Foam Columns for Countercurrent Surface—Liquid Extraction of Surface-Active Solutes

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The foam separation process uses differences in surface activity to separate components of a solution. Stable foams can flow upward countercurrent to liquid to give countercurrent differential separations with stripping, enrichment, or scrubbing similar to solvent extraction.

Six- and 24-in. I.D. foam columns were operated with sodium dodecylbenzenesulfonate solutions to measure height of transfer unit (HTU) values and foam densities and to develop satisfactory gas spargers, liquid feed distributors, foam drainage conditions, and foam condensation equipment. The HTU values for stripping of Sr-89 were about 1 cm. for the best conditions of uniform foams, liquid flows of 100 gal./sq.ft.hr. or less, and uniform liquid feed distribution with low inlet velocities. Variations of countercurrent column lengths within 10 to 28 cm. caused little variation in HTU values. The foams were condensed, with four types of pneumatic or mechanical foam breakers used. A pilot plant was designed for decontamination of a low level radioactive waste.

The foam separation process uses differences in surface activity to separate components of a solution. The physical chemistry and many of the principles of importance have been reviewed as part of a book on new separation techniques (*1*). The selection of foaming-complexing agents for the separation of metals has been studied (*2, 3*). This report will be on the experimental engineering studies to determine how to design and operate an efficient foam column system. One problem was to measure and improve the efficiency of mass transfer between the surface and the liquid flowing countercurrent to each other. This efficiency or mass transfer rate is commonly expressed in terms of HTU values. A second problem was to develop satisfactory gas spargers, liquid feed distributors, foam drainage conditions, and foam condensation equipment for operation of large foam columns.

The thermodynamics of interfaces was examined by Willard Gibbs, and the most common basic equation for foam separation is called the *Gibbs equation:*

$$d\gamma = -\Sigma\, \Gamma_i\, d\mu_i \tag{1}$$

The products of the surface excess Γ and the differential of the chemical potential $d\mu$ must be summed up for all components. For a dilute solution (where the activity coefficient is 1) and a two-component system, the Gibbs equation may be simplified to

$$\alpha = \frac{\Gamma}{x} = -\frac{1}{RT}\frac{d\gamma}{dx} \tag{2}$$

In deriving this form of the equation, the interface position is selected to make the surface excess of solvent equal to zero.

The quantity Γ/x is in the form of an equilibrium constant between the surface and the liquid and is similar to the distribution coefficient for a solvent extraction system. If two components of a solution are to be separated by foam separation, one component must have a high value of Γ/x as compared with the other; that is one must be relatively more concentrated at the surface.

The amount of solute present as surface excess in the absence of large amounts of foam is small compared with the amount in the bulk of the solution. This is true even for highly surface-active compounds such as soaps or detergents. In a foam, the ratio of surface to liquid can be high. Many compounds which have a high surface activity also have the characteristics which stablize liquid films and thus give stable foams. When foams are formed with such compounds, the amount of the surface-active solutes present in the foam as surface excess may be large compared with that which would be present in the same amount of solvent in the bulk solution. Countercurrent, multiple stage separation similar to solvent extraction or distillation is possible with these stable foams. In a foam column, solution flows down countercurrent to the surface (that is foam) flowing up. Operations corresponding to stripping, enrichment, or scrubbing in solvent extraction are possible. The equilibrium relationship is given by the Gibbs equation. For the case of dilute, two-component solutions, $d\gamma/dx$ is often constant with concentration, and the distribution coefficient Γ/x is a constant.

One distinctive characteristic of foam separation is that it becomes more effective as concentrations decrease. It can only remove or separate surface-active solutes which are present in relatively low concentrations. Values of the equilibrium constant in the Gibbs equations are 10^{-2} to 10^{-4} cm. for many surface-active materials (*3*). These values along with normal foam densities indicate that foam separation is likely to be effective only for removing solutes present at less than 10^{-3} *M* concentrations. Even if a particular solute has little surface activity, it is often possible to combine or complex it into a more surface-active form.

EXPERIMENTAL PROCEDURES AND EQUIPMENT

Dodecylbenzenesulfonate (DBS) and strontium which forms surface-active $Sr(DBS)_2$ were selected for test purposes. One important criteria was the selection of a chemical system of

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low solute concentrations so as to give a constant distribution coefficient Γ/x and thus simplify the mass transfer calculations. Strontium-89 is a cheap, convenient pure beta tracer, while Strontium-85 is a convenient gamma tracer. By using these radioactive tracers, accurate analyses for surface-active $Sr(DBS)_2$ is possible at very low concentrations (3). The $Sr(DBS)_2$ has a small ionization constant, and essentially all the strontium is present in this surface-active form if there is an excess of relatively highly ionized Na(DBS).

The HTU values were determined for stripping of Sr-89 with 0.001 N NaOH and Trepolate F-95 which is a commercial sodium salt of DBS. The strontium, added to the liquid feed as $SrCl_2$ tracer and $Sr(OH)_2$, was present as $2 \cdot 10^{-6}$ M $Sr(DBS)_2$ which was extracted by countercurrent contact with foam generated in a liquid pool at the bottom of the column (Figure 1). After flowing through a chamber designed to promote drainage of the liquid between the foam bubbles, the foam was separated into condensed foam and gas in a foam breaker. The operating line is straight if there is no loss of surface area, that is collapse of bubbles, in the countercurrent region. The chemical conditions were selected to give a constant distribution coefficient and thus a straight equilibrium line. The liquid pool was well mixed and was deep enough for the bubble surfaces to approach equilibrium. The liquid pool thus was approximately equivalent to one theoretical separational stage or $y_1 = \alpha x_B$. The liquid concentrations and flow rates were accurately measured by conventional methods The newly generated surface was equivalent to an inlet stream of zero solute concentration or $y_B = 0$. The surface flow rates were measured by estimating average bubble sizes from photographs of bubbles (Figure 2) and setting

$$V = va = 6v/d \tag{3}$$

The procedure for evaluating d allows for a distribution of bubble sizes, the nonspherical shape, and other approximations (6). Since the determinations of the distribution coefficient α required the same type of surface area measurement, any consistent approximation errors involved would cancel out. Since the surface concentrations determined from the condensed foam analyses and the surface area rates were the least accurately known quantities, the flow rates for HTU measurements were selected to give pinching at the bottom of the column and some divergence of the operating and equilibrium lines at the top. Thus any uncertainties in knowledge of the surface concentrations were of less importance. These strontium stripping studies were done in a 6-in. I.D. glass column with up to 10 mcuries of Sr-89 per run. Samples were taken after time steady state was approached, 20 to 120 min. depending on the flow rates, column length, and other conditions.

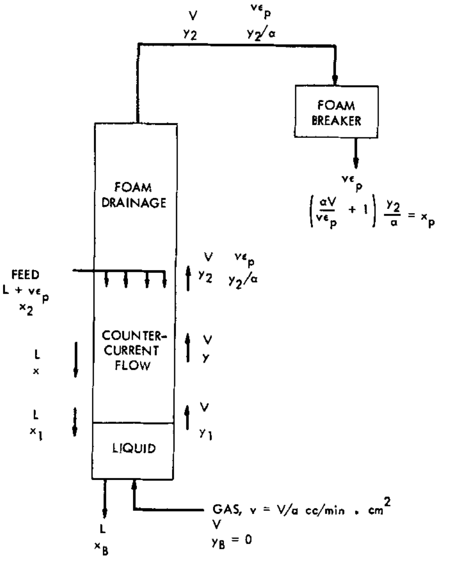


Fig. 1. Foam column flows and notation. Notation is per unit cross-section area of column.

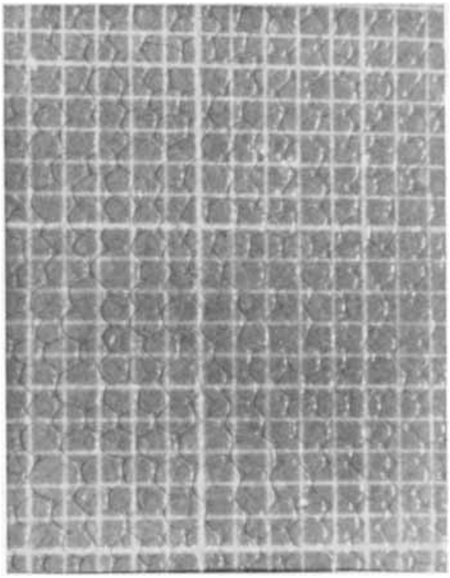


Fig. 2. Foam from nitrogen through 80-μ diameter holes of spinneret into 275 parts/million trepolate F-95 in 10^{-3} M NaOH, 1 mm. grid.

HTU DETERMINATIONS

The HTU values for stripping of Sr-89 were determined (see Appendix for method of calculation) for over a hundred combinations of conditions. The best HTU values were about 1 cm. These low values were obtained for conditions where there was plug flow of foam up the column, as indicated by visual observations and velocity measurements through the glass column wall and uniform flow of liquid down through the foam. The liquid flow rates and the dimensions of the liquid films between bubbles indicate low Reynolds numbers for the liquid, about 5 is a typical value. From this, one would expect streamline liquid flow and diffusion controlled mass transfer in the liquid.

The HTU values may be estimated for diffusion controlled mass transfer as follows:

$$\text{HTU} = L\left(\frac{l}{D}\right)\left(\frac{1}{a}\right) \tag{4}$$

The diffusion coefficient may be estimated to be $5 \cdot 10^{-6}$ sq.cm./sec. (4). The surface area per unit volume a is $6/d$. The average diffusion distance would be about 0.1 d from consideration of the bubble dimensions and foam densities (5, 6). Substitution of these values gives an expression for the diffusion controlled HTU values as a function of L and d:

$$\text{HTU} = 3{,}500\,Ld^2 \tag{5}$$

If the values of L corresponding to the lowest HTU values are substituted in Equation (5), the calculated HTU values would be about 2.9 cm. for $d = 0.1$ cm., 1.1 cm. for $d = 0.06$ cm., and 0.5 cm for $d = 0.04$ cm.

The effects of most variables on the HTU values appeared to be due to their effects on channeling. The lowest HTU values were obtained for what appeared to be plug flow of foam, and the foam had varying velocities for other conditions which gave high HTU values. For some of the worst conditions, large masses of foam flowed downward or liquid streamed down through one part of the column with most of the foam flow occurring at some other part of the column cross section.

Liquid Feed Distributors

One important requirement for avoiding channeling is that the liquid be distributed uniformly across the column cross section. For small columns of 2-in. I.D. or less, the liquid could simply be introduced through a tube at the column center line. Three types of liquid feed distributors were used for HTU studies in the 6-in. I.D. column. Results selected to illustrate the effect of these distributors (Table 1) show that uniform distribution of the liquid and low inlet velocities are necessary to obtain low HTU values. The single tube distributor *G* gave HTU values of 19 cm. for the 27-cm. countercurrent lengths. The weir type of distributor *E* gave a 14-cm. HTU value at a low flow rate, where the flows through the ten weir slots varied by ± 50% from the average flow but gave much better HTU values of 5 to 7 cm. for higher flow rates where the variations were about ± 30%. These flow variations were measured for discharge of water into air without foam. The *B* spider, which had 0.155-cm. I.D. capillary tubes, gave too-high liquid velocities which caused the liquid to jet down through the foam and thus resulted in high HTU values. The *C* and *F* spiders with capillaries of 0.240 and 0.376 cm. I.D., respectively, were the most effective sizes for the range of liquid flows used as shown by the low HTU values of 3 cm. or less. The *D* spider with 0.476-cm. I.D. tubes permitted siphoning at the lower flow rates tested and gave individual tube flow rates of ± 35% of the average at 720 cc./min. liquid flow. This siphoning caused a high HTU value of 8.2 cm. at 500 cm./min. but lower values of 1.5 to 2.9 cm. at higher flow rates. The effects of liquid feed distribution were controlling and almost completely masked the simultaneous effects of liquid rates.

The foam can distribute the liquid somewhat similarly to column packing. This effect was visible in both the 6- and 24-in. diameter columns and is shown by an HTU value of 2.2 cm. for a 57-cm. countercurrent length compared with 19 cm. for 27-cm. countercurrent lengths with the single tube distributor *G*. The use of screens across the column cross section to promote liquid distribution was not effective. A 20-mesh screen across the 6-in. diameter column resulted in accumulations of liquid which dumped through at irregular intervals.

Two liquid distributors were tested for visible channeling in a 24-in. diameter column. Nineteen capillary tubes with a 5-in. triangular spacing between tubes gave visible channeling as much as 30 in. below the tube ends even for relatively low flow rates. A distributor designed to give thirty-seven feed streams on approximately 3¾ in. triangular spacing did not cause significant channeling. This design used parallel, horizontal tubes spaced across the column cross section with 0.094-cm. diameter metering orifices drilled in the tubes. The orifice streams impinged on baffles and then dripped into the foam with little kinetic energy.

TABLE 1. EFFECT OF LIQUID FEED DISTRIBUTOR ON FOAM COLUMN HTU VALUES

Conditions: Stripping of Sr-89 from 0.001 N NaOH containing 275 parts/million Trepolate F-95, $\Gamma/x = 5.5 \cdot 10^{-3}$ cm.; spinneret gas spargers; 27- to 29-cm. column lengths

Liquid feed distributors Designation	Type	I.D., cm.	Liquid feed rates, cc./min.	HTU, cm.
B	Spider*	0.155	500	5.0
C	Spider*	0.240	500	2.8
			1,000-1,450	<0.5-1.8
F	Spider*	0.376	1,100	4.0
			1,450	2.1
D	Spider*	0.476	500	8.2
			1,100-1,450	1.5
G	Single tube	1.0	1,100-1,250	19.0
E	Weir†	—	1,100	14.0
			1,450	5.0

* Seven capillary tubes, one on the center line and six on a 4-in. diameter circle.
† Ten weir slots in a ring of tubing.

TABLE 2. EFFECT OF GAS SPARGER ON FOAM COLUMN HTU VALUES

Conditions: Stripping of Sr-89 from 0.001 N NaOH containing 275 parts/million Trepolate F-95, $\Gamma/x = 5.5 \cdot 10^{-3}$ cm.; spider liquid feed distributors; 19- to 45-cm. countercurrent column lengths

Gas sparger	Average pore diameter, μ	HTU, cm.
Spinneret *A*	50	<0.5 to 1.7
Spinneret *B*	80	0.5 to 1.8
EC fritted glass	*	2.3 to 5.7
Micrometallic *D*	65	4.7 to 5.6

* Maximum of 170 to 220 μ, average not reported.

Gas Spargers

The uniformity of the foam bubbles was important to the foam stability and to avoid channeling. The most uniform bubbles were obtained with spinnerets as used by the rayon spinning industry. Spinneret *A* had about 1,800 50-μ diameter holes and gave about 0.6-mm. diameter bubbles. Spinneret *B* had about the same number of 80-μ diameter holes and gave about 1.0-mm. diameter bubbles. The extra coarse porosity fritted glass gave about 0.4-mm. diameter bubbles which were considerably less uniform than the bubbles from the spinnerets. Sintered stainless steel gas spargers gave much less uniform bubbles than the fritted glass. The best HTU values with the spinnerets were in agreement with diffusion controlled mass transfer as previously mentioned. Smaller bubbles should give lower HTU values, since the distances for diffusion are smaller. However, the experimental HTU values for the fritted glass gas spargers were larger than those from the spinnerets and were never as small as would be expected for diffusion controlled mass transfer in the liquid (Table 2).

Column Length

There was little variation in HTU values with column length at good operating conditions for countercurrent lengths of 10 to 28 cm. If the liquid distribution is not uniform at the feed point, inefficient countercurrent contact for a distance below the feed point may result with efficient contact below this region. The HTU values for 50-, 60-, and 85-cm. countercurrent lengths scattered badly probably because the large number of transfer units is difficult to measure. About two-thirds of the HTU values were larger, and about one-third were smaller than the values for shorter countercurrent lengths at otherwise similar conditions.

Flow Rates

The experimentally observed effects of flow rates were a complex combination of effects from channeling, from liquid feed distribution differences, and from bubble diameter changes. These effects obscured the increase in HTU values with flow rates which would be expected for otherwise constant conditions. The flow rates at which excessive channeling begins to occur may be estimated from the following equation derived for the drainage of liquid through foam bubbles (*5*, *6*):

$$L + \frac{v}{1-\epsilon}\,\epsilon = 0.225\,\epsilon^2 d^2 \frac{\rho g}{32\mu} \tag{6}$$

This equation is otherwise dimensionally consistent if d has the units of centimeters. Channeling becomes excessive for conditions which would give values of $\epsilon > 0.30$ in the above equation. When the equation indicates values of $\epsilon < 0.26$, excessive channeling did not occur if the liquid feed was uniformly distributed and the foam bubbles were uniform in diameter. Fluidization of the foam bubbles would be expected at about $\epsilon = 0.26$, since this is the void volume of close packed spheres.

FOAM DRAINAGE

A low density is desirable for the foam discharged from a foam separation column in order to obtain a high volume reduction, that is in order to obtain the separated surface-active materials in a minimum volume of condensed foam. Since the foam leaving the countercurrent part of a foam column has a relatively high liquid content, a drainage section is usually desirable to promote drainage of liquid from the foam. The foam column conditions are picked to give a stable foam in the countercurrent region. Therefore the drainage occurs mostly by flow of liquid between the foam bubbles and not by loss of surface.

For foam columns of small diameter, drainage is conveniently obtained in vertical drainage sections (Figure 3). Drainage approaches equilibrium for a stable foam after several feet of vertical drainage section, since the downward liquid velocity with respect to the foam is opposed by the upward flow of foam. This vertical velocity may be reduced and better drainage obtained by increasing the column cross section to decrease the vertical foam velocity. From a model for foam drainage confirmed by experimental results (*5*, *6*), the exit foam density for a vertical drainage section may be estimated from

$$\epsilon_p = 3.2 \cdot 10^{-4} \frac{v}{d^2} \tag{7}$$

For low values of v (less than 0.1 cm./sec.), the foams are dry and less stable so that the average bubble diameter d increases as the foam flows through the drainage section.

For large diameter foam columns, horizontal foam drainage sections (Figure 3) are more practical than enlarged vertical sections. Foam tends to flow straight through the vertical drainage sections without expanding to give a lower vertical velocity. This is more probable as the diameter increases. A dry foam is more resistant to shear than a wet foam, so that any stagnant areas are self-perpetuating. In a horizontal drainage section, increased drainage is obtained by increasing the length instead of the diameter, and channeling through the drainage section is less likely.

The previously mentioned foam drainage model and experimental results (*5*, *6*) give the following equation for the exit foam densities for horizontal drainage sections:

$$\frac{1}{\bar{\epsilon}} - \frac{1}{\bar{\epsilon}_o} = \frac{2{,}800\, d^2 (t - t_o)}{h} \tag{8}$$

Horizontal baffles may be used to promote drainage by decreasing the effective value of h.

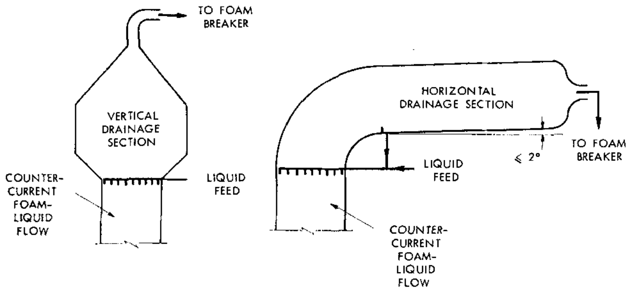
FOAM CONDENSATION

After the foam leaves the column, it must be condensed and separated into a liquid solution or slurry and a gas. Chemical and thermal methods of foam breaking are known, but mechanical condensation appeared more desirable for most foam separation systems. A sonic whistle operated by 40 lb./sq. in. air to give high intensity sound at 12,000 cycles/sec. was used for condensing foam during the HTU measurements. It was convenient and effective for this scale of work. Capacities of 0.2 cu. ft. of foam per standard cubic feet of operating air are reported in the technical literature, but the experimentally observed capacities were about 0.05 cu. ft. per standard cubic feet for the stable DBS foams. The capacity is further reduced if a diaphragm is used to separate the foam and the whistle. The power required for the operating air and the large volume of off gas may both be significant disadvantages for large systems.

Small, slow speed centrifuges with perforated bowls lined with 80- or 100-mesh screen were practical foam breakers. Lower speeds gave smaller volumes of uncondensed foam, while the capacity increased as the speed increased. The amount of uncondensed foam discharged was also greatly reduced by using a Teflon sheet instead of glass as the stationary wall on which the discharged liquid impinged.

Orifice Foam Breakers

From consideration of foam breaking mechanisms, condensation of foam by discharge through an orifice was considered and tested. Foams generated from Trepolate F-95 solutions in 6- and 24-in. diameter columns were drained to varying densities and drawn through an orifice by vacuum (Figure 4). The pressure drop across the orifice was controlled by venting the foam source to the atmosphere and controlling the vacuum into which the orifice discharged. The amounts of uncondensed foam were measured by operating the orifice for 2 to 5 min. and then venting the vacuum pot and discharging the liquid and foam into a graduate.



a. VERTICAL DRAINAGE b. HORIZONTAL DRAINAGE

Fig. 3. Foam column drainage section configurations.

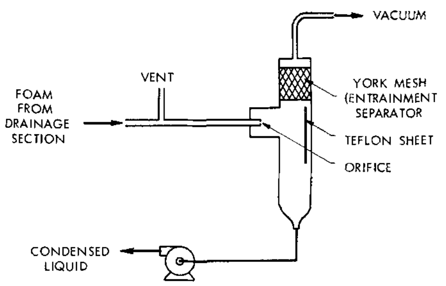


Fig. 4. An orifice foam breaker system.

The experimental results show that foams are easily condensed by an orifice with residual foam volumes of about 0.001 of the inlet volumes for the well-drained foams. Pressure drops from atmospheric for the inlet foam to ½ atm. in the vacuum pot were adequate. The same pressure ratio would probably apply at other pressures; that is an upstream to downstream pressure ratio of 2 is probably adequate. With the inlet foam at atmospheric pressure, condensation was less complete for 30 or 25 cm. of mercury pressure drop and became very poor for lower pressure drops.

The results indicate that the condensation occurs as the bubbles pass through the orifice and that orifices smaller than the bubble and impingement of the bubbles on a surface are not necessary. The condensation of foam was about equally efficient for 0.15-, 1.0-, and 2.5-mm. orifices. Since the foam bubbles were 0.5- to 0.8-mm. diameter, the 0.15-mm. diameter would be smaller than nearly all the bubbles, while the 2.5-mm. diameter would be larger than nearly all the bubbles. For most of the tests, the stream from the orifices impinged on a Teflon sheet placed 2 to 3 in. from the orifice. The amount of uncondensed foam was slightly decreased by placing the orifice 24 in. from the Teflon sheet. The amount of uncondensed foam was slightly greater for a glass surface in place of the Teflon sheet. It appeared that the foam bubbles broke before they hit the surface and that the liquid striking the surface caused some formation of new foam bubbles depending on the material and position of the surface.

The drier foams from lower foam rates or better drainage gave smaller fractions of uncondensed foam. This may have been due to less formation of new foam bubbles on the Teflon surfaces when the inlet foam was drier.

The capacities of the orifices as foam breakers appeared to be inversely proportional to the square root of the foam density as would be expected from orifice equations. The observed capacities agree with the following:

$$q = 6{,}000\, D_o^2 \sqrt{\frac{\Delta P}{\epsilon}} \tag{9}$$

This equation indicates somewhat higher flows than would be calculated for gases of the same densities as the foams.

PILOT PLANT

The results of these studies were applied to design of a foam separation pilot plant for decontamination of low level aqueous waste at the Oak Ridge National Laboratory. The controlling activity in terms of permissible concentrations is Sr-90.

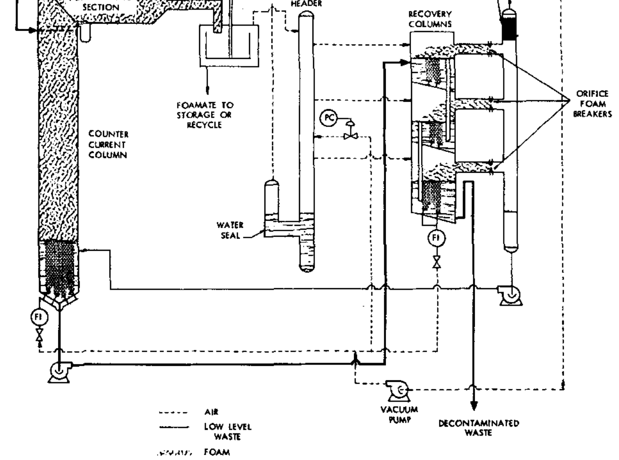


Fig. 5. Foam separation pilot plant.

The low level waste, after a pretreatment to remove part of the calcium and magnesium, flows through an 8 ft. high, 24-in. square foam column and three additional stripping stages (Figure 5). The stripping stages give additional removal of strontium and strip the DBS to the lowest concentration which will foam. The gas is recycled, and the only off gases are from pressure changes in the system. Both the centrifuge and orifice foam breakers are used to obtain scale-up data, since higher capital costs for a centrifuge may be less important than higher power costs for pumping gas for an orifice foam breaker.

NOTATION

a = surface area of dry foam, sq. cm./cc.
A = cross-section area of a column, sq. cm.
d = average foam bubble diameter, cm.
D = diffusion coefficient, sq. cm./sec.
D_o = orifice diameter, cm.
g = gravitational constant, cm./sec.^{2}
h = height of a horizontal drainage section, cm.
l = distance for diffusion, cm.
L = superficial liquid velocity, cm./sec.
ΔP = pressure drop, cm. of mercury
q = total foam flow rate, cc./min.
R = gas constant
$t - t_o$ = time in a horizontal drainage section, sec.
T = temperature
v = superficial gas velocity, cm./sec.
V = surface flow rate, sq. cm./sq. cm. sec.
x = bulk solution concentration of solute, amount/cc.
y = surface concentration of solute, amount/sq. cm.

Greek Letters

α = distribution coefficient, at equilibrium $\alpha = \Gamma/x$, cm.
γ = interfacial tension, dynes/cm.
$\Gamma(\Gamma_i)$ = surface excess (of ith component), amount/sq. cm.
ϵ = volume fraction of liquid in foam
ϵ_p = volume fraction of liquid in exit foam from vertical drainage section
$\bar{\epsilon}_o, \bar{\epsilon}$ = inlet and outlet volume fraction of liquid in foam for horizontal drainage section
μ = viscosity, poise
μ_i = chemical potential of ith component
ρ = solution density in g./cc.
See Figure 1 for meaning of subscripts

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APPENDIX TRANSFER UNIT CALCULATIONS

The number of transfer units based on the liquid phase N is calculated from the simple equation for linear operating and equilibrium lines.

$$N = (x_2 - x_1)\left[\frac{\ln\dfrac{x_2 - y_2/\alpha}{x_1 - y_1/\alpha}}{(x_2 - y_2/\alpha) - (x_1 - y_1/\alpha)}\right] \qquad (10)$$

$$N = \frac{x_2 - x_1}{(x - y/\alpha)_{\ln\ \mathrm{mean}}} = \frac{\text{height of contacting section}}{\text{HTU}} \qquad (10a)$$

While x_2 is measured directly, the other values needed to use Equation (10) must be calculated from other measurements. The volume flow rates of the liquid feed $L + v\epsilon_p$, the condensed foam $v\epsilon_p$, and the gas v were measured. The strontium tracer concentrations in the liquid feed x_2, the effluent liquid x_B, and the condensed foam x_p were measured. An average bubble diameter d was determined from photographs of the foam (Figure 2) by a counting procedure described in detail elsewhere (6). The surface flow rate was calculated from this diameter:

$$V = va = 6v/d \qquad (3)$$

Since the liquid pool is assumed to be equivalent to one theoretical stage, the streams leaving this pool are in equilibrium and

$$y_1 = \alpha x_B \qquad (11)$$

A solute material balance for this liquid pool can be rearranged to give

$$x_1 = x_B\left(1 + \frac{V\alpha}{L}\right) \qquad (12)$$

A solute material balance for the condensed foam can be rearranged to give

$$y_2 = \frac{v\epsilon_p x_p}{V + v\epsilon_p/\alpha} \qquad (13)$$

The values measured for calculation of N from these equations were checked for consistency by calculating solute balances for the whole column.

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Constitutive Equations for Viscoelastic Fluids with Application to Rapid External Flows

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A major problem in the analysis of complex flows of viscoelastic fluids lies in the development of a suitable constitutive equation relating stresses to the kinematics of deformation. In this paper an equation is developed from successive approximations to a very general theory of viscoelasticity. This equation, which predicts both a non-Newtonian viscosity coefficient and normal stress effects in simple laminar shearing flows, appears to reflect a reasonable compromise between simplicity and useful applicability to real materials.

The use of this equation is illustrated by means of a study of rapid flows about submerged objects. The results of this study are compared with the usual boundary-layer theory for Newtonian fluids, and the implications of this comparison are discussed in some detail.

One of the most important current engineering problems concerning non-Newtonian fluids involves the need for development of suitable constitutive equations with which to express the behavior of viscoelastic systems in complex flow fields, a problem to be distinguished from that of simple viscometric flow fields which have been studied extensively to date. While an understanding of viscometric flow fields does include a number of problems of engineering interest, at least as a useful approximation, most flow fields encountered in the processing of molten polymers are much more complex; an example of similarly complex flow fields involving dilute solutions occurs in the use of polymeric additives to reduce frictional drag in pipelines under turbulent flow conditions. In order to progress in the quantitative study of any of these flow fields by means of either mathematical analyses or experimental endeavors guided by dimensional analysis, it is necessary to have a suitably simple yet adequately general equation relating the stresses in the fluid to its deformational behavior.

In this paper new methods are introduced for obtaining approximate constitutive equations describing viscoelastic materials. The resulting equations are applied to the study of rapid external flows, and the results of this study are discussed in terms of the boundary-layer theory of Newtonian fluid dynamics.

CONSTITUTIVE THEORY

The full nonlinear significance of constitutive theories was first realized by Oldroyd (33) in 1950; an accurate history of recent developments has been published by Rivlin (37). It would appear that the best approach to be used in developing a constitutive theory is to limit all assumptions to those which experience would suggest to be general enough to describe the stress-deformation behavior of polymeric media; of several approaches attempted to date one of the most satisfactory appears to be that in which it is assumed that the stress depends not only upon the instantaneous strain from some arbitrary state but upon the entire history of the deformation, the dependence being in such a manner that strains in

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