segments spaced uniformly around the tank.

Underflow Arrangements   Concentrated solids are removed from the thickener by use of centrifugal or positive displacement pumps or, particularly with large-volume flows, by gravity discharge through a flow control valve or orifice suitable for slurry applications. Due to the risk to the thickener operation of a plugged underflow pipe, it is recommended that duplicate underflow pipes and pumps be installed in all thickening applications. Provision to recycle underflow slurry back to the feedwell is also useful, particularly if solids are to be stored in the thickener.
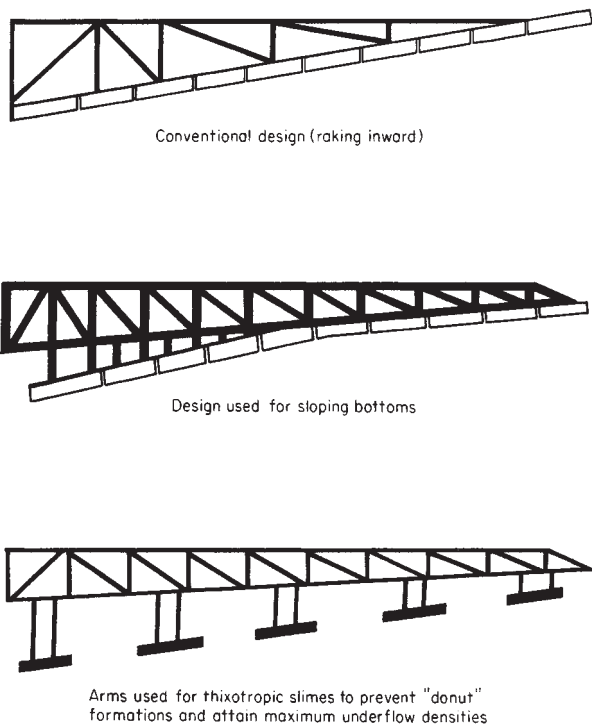
FIG. 18-92   E-Duc® Feed dilution system installed on 122-m-diameter thickener. (*EIMCO Process Equipment Co.*)

There are several basic underflow arrangements: (1) the underflow pump adjacent to the thickener sidewall with buried piping from the discharge cone, (2) the underflow pump under the thickeners or adjacent to the sidewall with the piping from the discharge cone in a tunnel, (3) the underflow pump adjacent to the thickener sidewall with a peripheral discharge from the tank sidewall, and (4) the underflow pump located in the center of the thickener on the bridge close to the drive mechanism, or at the perimeter, using piping up through the center column.

Pump Adjacent to Thickener with Buried Piping This arrangement of buried piping from the discharge cone is the least expensive system but the most susceptible to plugging. It is used only when the solids do not compact to an unpumpable slurry and can be easily backflushed if plugging occurs. Typically, two or more underflow pipes are installed from the discharge cone to the underflow pump so that solids removal can continue if one of the lines plugs. Valves should be installed to permit flushing with water and compressed air in both directions to remove blockages.

Tunnel A tunnel may be constructed under the thickener to provide access to the discharge cone when underflow slurries are difficult to pump and have characteristics that cause plugging. The underflow pump may be installed underneath the thickener or at the perimeter. Occasionally thickeners are installed on legs or piers, making tunneling for access to the center unnecessary. A tunnel or an elevated thickener is more expensive than the other underflow arrangements, but there are certain operational and maintenance advantages. Of course, the hazards of working in a tunnel (flooding and interrupted ventilation, for example) and related safety regulations must be considered.

Peripheral Discharge Peripheral discharge sometimes is used to permit the reduced installation cost of a flat-bottom tank on compacted soil. Because more torque is required to rake the solids to the perimeter of the tank, this arrangement is not suitable for service involving coarse solids or solids that become nonfluid at high concentrations.

Center-Column Pumping This arrangement may be used instead of a tunnel. Several designs are available. The commonest is a bridge-mounted pump with a suction line through a wet or dry center column. The pump selection may be limiting, requiring special attention to priming, net positive suction head, and the maximum density that the pump can handle. One design has the underflow pump located in a room under the thickener mechanism and connected to openings in the column. Access is through the drive gear at the top of the column.

INSTRUMENTATION

Thickener control philosophies are usually based on the idea that the underflow density obtained is the most important performance criterion. The overflow clarity is also a consideration, but this is generally not as critical. Additional factors which must be considered are optimization of flocculant usage and protection of the raking mechanism.

Automated control schemes employ one or more sets of controls, which will fit into three categories: (1) control loops which are used to regulate the addition of flocculant, (2) control loops to regulate the withdrawal of underflow, and (3) rake drive controls. Usually, the feed to a thickener is not controlled and most control systems have been designed with some flexibility to deal with changes in feed characteristics, such as an increase in volume or alteration in the nature of the solids themselves. In severe cases, some equalization of the feed is required in order to allow the control system to perform effectively.

Flocculant addition rate can be regulated in proportion to the thickener volumetric feed rate or solids mass flow in a feed-forward mode, or in a feed-back mode on either rake torque, underflow density, settling solids (sludge) bed level, or solids settling rate. Of these, feed-forward on mass flow or feed-back on bed level are probably the most common. In some feed-forward schemes, the ratio multiplier is trimmed by one of the other parameters.

Underflow is usually withdrawn continuously on the bases of bed level, rake torque, or underflow solids concentration in a feed-back mode. Most installations incorporate at least two of these parameters in their underflow withdrawal control philosophy. For example, the continuous withdrawal may be based on underflow solids density with an override to increase the withdrawal rate if either the rake torque or the bed level reaches a preset value. In some cases, underflow withdrawal has been regulated in a feed-forward mode on the basis of thickener feed solids mass flow rate. Any automated underflow pumping scheme should incorporate a lower limit on volumetric flow rate as a safeguard against line pluggage.

It is also important to consider the level of the sludge bed in the thickener. Although this can be allowed to increase or decrease within moderate limits, it must be controlled enough to prevent solids from overflowing the thickener or from falling so low that the underflow density becomes too dilute. The settling slurry within the sludge bed is normally free flowing and will disperse to a consistent level across the thickener diameter.

Rake drive controls protect the drive mechanism from damage and usually incorporate an alarm to indicate high torque with an interlock to shut down the drive at a higher torque level. They can have an automated rake raising and lowering feature with a device to indicate the elevation of the rakes.

A complete automated control scheme incorporates controls from each of the three categories. It is important to consider the interaction of the various controls, especially of the flocculant addition and underflow withdrawal control loops, when designing a system. The lag and dead times of any feedback loops as well as the actual response of the system to changes in manipulated variables must be considered. For example, in some applications it is possible that excessive flocculant addition may produce an increase in the rake torque (due to island formation or viscosity increase) without a corresponding increase in underflow density. Additionally, sludge bed level sensors generally require periodic cleaning to produce a reliable signal. In many cases, it has not been possible to effectively maintain the sludge bed level sensors, requiring a change in the thickener control logic after start-up. Some manufacturers offer complete thickener control packages.

Control philosophies for clarifiers are based on the idea that the overflow is the most important performance criterion. Underflow density or suspended solids content is a consideration, as is optimal use of flocculation and pH control reagents. Automated controls are of three basic types: (1) control loops that optimize coagulant, flocculant, and pH control reagent additions; (2) those that regulate underflow removal; and (3) rake drive controls. Equalization of the feed is provided in some installations, but the clarifier feed is usually not a controlled variable with respect to the clarifier operation.

Automated controls for flocculating reagents can use a feed-forward mode based on feed turbidity and feed volumetric rate, or a feed-back mode incorporating a streaming current detector on the flocculated feed. Attempts to control coagulant addition on the basis of overflow turbidity generally have been less successful. Control for pH has been accomplished by feed-forward modes on the feed pH and by feed-back modes on the basis of clarifier feedwell or external reaction tank pH. Control loops based on measurement of feedwell pH are useful for control in applications in which flocculated solids are internally recirculated within the clarifier feedwell.

Automated sludge withdrawal controls are usually based on the sludge bed level. These can operate in on-off or continuous modes and will use either single-point or continuous sludge level indication sensors. In many applications, automated control of underflow withdrawal does not provide an advantage, since so few settled solids are produced that it is only necessary to remove sludge for a short interval once a day, or even less frequently. In applications in which the underflow is recirculated internally within the feedwell, it is necessary to maintain sufficient sludge inventory for the recirculation turbine to pull from. This could be handled in an automated system with a single-point *low* sludge bed level sensor in conjunction with a low-level alarm or pump shutoff solenoid. Some applications require continuous external recirculation of the underflow direct to the feedwell or external reaction tanks, and an automated control loop could be used to maintain recirculation based on flow measurement, with a manually adjusted setpoint.

Control philosophies applied to continuous countercurrent decantation (CCD) thickeners are similar to those used for thickeners in other applications, but have emphasis on maintaining the CCD circuit in balance. It is important to prevent any one of the thickeners from pumping out too fast, otherwise an upstream unit could be starved of wash liquor while at the same time too much underflow could be placed in a downstream unit too quickly, disrupting the operation of both units as well as reducing the circuit washing efficiency. Several control configurations have been attempted, and the more successful schemes

have linked the solids mass flow rate of underflow pumping to that of the upstream unit or to the CCD circuit solids mass feed rate. Wide variations in the solids feed rate to a CCD circuit will require some means of dampening these fluctuations if design wash efficiency is to be maintained.

The following types of devices are commonly applied to measure the various operational parameters of thickeners and clarifiers. They have been used in conjunction with automatic valves and variable-speed pumps to achieve automatic operation as well as to simply provide local or remote indications.

Sludge Bed Level Sensors   Most of the more commonly used devices for detection of the sludge bed level operate on principles of ultrasound, gamma radiation, infrared or visible light, or simply with a float that is carefully weighted to float on the sludge bed level interface. There are basically two types of sensors, those that provide a single-point indication at a fixed height within the thickener or clarifier, and those that follow the sludge bed depth over a distance and provide a continuous indication of the level. Some devices are available that can provide a profile of the slurry concentration within the sludge bed.

Flowmeters   These are used to measure flocculant addition, underflow, and feed flow rates. For automatic control, the more commonly used devices are magnetic flowmeters and Doppler effect flowmeters.

Density Gauges   These are used to measure the density or suspended solids content of the feed and underflow streams. Gamma radiation devices are the most commonly used for automatic control, but ultrasonic devices are effective in the lower range of slurry density. Marcy pulp density scales are an effective manually operated device. A solids "mass flow" indication is usually obtained by combining a density gauge output with the output from a flowmeter.

Turbidity Gauges   These operate with visible light beams and detectors. They are used to monitor feed and effluent turbidity.

Streaming Current Detectors   These units produce a measurement closely related to the zeta potential of a suspension and are used successfully in optimizing the coagulant dose in clarification applications.

CONTINUOUS COUNTERCURRENT DECANTATION

The system of separation of solid-phase material from an associated solution by repeated stages of dilution and gravity sedimentation is adapted for many industrial-processing applications through an operation known as continuous countercurrent decantation (CCD). The flow of solids proceeds in a direction countercurrent to the flow of solution diluent (water, usually), with each stage composed of a mixing step followed by settling of the solids from the suspension. The number of stages ranges from 2 to as many as 10, depending on the degree of separation required, the amount of wash fluid added (which influences the final solute concentration in the first-stage overflow), and the underflow solids concentration attainable. Applications include processes in which the solution is the valuable component (as in alumina extraction), or in which purified solids are sought (magnesium hydroxide from seawater), or both (as frequently encountered in the chemical-processing industry and in base-metal hydrometallurgy).

The factors which may make CCD a preferred choice over other separation systems include the following: rapidly settling solids, assisted by flocculation: relatively high ratio of solids concentration between underflow and feed; moderately high wash ratios allowable (2 to 4 times the volume of liquor in the thickened underflows); large quantity of solids to be processed; and the presence of fine-size solids that are difficult to concentrate by other means. A technical feasibility and economic study is desirable in order to make the optimum choice.

Flow-Sheet Design   Thickener-sizing tests, as described earlier, will determine unit areas, flocculant dosages, and underflow densities for the various stages. For most cases, unit areas will not vary significantly throughout the circuit; similarly, underflow concentrations should be relatively constant. In practice, the same unit area is generally used for all thickeners in the circuit to simplify construction.

Equipment   The equipment selected for CCD circuits may consist of multiple-compartment washing-tray thickeners or a train of

individual unit thickeners. The washing-tray thickener consists of a vertical array of coaxial trays connected in series, contained in a single tank. The advantages of this design are smaller floor-area requirements, less pumping equipment and piping, and reduced heat losses in circuits operating at elevated temperatures. However, operation is generally more difficult and user preference has shifted toward unit thickeners despite the larger floor-area requirement and greater initial cost.

Underflow Pumping   Diaphragm pumps with open discharge are employed in some cases, primarily because underflow densities are readily controlled with these units. Disadvantages include the generally higher maintenance and initial costs than for other types and their inability to transfer the slurry any great distance. Large flows often are best handled with variable-speed, rubber-lined centrifugal pumps, utilizing automatic control to maintain the underflow rate and density.

Overflow Pumps   These can be omitted if the thickeners are located at increasing elevations from first to last so that overflows are transferred by gravity or if the mixture of underflow and overflow is to be pumped. Overflow pumps are necessary, however, when maximum flexibility and control are sought.

Interstage Mixing Efficiencies   Mixing or stage efficiencies rarely achieve the ideal 100 percent, in which solute concentrations in overflow and underflow liquor from each thickener are identical. Part of the deficiency is due to insufficient blending of the two streams, and attaining equilibrium will be hampered further by heavily flocculated solids. In systems in which flocculants are used, interstage effi-

TABLE 18-7   Typical Thickener and Clarifier Design Criteria and Operating Conditions

	Percent solids		Unit area, $m^2/(t/d)$°†	Overflow rate, $m^3/(m^2 \cdot h)$°
	Feed	Underflow		
Alumina Bayer process				
Red mud, primary	3–4	10–25	2–5	
Red mud, washers	6–8	15–35	1–4	
Hydrate, fine or seed	1–10	20–50	1.2–3	0.07–0.12
Brine purification	0.2–2.0	8–15		0.5–1.2
Coal, refuse	0.5–6	20–40	0.5–1	0.7–1.7
Coal, heavy-media (magnetic)	20–30	60–70	0.05–0.1	
Cyanide, leached-ore	16–33	40–60	0.3–1.3	
Flue dust, blast-furnace	0.2–2.0	40–60		1.5–3.7
Flue dust, BOF	0.2–2.0	30–70		1–3.7
Flue-gas desulfurization sludge	3–12	20–45	0.3–3†	
Magnesium hydroxide from brine	8–10	25–40	5–10	
Magnesium hydroxide from seawater	1–4	15–20	3–10	0.5–0.8
Metallurgical				
Copper concentrates	14–50	40–75	0.2–2	
Copper tailings	10–30	45–65	0.4–1	
Iron ore				
Concentrate (magnetic)	20–35	50–70	0.01–0.08	
Concentrate (nonmagnetic), coarse: 40–65% −325	25–40	60–75	0.02–0.1	
Concentrate (nonmagnetic), fine: 65–100% −325	15–30	60–70	0.15–0.4	
Tailings (magnetic)	2–5	45–60	0.6–1.5	1.2–2.4
Tailings (nonmagnetic)	2–10	45–50	0.8–3	0.7–1.2
Lead concentrates	20–25	60–80	0.5–1	
Molybdenum concentrates	10–35	50–60	0.2–0.4	
Nickel, $(NH_4)_2CO_3$ leach residue	15–25	45–60	0.3–0.5	
Nickel, acid leach residue	20	60	0.8	
Zinc concentrates	10–20	50–60	0.3–0.7	
Zinc leach residue	5–10	25–40	0.8–1.5	
Municipal waste				
Primary clarifier	0.02–0.05	0.5–1.5		1–1.7
Thickening				
Primary sludge	1–3	5–10	8	
Waste-activated sludge	0.2–1.5	2–3	33	
Anaerobically digested sludge	4–8	6–12	10	
Phosphate slimes	1–3	5–15	1.2–18	
Pickle liquor and rinse water	1–8	9–18	3.5–5	
Plating waste	2–5	5–30		1.2
Potash slimes	1–5	6–25	4–12	
Potato-processing waste	0.3–0.5	5–6		1
Pulp and paper				
Green-liquor clarifier	0.2	5		0.8
White-liquor clarifier	8	35–45	0.8–1.6	
Kraft waste	0.01–0.05	2–5		0.8–1.2
Deinking waste	0.01–0.05	4–7		1–1.2
Paper-mill waste	0.01–0.05	2–8		1.2–2.2
Sugarcane defecation			0.5‡	
Sugar-beet carbonation	2–5	15–20	0.03–0.07‡	
Uranium				
Acid-leached ore	10–30	25–65	0.02–1	
Alkaline-leached ore	20	60	1	
Uranium precipitate	1–2	10–25	5–12.5	
Water treatment				
Clarification (after 30-min flocculation)				1–1.3
Softening lime-soda (high-rate, solids-contact clarifiers)				3.7
Softening lime-sludge	5–10	20–45	0.6–2.5	

°$m^2/(t/d) \times 9.76 = ft^2/(\text{short ton/day})$; $m^3/(m^2 \cdot h) \times 0.41 = gal/(ft^2 \cdot min)$; 1 t = 1 metric ton.
†High-rate thickeners using required flocculant dosages operate at 10 to 50 percent of these unit areas.
‡Basis: 1 t of cane or beets.

ciencies often will drop gradually from first to last thickener, and typical values will range from 98 percent to as low as 70 percent. In some cases, operators will add the flocculant to an overflow solution which is to be blended with the corresponding underflow. While this is very effective for good flocculation, it can result in reflocculation of the solids before the entrained liquor has had a chance to blend completely with the overflow liquor. The preferable procedure is to recycle a portion of the overflow back to the feed line of the same thickener, adding the reagent to this liquor.

The usual method of interstage mixing consists of a relatively simple arrangement in which the flows from preceding and succeeding stages are added to a feed box at the thickener periphery. A nominal detention time in this mixing tank of 30 to 60 s and sufficient energy input to avoid solids settling will ensure interstage efficiencies greater than 95 percent.

The performance of a CCD circuit can be estimated through use of the following equations, which assume 100 percent stage efficiency:

$$R = \frac{O/U[(O/U)^N - 1]}{[(O/U)^{N+1} - 1]} \tag{18-49}$$

$$R = 1 - \left(\frac{U}{O'}\right)^N \tag{18-50}$$

for O/U and $U/O' \neq 1$. R is the fraction of dissolved value in the feed which is recovered in the overflow liquor from the first thickener, O and U are the overflow and underflow liquor volumes per unit weight of underflow solids, and N is the number of stages. Equation (18-49) applies to a system in which the circuit receives dry solids with which the second-stage thickener overflow is mixed to extract the soluble component. In this instance, O' refers to the overflow volume from the thickeners following the first stage.

For more precise values, computer programs can be used to calculate soluble recovery as well as solution compositions for conditions that are typical of a CCD circuit, with varying underflow concentrations, stage efficiencies, and solution densities in each of the stages. The calculation sequence is easily performed by utilizing material-balance equations around each thickener.

DESIGN OR STIPULATION OF A SEDIMENTATION UNIT

Selection of Type of Thickener or Clarifier   Selection of the type of unit thickener or clarifier depends primarily on the optimization of performance requirements, installation cost and operating cost. For example, the inclined-plate type of clarifier provides for less solids-holding capacity than a circular or rectangular clarifier, but at a lower installation cost. The high-density thickener maximizes underflow solids concentration, requiring a higher torque rating than conventional thickeners.

Most manufacturers have overlapping sizes in the bridge-supported, center-column-supported, and traction types even though an optimum economical size range exists for each type. Bridge-supported thickeners are generally selected for diameters less than 30 m (100 ft) and center-column-supported thickeners are selected for greater diameters. Traction units often are least expensive in sizes over 75 m (250 ft) if ground conditions permit installing proper supporting walls to carry the loads.

Special conditions affect the choice of thickener or clarifier type. For example, if a unit must be covered to conserve heat, the bridge-supported type may be more economical up to about 45 m (150 ft) in diameter, although 30 m (100 ft) may be the economic limit for an uncovered unit.

Materials of Construction   A wide variety of materials is available for tanks, as indicated earlier. Most mechanisms are made of steel; however, submerged parts may be made of wood, stainless steel, rubber-covered or coated steel, or special alloys.

Design Sizing Criteria   Table 18-7, which lists typical design sizing criteria and operating conditions for a number of thickener and clarifier applications, is presented for purposes of illustration or preliminary estimate. Actual thickening and clarification performance is dependent on particle size distribution, specific gravity, sludge bed compaction characteristics, and other factors. Final designs should be based on bench-scale tests involving the methods previously discussed.

If a solids-contact clarifier is required, the surface-area requirement must exclude the area taken up by the reaction chamber. The reaction chamber itself is normally sized for a detention time of 15 to 45 min, depending on the type of treatment and the design of the unit.

Torque Rating   The choice of torque rating has been discussed earlier. Torque is a function of such factors as quantity and quality of underflow (therefore, of such parameters as particle characteristics and flocculant dosage that affect underflow character), unit area, and rake speed; but, in the final analysis, torque must be specified on the basis of experience modified by these factors. Unless one is experienced in a given application, it is wise to consult a thickener or clarifier manufacturer.

THICKENER COSTS

Equipment   Costs vary widely for a given diameter because of the many types of construction. As a general rule, the total installed cost will be about 3 to 4 times the cost of the raking mechanism (including drivehead and lift), plus walkways and bridge or centerpier cage, railings, and overflow launders. Figure 18-93 shows the approximate installed costs of thickeners up to 107 m (350 ft) in diameter. These costs are to be used only as a guide. They include the erection of mechanism and tank plus normal uncomplicated site preparation, excavation, reinforcing bar placement, backfill, and surveying. The price does not include any electrical work, pumps, piping, instrumentation, walkways, or lifting mechanisms. Special design modifications, which are not in the price, could include elevated tanks (for underflow handling); special feedwell designs to control dilution, entrance velocity, and turbulence; electrical and drive enclosures required because of climatic conditions; and mechanism designs required because of scale buildup tendencies.

Operating Costs   Power cost for a continuous thickener is an almost insignificant item. For example, a unit thickener 60 m (200 ft) in diameter with a torque rating of 1.0 MN·m (8.8 Mlbf·in) will normally require 12 kW (16 hp). The low power consumption is due to the very slow rotative speeds. Normally, a mechanism will be designed for a peripheral speed of about 9 m/min (0.5 ft/s), which corresponds to only 3 r/h for a 60-m (200-ft) unit. This low speed also means very low maintenance costs. Operating labor is low because little attention is normally required after initial operation has balanced the feed and underflow. If chemicals are required for flocculation, the chemical cost frequently dwarfs all other operating costs.
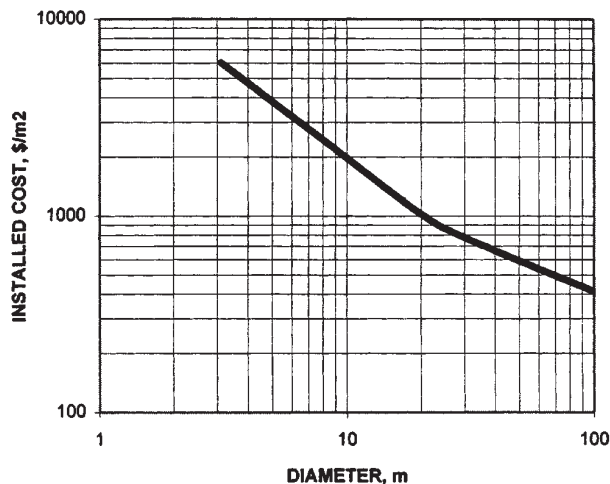

FIG. 18-93   Approximate installed cost of single-compartment thickeners (1995 dollars). To convert to ft and ft^2 units, multiply diameter in meters by 3.28 and divide cost by 10.76.