Separation & Purification Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

Foam Separation Methods

P. Somasundaran[a]
[a] Henry Krumb School of Mines Columbia University, New York, N. Y.

To cite this Article Somasundaran, P.(1973) 'Foam Separation Methods', Separation & Purification Reviews, 1: 1, 117 — 198
To link to this Article: DOI: 10.1080/03602547308068939
URL: http://dx.doi.org/10.1080/03602547308068939

FOAM SEPARATION METHODS

P. SOMASUNDARAN[240]
Henry Krumb School of Mines
Columbia University
New York, N. Y. 10027

An overview of various foam separation techniques--foam fractionation, ion flotation, foam flotation, microflotation, precipitate flotation and, particularly, froth flotation—based on preferential concentration at the liquid/gas interface of detergents, proteins, microorganisms, minerals, and surfactant-ion complexes containing, for example, such radioactive impurities as radium and strontium or such inorganic wastes as dichromate, phosphate and lead is presented. Recent theoretical and developmental work in the area is summarized. The relationship between adsorption at various interfaces and froth flotation of minerals is examined along with a brief analysis of the physical principles involved. Finally, a discussion of various foaming devices and a summary of reported applications of the techniques are given.

INTRODUCTION

The separation of soluble or insoluble materials from solutions is difficult when their concentrations are relatively small as most of the separation techniques then become inefficient. The problem is all the more serious if the components to be separated are sensitive, like enzymes, to changes in the operating conditions like temperature. A group of methods which appear to be useful for separating almost any material, particularly when its bulk concentration is low, are what have been called foam separation techniques and more recently adsorptive bubble separation techniques(1,2). These methods are based primarily on the tendency of the organic components of a solution to preferentially concentrate at the liquid/gas interface and the tendency of certain other components to associate with these organic compounds. In most adsorptive bubble separation techniques, the amount of liquid/gas interface available for the above components to adsorb is increased by generating foam, and then the components are separated by simply removing the foam mechanically. These techniques are listed and classified in Table I on the basis of the particle size of the material and the mechanism by which it is separated. The nomenclature used here is derived from the suggestions of Karger et al(1), Pinfold(3), and Rubin(4) for the various foam separation techniques. If a species is naturally surface active, it can be separated simply by providing enough liquid/gas interface and by collecting the resultant foam. Such a separation is called "foam fractionation" for the separation of surface-active molecules, "foam flotation" for that of hydrophobic colloids, and "froth flotation" for that of sieve-size particles of crushed naturally hydrophobic minerals such as sulphur and graphite. If the species to be separated is not naturally surface active, a surface active agent that would associate with the species in some manner is added and then foaming conducted to remove the surfactant-species complex. This process is called "molecular flotation" or "ion flotation" for the separation of submicro species (ex: complexes of strontium, lead, cyanides, and phosphates with surfactants). The separation of particulates of colloid size by this technique is called "microflotation" and of sieve-size particles of naturally hydrophilic minerals such as silica and alumina is called "froth flotation". Finally, there is the interesting technique called "precipitate flotation", where the species to be separated is first precipitated, usually by changing the pH of the bulk solution, and then floated

TABLE 1. VARIOUS ADSORPTIVE BUBBLE SEPARATION METHODS CLASSIFIED ON THE BASIS OF MECHANISM OF SEPARATION AND SIZE OF THE MATERIAL SEPARATED

MECHANISM	SIZE RANGE		
	MOLECULAR	MICROSCOPIC	MACROSCOPIC
Natural surface activity	FOAM FRACTIONATION ex: detergents from aqueous solutions	FOAM FLOTATION ex: micro-organisms, proteins, dyes	FROTH FLOTATION of non-polar minerals ex: sulfur
In association with surface active species	ION FLOTATION MOLECULAR FLOTATION ex: Sr^{++}, Ag^{++}, Pb^{++}, Hg^{++} cyanides, phosphates	MICRO FLOTATION ex: particulates in waste, micro-organisms	FROTH FLOTATION ex: minerals such as silica PRECIPITATE FLOTATION (1st and 2nd kind) ex: ferric hydroxide

with the help of surfactants which adsorb on the precipitates. It has been shown by researchers in this area that it is possible to separate a large number of materials using one or the other of the above techniques, sometimes even when the concentration of the material to be separated is as low as 10^{-10} M/l(5). The reason for this becomes evident when the basic principles of foam separation are examined.

BASIC PRINCIPLES

As stated earlier, foam separation is possible because either the material to be separated or a complex of it with another reagent selectively concentrates at the liquid/gas interface. An understanding of the mechanisms of various interfacial phenomena is therefore essential for obtaining best results using these separation techniques. The principles of the adsorption of surfactants at the liquid/gas interface are understood well and utilized ingeniously in this area. However, the mechanisms by which various materials interact with the surfactants leading to their separation, even though well established in some areas like froth flotation, are not yet fully utilized in other foam separation techniques such as precipitate flotation and microflotation. These mechanisms will therefore be reviewed in detail in this paper, after a brief discussion of the relevant theories of adsorption at the liquid/gas interface.

Positive adsorption of surfactants at the liquid/gas interface results when the interaction energy among the solvent water molecules themselves is greater than that between the solvent water molecules and the solute surfactant molecules or ions, and hence the existence of the surfactant molecules in the bulk is less favorable than their existence at the surface. When the size of the nonpolar part of the surfactant molecules is increased, they interfere with the interaction of the water molecules to a greater extent and thus cause it to be less favorable for them to stay in the bulk. Therefore such an increase in size should cause an increase in adsorption. This is actually found to be the case as shown by the results for the adsorption of alkyl ammonium acetates of various chain lengths at the liquid/gas interface(6) (Figure 1). It can be seen

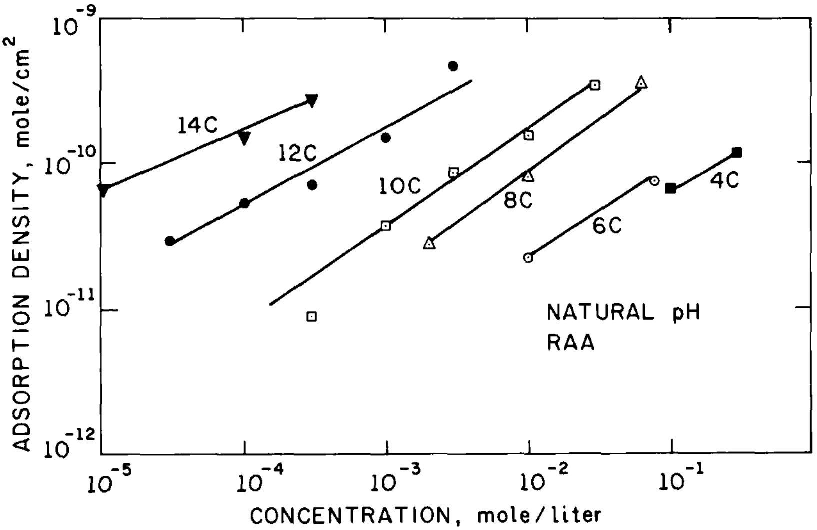

Figure 1. Adsorption density of various long-chain alkyl ammonium ions at the liquid/gas interface(6).

that the increase in chain length causes an increase in the surface excess of the reagent; this in turn can be expected to lead to an increased separation of the reagent if foam is generated and removed. On the other hand, increase in the number of polar groups or the number of double and triple bonds on the surfactant willdecrease its incompatibility with a polar medium such as water and hence its adsorption at the liquid/gas interface(7). Solution properties such as ionic strength and temperature also play a role in determining the nature of the distribution of surfactants between the bulk and the various interfaces. In general, an increase in ionic strength or a decrease in temperature increases the segregation of the surfactants at various interfaces(8,9). There are, however, several exceptions to the above statement in regard to the adsorption of the surfactants at the solid/liquid interface, and these will be discussed elsewhere.

Several theoretical models are available for describing the adsorption of surfactants at the liquid/gas interface. Most popular among them is that based on the Gibbs adsorption isotherm. Its application to foam separation methods has been discussed in detail by various authors including Rubin and Gaden(10), Lemlich(11,12), and Karger and Devivo(13). For solutions containing only one surface active agent, the Gibbs equation relates the interfacial excess Γ_i to its bulk concentration C_i by the expression:

$$\Gamma_i = (a_i/RT)(d\gamma/da_i) = (C_i/\beta RT)(d\gamma/dC_i) \qquad (1)$$

where γ is the surface tension of the solution under consideration and a_i is the activity of the surfactant species i and is equal to concentration C_i for the dilute solutions usually considered. β is 1 for solutions containing nonionic surfactants only or ionic surfactants in the presence of excess electrolytes and is 2 for those containing an ionic surfactant without any excess electrolyte present. Equation (1) is based on the Gibbs convention of zero surface excess for the solvent. Its application under various conditions has been discussed by several workers including Chattoraj(14). The distribution coefficient Γ_i/C_i which determines the extent of removal of the surfactant by foams, is given in Figure 2 as a function of the concentration of the surfactant. It can be seen from an examination of this figure that the relative segregation of the surfactant will actually be higher at lower surfactant concentrations. The de-

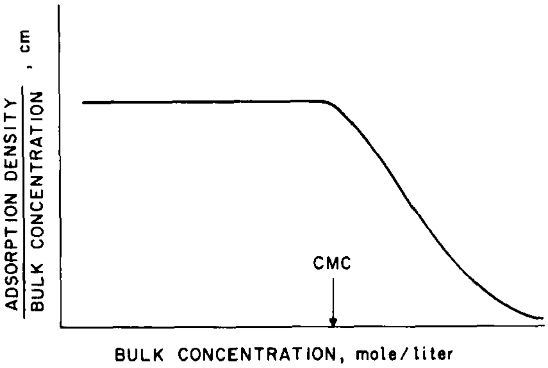

Figure 2. Distribution coefficient as a function of bulk surfactant concentration.

crease in coefficient after a particular concentration is due to the formation of micelles at this concentration. Above the critical micelle concentration (CMC), increase in the activity and adsorption of the surfactant at the liquid/gas interface with increase in the total concentration of the surfactant is very much smaller than the increase below the CMC$^{(15)}$. This higher distribution factor at lower concentration, an experimentally verified fact$^{(16,17)}$, is responsible for the success of foam separation methods at very low concentration of the material to be separated, the only condition being that there be enough surfactant of one kind or another for generating the foam.

For solutions containing nonionic surfactants, or ionic surfactants at very low concentrations, the Langmuir isotherm is applicable. On the basis of this, the distribution coefficient for the surfactant i is:-

$$\frac{\Gamma_i}{C_i} = \frac{k_1}{k_2 C_i + 1} \tag{2}$$

where k_1 and k_2 are constants for the system under consideration. At very low concentrations, k_2C_i becomes negligible in comparison with 1. Equation (2) then leads to the same conclusion as that obtained using the Gibbs equation regarding the constancy of the distribution coefficient.

When the reagent under consideration is a long chain surfactant, the enhancing effect on adsorption of the lateral van der Waal's attraction between the chains adsorbed at the interface must be considered, particularly at high adsorption densities, the retarding effect on adsorption of the repulsion between the polar heads of the adsorbed surfactant must also be considered if the surfactant is ionic. An equation that would be valid for the adsorption of such ionic long chain surfactants has been derived by Davies and Rideal$^{(7)}$. The distribution coefficient for the surfactant on the basis of this equation is:

$$\frac{\Gamma_i}{C_i} = \frac{(B_1/B_2)\exp[(W - z_i e\,\psi_o)/k\,T]}{1 + (B_1/B_2)\,A_o\,C_i\,\exp\,[(W - z_i e\,\psi_o)/k\,T]} \tag{3}$$

where W is the van der Waals' energy of desorption of 1 molecule of a long-chain hydrocarbon, z_i is the valency of the long chain ion i, ψ_o is the surface potential, A_o is the limiting area available to each long chain ion at the surface and B_1 and B_2 are constants. W is related to the number of $-CH_2-$ groups, n, in the chain by the equation:-

$$W = n\left(\frac{600}{N} + \frac{1200}{A^{1/2}} - 53.5\right) \qquad (4)$$

where A is the area in $Å^2$ available at the surface to each ion and N is the Avogadro's number. The main advantage of this expression over the others discussed earlier is that it takes into account the decrease in adsorption at higher concentrations due to the electrical double layer created at the interface by the process of adsorption itself. This decrease in adsorption is reduced if excess electrolyte is present in the solution to provide a large amount of counter ions. However, this is reflected in the equation only if ψ_δ, the potential at the plane of closest approach of the counter ion to the adsorbed long chain ions, is used instead of ψ_o. Also, the transfer energy of the long chains from the interface to the bulk will increase with an increase in ionic strength of the bulk solution(18). The numerical constants in equation (4) are hence not strictly applicable when external ions are present, as they would be in the case of ion flotation. The distribution coefficients of the surfactants can be expected to increase with an increase in ionic strength. The distribution coefficients for a particular inorganic ion associating with the adsorbed surfactant cannot, however, be expected to increase under these conditions. If the ionic strength increase is due to increase in concentration of other ions, the competition presented by them for association with surfactant species will reduce the separation of the particular inorganic ion under consideration at the interface. On the other hand, if the increase in ionic strength is due to the particular inorganic electrolyte itself, its separation at the interface will increase (provided the increase in ionic strength has not caused the formation of micelles of the surfactant), but not at a rate that is larger than the increase in the bulk concentration. Its distribution coefficient, Γ_i/C_i, could not be expected to improve under those conditions where the ionic strength has increased due to an increase in its own bulk concentration. It must be remembered at this point, that ionic strength and such variables will also affect such factors as the stability of foams and the drainage of the bulk liquid from in between the foams, and that it is the total of all these effects that is important for the separation itself. Indeed, a good distribution coefficient is the first necessary condition for good separation.

If two or more surfactants are present in the system, separation of one from the other is best conducted just below the critical micelle concentration of the reagent that is present in relatively large quantity. The reason for this becomes evident if we examine a surface tension versus concentration curve for a surfactant solution containing an additional surfactant as impurity. Such a curve is given in Figure 3. Initially, the surface tension is seen to decrease steadily with increase in concentration of the major surfactant as all surfactants are adsorbing at the liquid/gas interface in increasing quantities. Once the critical micelle concentration of the surfactant is reached, the impurity is solubilized by the micelle and the concentration of the impurity at the liquid/gas interface decreases causing an increase in the surface tension of the

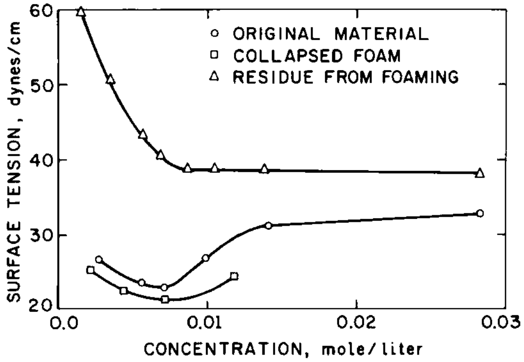

Figure 3. Surface tension of impure and foam-fractionated sodium lauryl sulfate solutions(19).

solution. If it is desired to remove the impurity, it is therefore helpful to foam the solution below the CMC of any of the surfactants present in the solution. When the solution has been foamed a sufficient number of times below such CMC's and the foam containing the impurity removed, the minimum in surface tension will gradually disappear and the resultant solution can be considered to contain a pure surfactant. The foamate collected will contain a relatively higher concentration of the impure surfactant in it than in the original solution. This technique has been used by several workers(15) to purify their surfactant solutions. Rubin and Jorne(20) have recently described expressions for the distribution coefficient of a surfactant in the presence of other surfactants. They have also derived theoretical expressions for the distribution coefficient of one surfactant relative to that of another on the basis of the Gibb's isotherm, the Langmuir isotherm, and the Davies and Rideal isotherm. These expressions have direct application in the separation of one surface active agent from another and are given below. The relative distribution coefficient α_{AB} for two surface active species A and B defined as $\frac{\Gamma_A}{C_A}/\frac{\Gamma_B}{C_B}$ on the basis of Gibb's isotherm is given by:

$$\alpha_{AB} = \frac{2\,C_B + C_A\left[\frac{\partial\gamma}{\partial \ln(C_A + C_B)} + RT\,\Gamma_B\right] C_A}{2\,C_A + C_B\left[\frac{\partial\gamma}{\partial \ln(C_A + C_B)} + RT\,\Gamma_A\right] C_B} \qquad (5)$$

in the absence of excess counter ions and by:

$$\frac{\left(\frac{\partial\gamma}{\partial \ln C_A}\right) C_B}{\left(\frac{\partial\gamma}{\partial \ln C_B}\right) C_A} \qquad (6)$$

in the presence of excess counter ions. Γ_A and Γ_B are again adsorption densities of species A and B at the liquid/gas interface at bulk concentrations C_A and C_B respectively. On the basis of the Langmuir isotherm, the relative distribution coefficient is a constant and on the basis of the Davies and Rideal isotherm, it is given by:

$$\alpha_{AB} = K \exp \left[(n_A - n_B) \left(\frac{521}{RT} + \frac{1200 \times 7750}{kT} \Gamma_{A,B}^{1/2}\right) \right] \quad (7)$$

where $\Gamma_{A,B}$ is the total surface excess of the two solutes, and K is a constant. Equation (7) indicates that the relative distribution coefficient will not be a constant, but will be proportional to the square root of the total adsorption density. Furthermore, n, the effective number of $-CH_2-$ groups, should not be considered as a constant but rather as a function of the total adsorption density. The relative distribution coefficient obtained by Rubin and Jorne on the basis of various adsorption models is reproduced in Figure 4 along with some of their experimental data for the selective removal of sodium laurylsulfate from sodium dodecylbenzenesulfonate. In spite of the large scattering of data, it could be seen that the relative distribution coefficient is not constant. For separation of A from B, one must then conduct foaming under condition of maximum α_{AB}. Since it is found that α_{AB} increases with increase in concentration of either surfactant until a CMC is reached and then decreases sharply, best separation could be expected just below the CMC of either compound.

While successful separation of surface active materials depends on their adsorption at liquid/gas interfaces, that of the nonsurface active materials by foam separation techniques depends on the extent of association that is possible between these nonsurfactive materials and a surfactant that can be safely added to the system. For example, in ion flotation the association between the ions to be separated and the oppositely charged surfactants due to the electrostatic attraction between them is put to use. In the absence of excess electrolyte, adsorption of the ions due to electrostatic attraction alone will be given on the basis of the Boltzmann distribution equation as:

$$\Gamma_{(+)(-)} = k' \, C_{(+)(-)} \exp \left[(-z_{(+)(-)} e \, \psi_\tau + \varnothing_{(+)(-)})/kT \right] \quad (8)$$

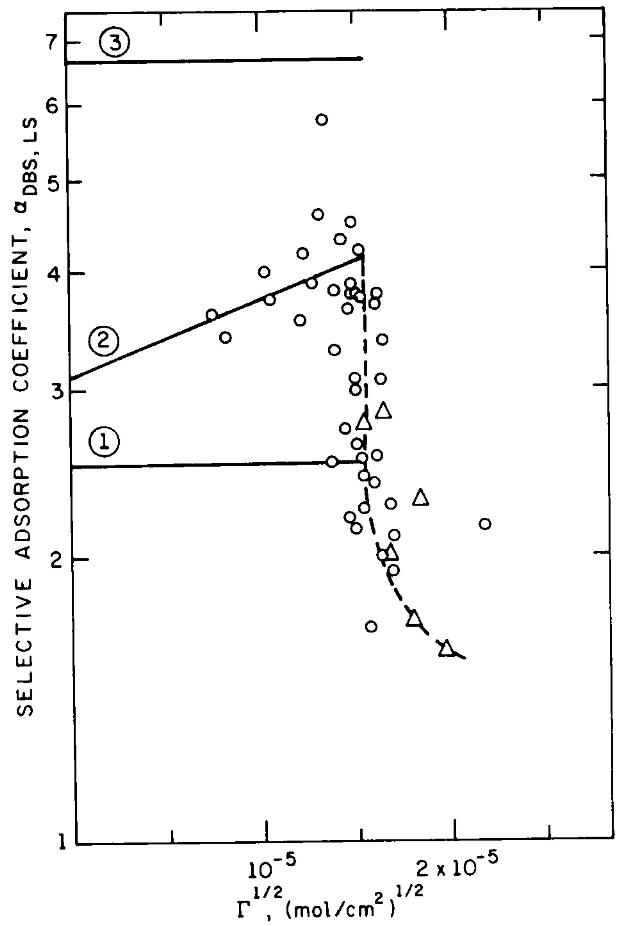

Figure 4. Adsorption coefficient of docecylbenzene sulfate (DBS) relative to that of lauryl sulfate (LS) as a function of total surface excess.(20)

1. Langmuir model (foaming experiment),
2. Long-chain ions model,
3. Langmuir model (surface tension).

where $C_{(+)(-)}$ is the bulk concentration of the positive or negative counter ions under consideration, z is its valency including sign, ψ_T is the potential at the plane of closest approach of these ions to the interface and generated due to the adsorption of the surfactant and k' is a constant for converting moles/unit volume into moles/unit area. $\emptyset_{(+)(-)}$ is the specific adsorption potential due to reasons other than the electrostatic attraction. The above adsorption can also be expressed with the help of Gouy-Chapman equation of the form:

$$\Gamma_{(+)(-)} = \sqrt{\frac{2\epsilon kT}{\pi z^2 e^2 N} \qquad C_{(+)(-)}} \; \sinh \; (ze\psi_T/kT) \qquad (9)$$

On the basis of equation 8 or 9, adsorption of the ions at the liquid/gas interface is a function of their valency and bulk concentration as well as the potential at the interface. If the counter ions can penetrate into the complete interface, this potential can be considered the same as the surface potential, usually designated as ψ_o. If they cannot penetrate, ψ_T will be essentially the potential at the plane of closest approach, and may or may not be equal to ψ_δ, the Stern layer potential. A factor having a major effect on the adsorption of ions and their separation by foaming techniques is the concentration of other ions in solution, and the extent of competition that they face from these foreign ions to occupy the adsorption sites. One way to study this is to examine the reduction in ψ_T that is caused by the adsorption of the foreign ions and the resultant reduction in the adsorption of the ion under consideration according to equation 8 or 9. According to equation 9, adsorption of ions in the complete diffuse layer at the liquid/gas interface should increase linearly with the square root of its concentration when ψ_δ can be assumed to be fairly constant. This is indeed applicable only in the absence of excess electrolyte. If excess electrolyte is present in the solution, adsorption of the ion under consideration will be linearly proportional to the concentration, since the adsorption can now be considered to be taking place by mere ion exchange(21).

Other factors that could be expected to have significant effects on the performance of ion flotation are pH which will determine the extent of hydrolysis and hence the charge of the species, and the activation or depression of the adsorption of the ions by other chemical species present in the system. As pointed out by Sebba(22), the concentration of the adsorbed ions at the liquid/gas interface can often be above the solubility limit and therefore can cause its own precipitation at the interface. Such precipitation is of course advantageous, since it makes it easy to collect the materials from the foamate by simple filtration or similar techniques. When the surfactant species responsible for the double layer at the liquid/gas interface is of the anionic type hydrogen ions will adsorb at the interface as counter ions along with other cations. Foaming and the separation of the foams can lead in such cases to a change in pH, which in turn can affect the surface tension of the solution and hence the efficiency of the foam separation. Such effects have been observed in practice in the separation of metal ions(10) and in the foam separation treatment of sewage effluents(23). If the hydrogen ions preferentially adsorb at the interface, it can also lead to surface hydrolysis of anionic surfactants which in turn can enhance the pH changes sufficiently to cause the formation of precipitates, and this also can affect the foam properties and the efficiency of the separation(24). If the pH of the bulk solution itself is above the precipitation pH of the ions to be separated, a precipitate is naturally formed, and this is separated by precipitate flotation. The principles of precipitate flotation have been used by several workers extensively to remove such materials as chromium hydroxide(25,26), cyanide(27), nickel(28), palladium(29), strontium(30), silver, uranium, gold(31), copper(32), zinc(33) and iron(34). The main advantage of precipitate flotation over ion flotation is that it does not need a stoichiometric concentration of the surfactant. It needs only enough surfactant to impart hydrophobicity to the colloidal particles of the precipitate by covering a fraction of the surface of the particles and to impart stability to the foams by adsorbing at the liquid/gas interface. However precipitate flotation, unlike ion flotation, requires the addition of alkali or other reagents to cause the precipitation of ions under consideration.

Apart from the above considerations, the basic principles of precipitate flotation are similar in a number of ways to those of froth flotation. It is important to realize this similarity, and to use the significant amount of basic knowledge developed in recent years in the area of froth flotation for a basic understanding of precipitate flotation.

FROTH FLOTATION

In froth flotation, particles to be separated are agitated by rotating impellers and the gas is either introduced through the central pipes or precipitated near the impellers. Gas bubbles stick to those particles that are hydrophobic and carry them towards the surface where they are separated from the main body usually by mechanical skimming. The froth flotation of minerals or precipitates is possible only if the particles could preferentially be wetted by gas rather than by water. Only a very small fraction of the minerals and precipitates of the "second kind"(3) (formed by reaction between ions and certain organic reagents) are naturally hydrophobic and attach to gas bubbles by themselves. Most minerals and precipitates have to be made hydrophobic for flotation purposes, and this is achieved by selectively adsorbing surfactants on them. A surface coverage of only 2 to 5% is found necessary for imparting floatability to minerals(35). In order to impart floatability to minerals, they are treated with heteropolar reagents called "collectors". These reagents possess at least one nonpolar and one polar portion. The acquired hydrophobicity of the minerals is the result of the adsorption of those reagents on the mineral particles with their nonpolar end oriented towards the bulk solution. The surfactant species adsorb on the bubble surface and this is also directly responsible for the attachment of bubbles on the mineral particles(6). This can be easily seen by examining the Young's equation given below which relates the various interfacial energies to the contact angle created by a gas bubble on a particle surface in solution.

$$\gamma_{sg} - \gamma_{sl} = \gamma_{lg} \cos \theta \qquad (10)$$

where γ_{sg}, γ_{sl}, and γ_{lg} are solid/gas, solid/liquid, and liquid/gas interfacial tensions respectively, and θ is the contact angle. For the adhesion of the gas bubble to the particle in solution, a contact angle that is fairly larger than zero is required. One then obtains the following condition from Young's equation for bubble - particle attachment: $\gamma_{sg} - \gamma_{sl} < \gamma_{lg}$

From this, it can be seen that a change in the surface tension of the liquid/gas interface is as much important for establishing the attachment of the bubble to the particle as a change in γ_{sg} or γ_{sl}. The extent of changes produced by a surfactant on various interfacial energies will be determined by the nature of the surfactant. For example, a nonionic surfactant will change γ_{lg} more than an ionic surfactant while the latter will be more influential in affecting the interfacial tension between the solution and a polar surface which is charged oppositely to the surfactant species. This is due to the fact that while at the liquid/gas interface adsorption would be retarded by repulsion between the ionic heads of the adsorbed surfactant species, at the solid/liquid interface, it would be enhanced by the electrostatic attraction between the ionic heads and the oppositely charged surface sites. Indeed, repulsion between the charged heads of the adjacently adsorbed surfactant species would tend to slightly retard the adsorption even at the solid/liquid interface as shown indirectly by the experiments of Yamada and Fuerstenau(36) and Somasundaran and Fuerstenau(37) on the effect of neutral surfactant molecules on the froth flotation of minerals using ionic surfactants. Our past experiments (6,37) have indicated that significant transfer of surfactant species from the liquid/gas interface to the solid/gas interface is possible during particle-bubble attachment. Since adsorption at the liquid/gas interface is usually significantly higher than that at the solid/liquid interface (see Figure 5), the adsorption at the liquid/gas interface has a larger role in effecting bubble-mineral attachment.

The separation of one mineral from another, or one precipitate from another using flotation is certainly dependent on the selective adsorption of surfactants on only the ones to be floated. An understanding of the mechanism of adsorption is therefore essential to select the appropriate conditions for separation.

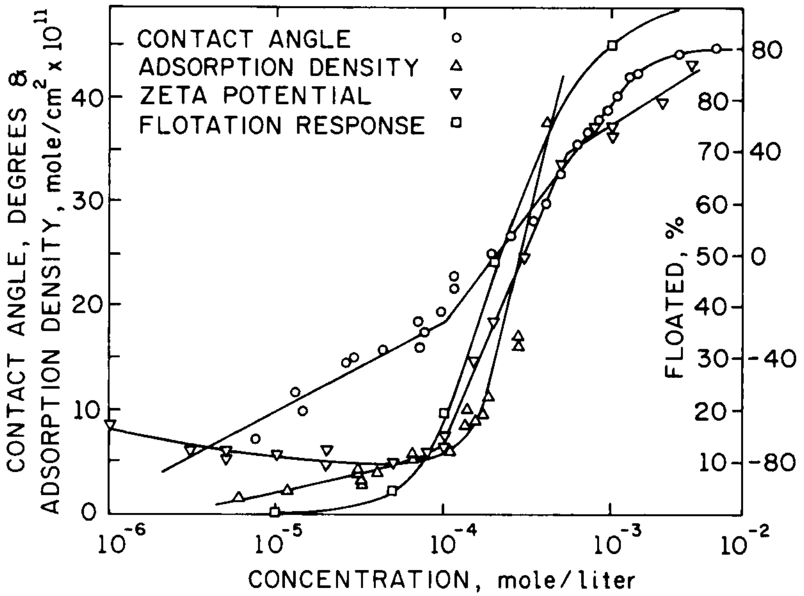

Figure 5. Adsorption density of dodecylammonium acetate at different interfaces(6).

RELATIONSHIP BETWEEN INTERFACIAL ADSORPTION AND FROTH FLOTATION

Most surfactants adsorb on nonmetallic minerals such as silica and alumina due to the electrostatic attraction between the polar heads of the surfactant and the charged mineral surface(38–42). Selective adsorption and flotation in the case of such minerals is essentially the result of the difference between their electrical characteristics in aqueous solution. For oxides and silicate minerals, hydrogen and hydroxyl ions have been considered to be the potential-determining ions(41), and therefore, the solution pH will determine the sign and magnitude of the charge on the mineral surface. Below the pH of the point of zero charge (pzc), the particle surface will be positively charged and will preferentially adsorb anions including anionic surfactants. Above the point of zero charge, the surface will be negatively charged and will preferentially adsorb cations. While ions such as sodium, potassium, nitrate and perchlorate adsorb at oxide-solution interfaces exclusively due to electrostatic attraction, other forces such as van der Waals' interaction between adsorbed species, covalent bonding and hydration effects at the interface are important in the adsorption of certain other ionic species. These adsorptions are usually referred to as specific adsorptions. Examples of the species that are found to specifically adsorb on minerals are polyvalent ions, such as calcium and sulfate, and long-chain surfactants like laurylsulfate. Because of the specific adsorption, the above ions can adsorb in the innermost layer of the diffuse layer in concentrations larger than that which is needed to neutralize the charge on the surface. Consequently, they reverse the sign of the potential at this plane, commonly referred to as ψ_β or ψ_δ potential as the case may be. Since the sign and magnitude of ψ_δ will determine the further adsorption on the particle, it is important to examine the effects of all the ions normally present in a system on the electrical double layer characteristics like ψ_δ potential. Such an examination would help in choosing the optimum conditions for processes such as flotation and flocculation.

The fact that there is good correlation between froth flotation and other interfacial phenomena becomes evident on examining Fig. 6. The flotation recovery of quartz particles is plotted here as a function of surfactant concentration along with zeta potential, surfactant adsorption and contact angle. A sharp rise in all the interfacial phenomena occurs at a dodecylammonium acetate concentration of 10^{-4} mole/liter. For a system containing a mineral like quartz (the potential determining ions of which are hydrogen and hydroxyl ions) in aqueous solution containing no specifically adsorbing ions other than the collector, froth flotation using a cationic surfactant should be possible if its pzc is below the solution pH and not possible if its pzc is above the solution pH. Similarly, significant flotation with anionic surfactants is possible only for those minerals which have a pzc above the solution pH. The significance of the relation between the solution pH and point of zero charge is il-

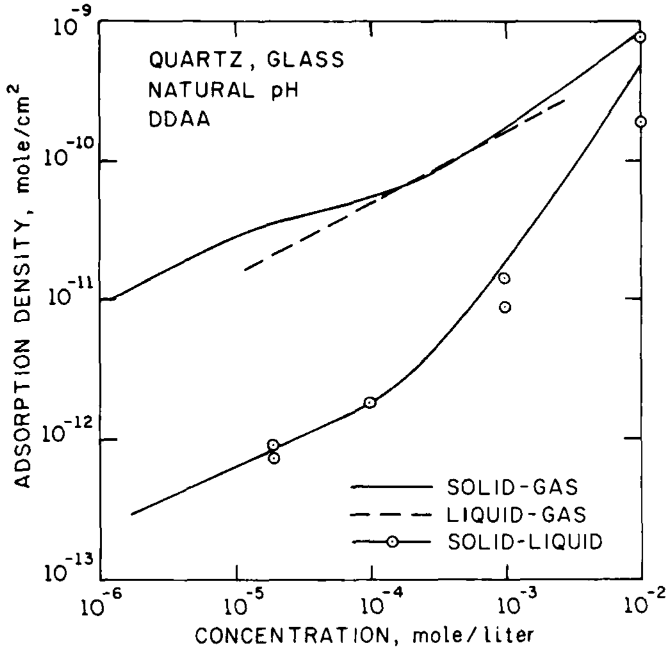

Figure 6. Correlation diagram of contact angle, adsorption density, flotation, and zeta potential for quartz as a function of dodecylammonium acetate concentration at pH 6 to 7, 20 to 25° C(21).

lustrated in Figure 7 where flotation of calcite with anionic and cationic collector is given as a function of pH(43). The point of zero charge of calcite lies within the range of 8 to 9.5 (43). It can be seen that significant flotation with the anionic collector, sodium dodecyl sulfate, is possible only below pH9 where the mineral particles are positively charged and, with the catonic collector, dodecylammonium acetate, only where the mineral particles possess a net negative surface charge. If calcite was present in solution, for example, mixed with quartz (pzc =~ pH2), preferential flotation of calcite leaving quartz in the suspension is possible using anionic surfactants at about pH 5 to 7. It must be noted at this point that materials differ significantly in their properties depending on their source as well as the method of

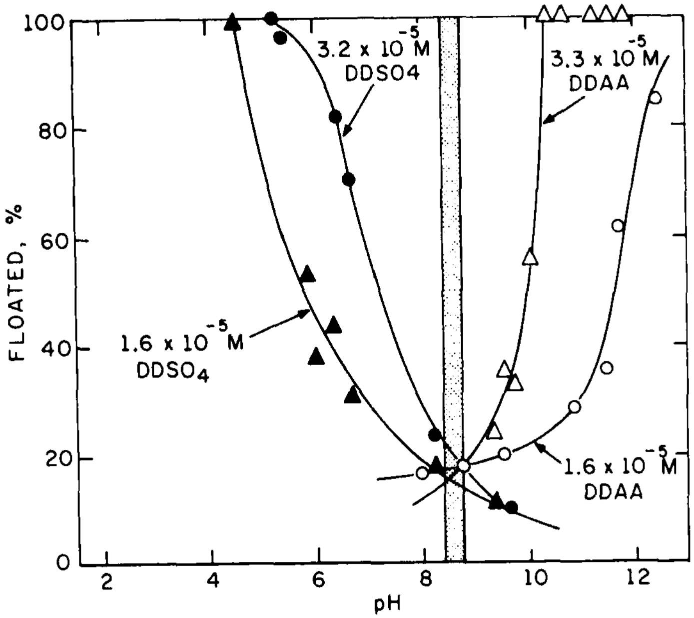

Figure 7. Flotation of calcite with dodecylammonium acetate (DDA) and sodium dodecylsulfate ($DDSO_4$) solutions(43).

preparation. Such differences can contribute significantly to variations in surface properties and hence their response to separation processes. Variations in surface properties as well as flotation response due to various mechanical and chemical treatments including leaching, drying, and doping have been recently discussed by the author(44).

It is also evident from Figure 7 that flotation obtained at any given pH increases with bulk surfactant concentration. This is in agreement with the Stern-Graham's equation, given below for adsorption at the solid/liquid interface which predicts an increase in the adsorption due to electrostatic attraction with an increase in bulk concentration. The adsorption density in mole/cm^2, Γ_δ, in the Stern plane at the interface is given by:

$$\Gamma_\delta = 2r\ C_B \exp\left(\frac{\Delta \bar{G}^o_{ads}}{RT}\right) \qquad (11)$$

where r is the radius of the adsorbed ion, C_B is the bulk concentration of the adsorbent, and $\Delta \bar{G}^o_{ads}$ is the standard free energy of adsorption of the ion at the interface and is given by Fuerstenau$^{(41)}$ as

$$\Delta \bar{G}^o_{ads} = \Delta G^o_{elect} + \Delta G^o_{hydroph} + \Delta G^o_{chem} \qquad (12)$$

ΔG^o_{elect} is equal to $zF\psi_\delta$, with F as Faraday's Constant and ψ_δ as the potential at the Stern plane. $\Delta G^o_{hydroph}$ is equal to $n\phi$ the interaction energy due to the association of the adsorbed surfactant ions containing n $-CH_2-$ or $-CH_3$ groups with ϕ as the standard free energy for removing one mole of $-CH_2-$ groups from water through association$^{(38-40)}$. ΔG^o_{chem} is the free energy change due to chemical reactions between the surface species and the adsorbing species. Equation (11) in the absence of any chemisorption becomes

$$\Gamma_\delta = 2r\, C_B \exp \frac{(-zF\psi_\delta - n\phi)}{RT} \qquad (13)$$

The extent of adsorption and, hence, flotation obtained at any given pH, ionic strength and surfactant bulk concentration is dependent on the length of the chain as well as its shape which will determine the effective number of $-CH_2-$ groups that can be removed from water by lateral cohesive interaction. This is indeed the case as shown by the data in Figure 8 for the flotation recovery of quartz with alkylammonium acetates of varying chain length. It can be seen that flotation is obtained at lower surfactant concentrations as the chain length is increased.

Variables like solution pH, in addition to their influence on flotation due to their effect on surface charge, have also other important effects on the surfactant performance. For example, above pH 12.1, even though quartz is still negatively charged, its flotation with cationic alkylammonium acetates is found to cease completely$^{(37)}$. This is because above this pH almost all the amine is in its neutral molecular form which by itself is unable to adsorb at the solid/solution interface and act as collectors. At least a good fraction of the surfactant should be present in its ionic form in order to cause good flotation. However, when present with ionic collectors, neutral surfactant

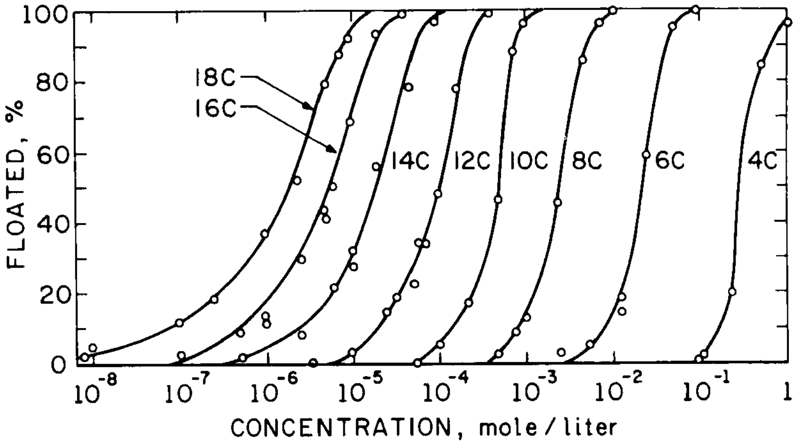

Figure 8. The effect of alkyl chain length on the flotation of quartz in alkylammonium acetate solutions(21).

species can act as very good collectors, since total adsorption in a system containing both ionic and neutral species is higher than in one containing only one kind. This is due to the fact that the neutral molecules that coadsorb due to the cohesive attraction between the chains can actually screen the repulsion between the charged heads of the adsorbed surfactant ions. Other noteworthy effects of the structure of the molecules include the positive effect of benzyl radicals in the chain and the negative effects of double bonds and triple bonds as well as of branching of chains.

The solution properties which have important effects on the surfactant adsorption or flotation include temperature, ionic strength, and the presence of specifically adsorbing inorganic ions and certain colloids or macromolecular reagents. The ionic strength effect is based on the fact that electrostatic adsorption of the surfactant at the solid/liquid interface is in competition with other ions carrying charges like those of the surfactant ions. A significant increase in the concentration of other ions will, decrease the adsorption of the surfactant on the solid and, as a result, its flotation. The data of Modi and

Fuerstenau(45) for flotation recovery of alumina at pH6 with 4 x 10^{-5} mole/liter sodium dodecylsulfate as collector is given in Figure 9 as a function of the the concentration of sodium chloride. It can be seen that sodium chloride, when present in concentrations above 10^{-4} M, has a deleterious effect on flotation. In Figure 9, data for flotation in the presence of sodium sulfate is also presented. The effect of sodium sulfate in depressing the flotation of the positively charged alumina at pH6 is almost 500 times larger than that of sodium chloride. The greater effect of sulfate over that of chloride is the result of the tendency of the bivalent sulfate to specifically adsorb strongly and to compete with dodecyl sulfonate to a greater extent than the monovalent chloride. Similar effects have been observed by various workers for bivalent calcium and magnesium on the flotation of negatively charged minerals using dodecylammonium chloride. As pointed out by Fuerstenau(41), such effects become important if flotation separation is being conducted in a medium like sea water which contains large concentrations of polyvalent ions. It must however be noted that the specific adsorption properties of bivalent ions can

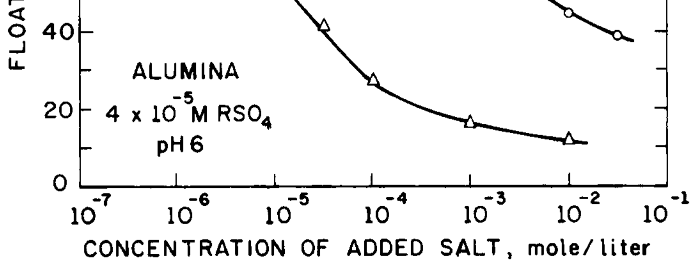

Figure 9. The depression of flotation of alumina by NaCl and Na_2SO_4 with sodium dodecylsulphate as the collector at pH 6(41).

be used to enhance flotation when the surfactant has a charge opposite to that of the ions. This is illustrated in Figure 10, where flotation of alumina at pH6 with a cationic surfactant, dodecylammonium acetate, in water and in 10^{-2} mole/l Na_2SO_4 solution are plotted as a function of the concentration of the surfactant. At pH6, alumina is positively charged and, hence, there is no flotation with the above cationic surfactant. However, in the presence of bivalent sulfate ions, flotation occurs as the specifically-adsorbing sulfate ions adsorb in quantitites larger than not only what is necessary to negate the surface charge, but even enough to reverse the sign of the charge of the Stern plane and thus make it possible for the cationic surfactant to adsorb and make the particles hydrophobic and flotable. Similarly, flotation of negatively charged mineral particles with anionic collectors is possible if the solid particles are first activated by means of divalent cations such as that of calcium and magnesium. These ions are found to function most effectively in the pH range where they are in hydrolyzed soluble form(46-48). Another type of reagent which affect flotation operations are polymers like starch. An ex-

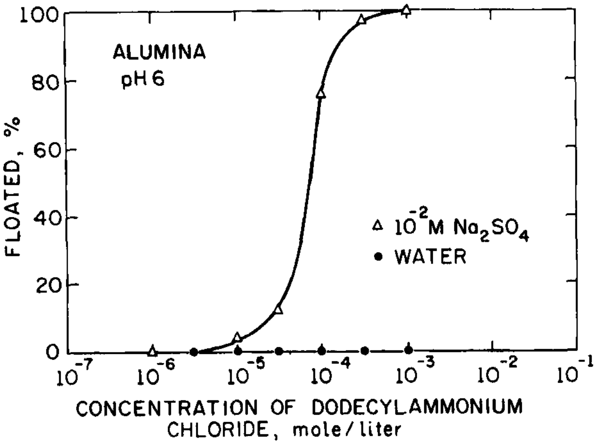

Figure 10. The activation of alumina flotation by Na_2SO_4 with dodecylammonium chloride as collector at pH 6(41).

ample of the effect of this type of reagent is illustrated in Figure 11. Flotation data(49) for calcite with sodium oleate as collector is presented in this figure as a function of the starch concentration. It can be seen that starch acts as a depressant for the flotation of calcite. The mechanism by which starch acts appears to be, however, different from the way in which most depressants act. Most reagents depress flotation normally by adsorbing on the mineral particles, making their surface unavailable or unsuitable for the adsorption of the surfactant. However, on the basis of the data in Figure 12 for the adsorption density of oleate on calcite as a function of starch concentration, it is evident that starch, which prevented the flotation of calcite with oleate, has actually enhanced the adsorption of oleate on the mineral. In other words, even though the mineral adsorbed more surfactant in the presence

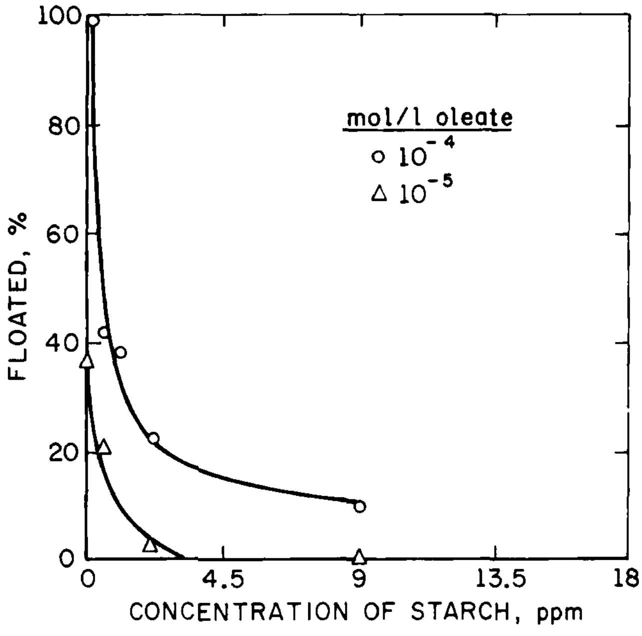

Figure 11. Percent of calcite floated as a function of starch in 10^{-4} mole/liter sodium oleate solutions(49).

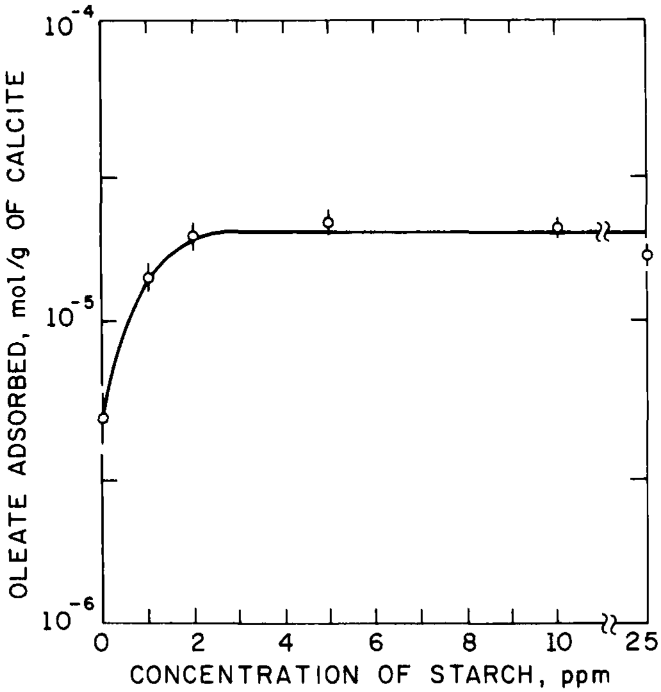

Figure 12 Adsorption density of oleate on calcite at natural pH 9.6-9.8 as a function of starch added prior to the oleate addition; vertical lines indicate the standard deviation in adsorption density due to the variation in the scintillation counting(49).

of starch, the mineral surface remained hydrophilic. This was ascribed by the author to the peculiar helical structure that starch assumes in the presence of hydrophobic materials or in alkaline solutions and to the fact that this helix interior is hydrophobic and the exterior is hydrophilic(50). The mutual enhancement of adsorption was apparently due to the formation of helical starch-oleate clathrate with the hydrophobic oleate held inside the starch helix. The hydrophilic nature of calcite in the presence of oleate and starch results because the adsorbed oleate is obscured from the bulk solution by such wrapping by starch helixes whose exterior is hydrophilic and also by simple overwhelming by the massive starch species.

Another important variable in flotation systems is temperature. Figure 13 shows the effect of temperature on the surfactant adsorption(51,52) on alumina as aqueous solution. As expected for physical adsorption, surfactant adsorption decreased with temperature. Flotation can also be expected to de-

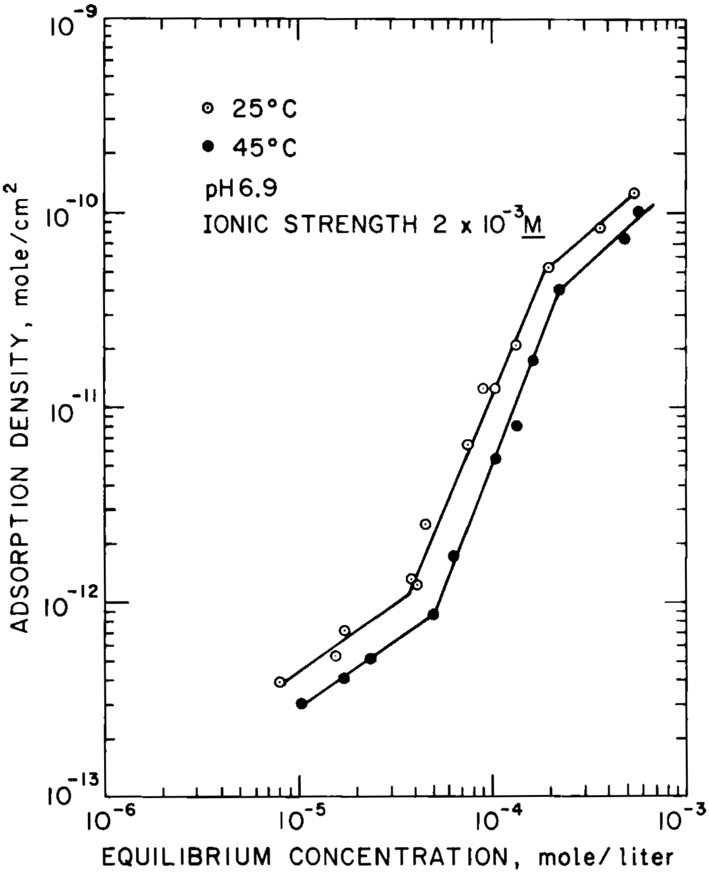

Figure 13. The effect of temperature on adsorption density of sodium dodecylsulfonate on alumina(51).

crease with temperature, especially since the effect of temperature on other parameters like adsorption density at liquid/gas interface will not be conducive to flotation. It must be noted at this point that if the adsorption is of a chemical nature, as in the case of stearic acid on iron oxide minerals or xanthates on sulfide minerals, it would increase with temperature. In practice flotation in such cases is also found to increase with temperature(53-55).

It is important to realize that the varibales discussed above have similar effects on other foam separation techniques. For example, the results of Karger and co-workers(56), shown in Figure 14, for the effect of pH on the distribution factor of mercury and iron show that separation can be obtained in this case by choosing the appropriate pH conditions under which only one

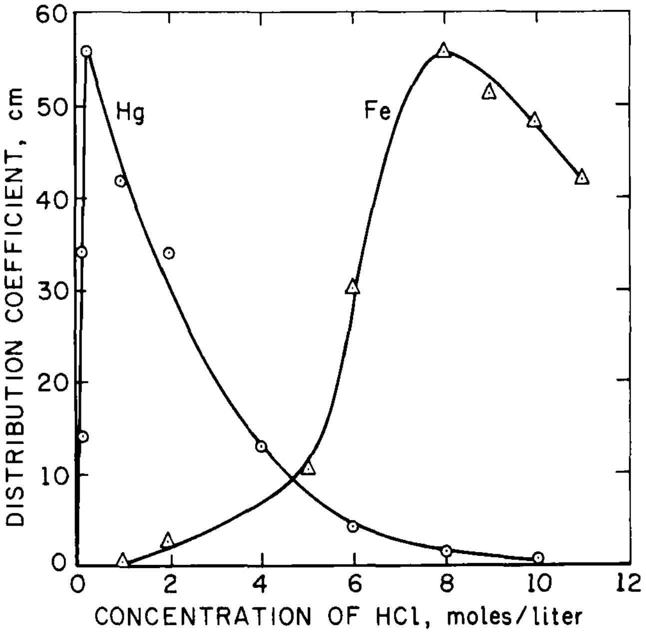

Figure 14. Distribution coefficients for Fe and Hg as a function of HCl concentration. a) Fe = $2 \times 10^{-}$ H/l, surfactant (HDT) = 10^{-3} H/l
b) Hg = 2×10^{-7} H/l, surfactant (HDT) = 10^{-} H/l

of the species is in hydrolyzed soluble form. Figure 15 contains similar results of Rubin and co-workers(57) for the effect of pH on the flotation of micro-organism E. coli using lauric acid, and Figure 16 on the ion flotation of iron using sodium laurylsulfate(3). The next Figure (figure 17) shows the activating effects of an external electrolyte like aluminium sulfate on the flotation of B. cereus using lauric acid(58) and Figure 18 shows that of ferric chloride on the removal of phosphate from waste-water by foam fractionation(59). It is evident that, as in the case of froth flotation of minerals, these polyvalent electrolytes can influence the performance of foam separations significantly.

PHYSICAL PRINCIPLES OF FLOTATION

As opposed to the chemistry of flotation, the physics and mechanics involved in the generation of bubbles and the attachment of bubbles to particles are not well understood. Furthermore, the physical conditions inside a conventional ore flotation cell and a cell used for precipitate flotation or ion flotation are significantly different from each other since, unlike in the case

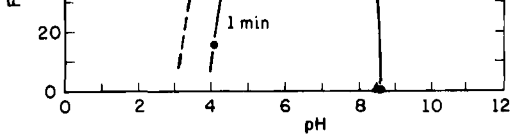

Figure 15. The effect of pH on the microflotation of E. Coli. Initial concentration of organisms, 7.2×10^8/ml.; gas flow rate, 10.8 ml./min; collector concentration (lauric acid), 40 mg./l.; alcohol frother dose, 1 ml./400 ml; $Al_2(SO_4)_3\ 18H_2O$ concentration, 100 mg/l(57).

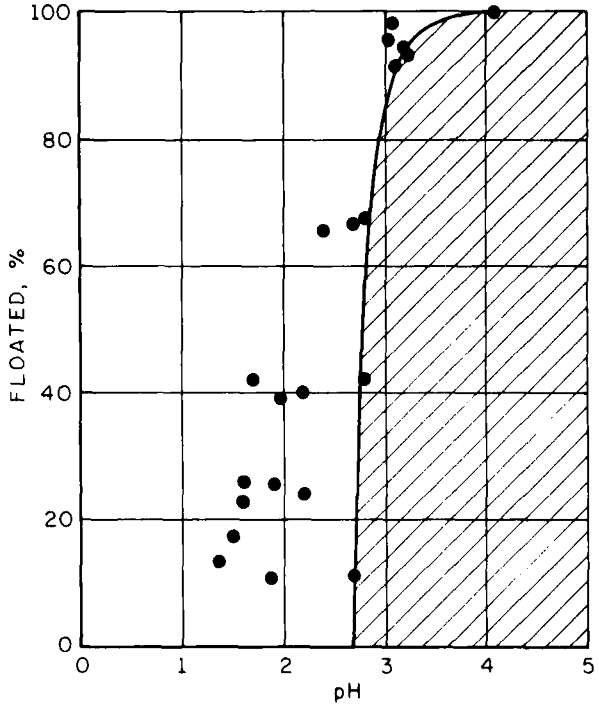

Figure 16. The effect of pH on flotation of iron species using sodium laurylsulfate. Precipitation occurs in the hatched region(4).

of precipitate or ion flotation, ore flotation makes use of a high flowrate of air and a high degree of mixing by intense agitation. The mechanism of bubble generation in the case of precipitate flotation and other such techniques is relatively simple since the bubbles are formed by the mere forcing of air through a sparger and the bubble size distribution is governed mainly by the size distribution of the sparger pores and the gas flowrate(60). For the case of froth flotation of ores, the recent study of Grainger-Allen(61) using high speed photographic and stroboscopic techniques suggest that bubble formation is brought about by flow separation and formation of a ventilated cavity attached to the trailing edge of the impeller blade used for the agitation of the suspension followed by vortex shedding of the air cavity to generate

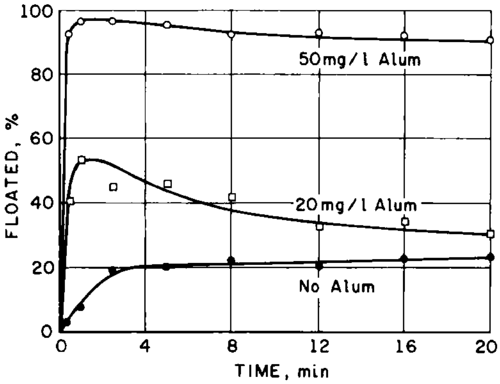

Figure 17. The effect of alum on the microflotation of B. cereus at pH 7 using 20 mg./liter lauric acid(58).

very small bubbles. The small size of the bubble seems to generate due to the implosion of the bulk liquid into the cavity and further division of the bubbles into the general turbulence. Grainger-Allen observed striations of larger bubbles attributed to large-scale vibrations of the bubble surface. The signi-

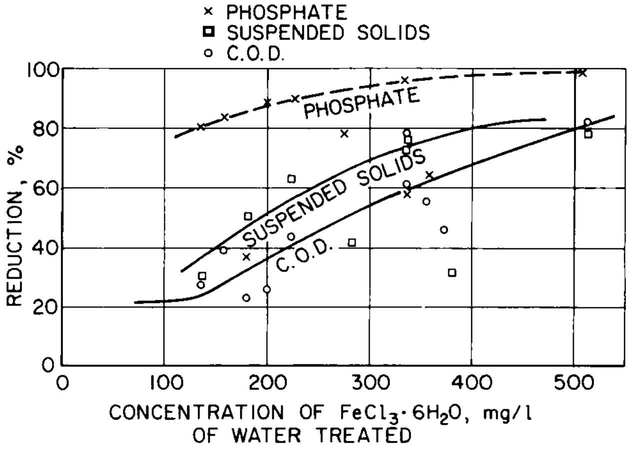

Figure 18. The effect of ferric chloride on the removal of phosphate and suspended matter(59).

ficance of such vibrations(62) in making the collisions between particles and bubbles fruitful and in decreasing the coalescence between bubbles suggests that the use of such techniques as ultrasonic vibration in foam separation techniques that involve no high degree of turbulence might increase the efficiency of separation, particularly those involving fine precipitates.

The mechanics of the attachment of particles to bubbles have been subjected to only a few quantitative studies(63-68). The attachment of bubbles to particles is dependent, among other things, on the relative velocity of the particle, the contact angle and the interfacial tensions of the system, the viscosity of the liquid film between the bubble and the particle, and the internal pressure of the bubble. Relative velocity of the particle should be high enough to overcome the small energy barriers to attachment brought about by the internal pressure of the bubble, but not large enough to exceed the energy barrier for detachment. A finite contact angle is a necessary condition for attachment. In addition, the properties of the liquid film between the bubble and the particle should be such that it can thin, rupture and recede within the period of the collision between the bubble and the particle. Sheludko(67) has evaluated the critical speed at which the liquid film should move in order for the attachment to occur. From the practical point of view, the design of impellers and other parts of the flotation cell and the power consumption during the operation have been studied by several workers. These studies have been discussed by Harris and co-workers(69); it must be said that this area of froth flotation is relatively dark and that further work is called for to shed some light.

In the field of foam separation techniques, there has been only limited work done to study the effects of bubble size, agitation or other such physical parameters on the separation operations. In general, agitation is avoided lest the materials which have concentrated at the surface of the bubble become detached from it. However, the general optimum requirements of mixing or of the size distribution of bubbles and its residence time for best separation have not been established. In this connection, it might be noted that Haberman and Morton(70) have observed the terminal velocity of bubbles to increase with size up to a size of about 0.7mm radius in filtered tapwater and then to decrease with size until a size of 3mm radius is reached. Increase in bubble size above 3mm causes further slight increase in the terminal velocity. Experiments on bubbles in unfiltered tapwater yielded similar results, except for the fact that the decrease of the terminal velocity with increase in bubble size in the range of 0.7mm to 3mm was absent. It might be pointed out that Shah and Lemlich(60) have reported the gas velocity to decrease with bubble size in the complete range of their study, but their study is restricted to the narrow range where Haberman and Morton also observed a decrease. In any case, bubbles smaller than 0.7mm could be expected to have a larger residence time in the solution and, therefore, also a larger collection of surfactant species on its surface. The difference in behavior between filtered and unfiltered tapwater was ascribed to the presence of particulate matter in the tapwater(70). The particulate matter is in general found to have a beneficial effect on foam stability which is a desired property when foaming methods are used for separation, since it is essential to give the foams on the liquid surface enough time to drain the bulk liquid as much as possible and thus improve the grade of the product collected in the foam.

The principles of formation of foam films, their structure and stability and the drainage of foam have been discussed by Rubin and Gaden(10) in early 1962, by Kitchener(71) in 1964, by Lemlich(11) in 1968, and recently by Ross(72). Drainage and thinning of films are also discussed in detail in a monograph by Mysels et al(73) on their research on soap films. Drainage takes place by downward flow under gravity as well as by suction into plateau borders. When the foam is fairly dry, they collapse by rupture as well as coalescence. Transient-type foams, which are beneficial for separation under certain conditions, collapse mainly by rupture of the thin films in a regular manner. Metastable foams, such as those usually employed in foam separation techniques, collapse mainly due to thermal, mechanical or radiational disturbances. Collapse of the foamate is often achieved by purposely disturbing the foam using various devices described elsewhere. Since the amount of bulk liquid in the foamate would be determined by the thickness of the metastable lamellae, it is important to maintain suitable conditions that would yield fairly thin lamellae. The thickness of the lamellae is controlled by the electrical double-layer repulsion between the two liquid/gas interfaces binding the films, the long-range van der Waal's pressure, the Laplace capillary suction pressure and, to some extent, by the steric hindrance of the close-packed monolayers. The stability of the lamellae has been identified by Kitchener(71, 74) to be governed mainly by film elasticity, fluid viscosity and double-layer repulsion. Film elasticity can be considered as a type of restoring force that occurs when the film is extended due to sudden mechanical or thermal fluctuations in the film. It results from the increase in surface tension produced by the decrease in surfactant concentration at the interface during the sudden extension of the film and from the inability of the bulk solution to restore the concentration back to its original value instantaneously. In order that there is a significant change in surface tension on extension, it is necessary for the bulk surfactant concentration to be in the range where change in surface tension with change in surfactant concentration is significant. Also, in order that the surface tension fluctuation is not restored instantaneously, the type of surfactants and their bulk concentration should be such that there will be no significant rapid diffusion of the surfactant from the subsurface region to the extended interfacial region. Furthermore, enhanced surface viscosity is required to reduce the transport of the surfactant species instantaneously over the surface to expanded areas as well as to minimize frequent extension or any such damage of the interfacial region. Bulk fluid viscosity should also be optimum so that the drainage of the liquid from the lamellae will not be either too rapid to damage the stability of the foam or too slow to prevent the drainage of the bulk liquid.

FACTORS IN FOAM SEPARATION

The factors that have been experimentally investigated for their influence on foam separation techniques include basic variables such as concentration of the surfactant and auxiliary reagents, pH, ionic strength, temperature, viscosity and other operating variables like gas flow rate, feed rate, reflux ratio, foam height, and equipment design. The effects of factors which were recently investigated by various workers are summarized in the following sections.

Surfactant Concentration

A large number of workers have found that the lowest surfactant concentration, which would still possess desirable foaming properties, is the most suitable for separation(5,75-77). Recently Robertson and Vermeulen(78) during their foam fractionation study of rare-earth elements have noted transiency of the foam, which is higher at lower surfactant concentrations, as a desirable property for effective extraction. It must be noted that flotation of ions and minerals is essentially dependent on their association with surfactants and hence their extraction can be expected to increase with surfactant concentration at least until the critical micelle concentration of the constituent surfactants is reached. Rubin and co-workers(32,33) have, in fact, found the removal of zinc and copper by ion flotation using sodium laurylsulfate as collector to increase with surfactant concentration. Removal of these metals as precipitate was, however, not as sensitive to the concentration of the surfactant, provided enough surfactant was present to produce a stable foam. Increase in the flotation of minerals with concentration of the collector is a rather common observation(63,64).

Concentration of Auxiliary Reagents

Various auxiliary reagents are being used successfully in foam separation techniques for improved extraction. The effects are, in most cases, due to the flocculation of the particulates or the activation of collector adsorption on them. Most commonly used auxiliary agents in foam separation techniques are alum and ferrous sulfate. Garrets(59) has used them for enhancing the removal of phosphate and suspended solids from waste water, and Rubin and coworkers(57,58) have used them beneficially for the separation of E. coli and B. cereus by microflotation. In the flotation of B. cereus with lauric acid as collector, addition of alum caused broadening of the pH range of flotation. The extent of broadening was found to be proportional to the amount of alum added. With the addition of 150 mg of alum per liter of solution, the pH range of flotation was broadened from 3 to 5 to as much as 3 to 9. Below pH 4.5 however, removal of B. cereus by both lauric acid and laurylamine is reported to be better without alum than with it. Brummer and Stephen(79) have found during their study of the decontamination of municipal waste waters that the addition of certain commercial polyelectrolytes to the system is useful. Only two of the fourteen polyelectrolytes investigated (prima floc C-7 from Rohm and Haas and UCAR Resin C-149 from Union Carbide) was, however, found to show any significant effect. In this connection, it might be noted that Devivo and Karger(79) in their studies of flotation of kaolinite and montmorillonite, have found aggregation to have opposite effects in two systems; one employing bubbles of 1 to 2 mm. diameter and the other using bubbles of 0 to 2 mm. diameter for coagulated clays. Flotation was found to be better with the finer bubbles than with the coarser ones. Grieves(81) also has reported alum and ferric salts to have detrimental effects in the cleaning of synthetic water (containing distilled water, clay and surfactants) using cationic surfactants. Sheiham and Pinfold(82) have studied the flotation of very dilute solutions of two cationic collectors, hexadecyltrimethylammonium chloride and dodecylpyridinium chloride, in the presence of various electrolytes and have found the concentration, charge and nature of the electrolytes to have a pronounced effect on the rates of foam separation. Furthermore, improved extraction was obtained, by Robertson and Vermeulen(78) in their foam fractionation of rare earth elements with cationic surfactant and EDTA by the addition of selected chelates and, except at low pH values, by Dick and Talbot(83) in their foam separation of copper with sodium laurylsulfate by the addition of a substituted ethylene diamine. The diamine used is a neutral liquid capable of complexing with copper in ionic form. In the froth flotation of minerals, the use of additives like calcium(84) and depressants like cyanide(85) is a common practice for the effective separation of one mineral from the other.

Solution pH

As mentioned earlier, the pH of the solution will determine the sign and the magnitude of the charge on a variety of inorganic particulates. Therefore, adsorption of the surfactants and the extent of removal of the particulates by foam separation techniques will be controlled by solution pH as well as other important variables. The effect of pH on the froth flotation of minerals is most significant(63,86). Excellent separations of minerals from one another is achieved in practice by choosing appropriate pH conditions. The effect of pH on ion flotation and precipitate flotation has been examined by Rubin and co-workers(32-34,87) and Grieves and co-workers(88,89). Indeed, the initial pH of the solution will determine whether the process to be used is precipitate flotation or ion flotation. For example, 8 being the precipitation pH for zinc, it can be removed below pH 8 by ion flotation and above by precipitate flotation. Grieves noted that precipitate flotation is most efficient when the sign of the charge of the precipitate is opposite to that of the collector and when the amount of soluble species is minimum. For the ion flotation of copper using sodium laurylsulfate, Rubin and co-workers(32) observed significant effect of pH only when the ionic strength was 10^{-2} N or higher. The difference in behavior between high and low ionic strength was attributed by the authors to the difference in the state or type of the cations predominating at each pH. Flotation of microorganisms is often found to occur in a particular pH range only. For example, removal of E. coli using lauric acid and alcohol is maximum in the pH range of 4 to 8(57) and that of aerobactor aerogenes using lauric acid or lauryl amine below pH8(90).

Ionic Strength

The effects of increase in ionic strength on different foam separation techniques are apparently not of similar nature, the major reason for this probably being that increase in ionic strength has different effects on the adsorptions at various interfaces that are responsible for various separations. Increase in ionic strength is in general detrimental to froth flotation, since the adsorption of surfactant on particulates usually decreases when the concentration of the counter ions competing with the surfactant is increased. Even though increase in concentration of the activating ions or potential determining ions would cause an increase in ionic strength, the beneficial effects on flotation due to such changes cannot, of course, be attributed to the increase in ionic strength. It must, on the other hand, be ascribed to favorable changes in the surface potential or Stern layer potential of the particles.

Since surfactant adsorption at the liquid/gas interface increases with increase in ionic strength, foam separation of surfactant itself might be assisted to some extent by an increase in ionic strength, provided that the critical micelle concentration of the surfactant is not lowered below the concentration of the surfactant and that the effects of ionic strength on the other foam properties are not of a detrimental nature. Rubin(29) has reported that the removal of surfactants by foam separation was not affected significantly in their experiments by a change in ionic strength. Increase in ionic strength was found to have no deleterious effects also on the precipitate flotation of the "second kind" of nickel and palladium with nioxime(29,91). However, in the case of the precipitate flotation of the "first kind", recovery of strontium using dodecylpyridinium chloride, hexadecyltrimethylammonium chloride and a dialkyammonium chloride was reduced by an increase in ionic strength(30). The reduction in recovery was attributed to slower precipitation, less secure attachment of the collector to the precipitate, rapid flotation of the collector and higher foam drainage and redispersion. Rubin and co-workers(32,33) reported the ionic strength to have very little effect on the precipitate flotation of zinc or copper, but to have a detrimental effect on their ion flotation. In addition, ionic strength increase magnified the effect of pH on the flotation of copper using sodium laurylsulfate. Finally, Grieves(89) has reported that increase in the solution concentration of chloride and sulfate have detrimental effects on the foam fractionation of phenol and phosphate using ethylhexadecyldimethylammonium bromide. The removal of the anionic orthophosphate was in fact more affected by the presence of the above anions than that of the phenol.

Temperature

Temperature has been suggested as an operating variable for cases where the foam stability of surface active components is different at different temperatures(92). In the case of froth flotation of minerals, surfactant adsorption and hence flotation could be expected to decrease with increase in temperature if the binding of the collector to the mineral surface is due to physical adsorption(51). If the adsorption is due to chemical forces between the surfactant and the mineral particles, opposite effects could be expected(93). For the case of foam fractionation, Grieves reports increase in temperature to be beneficial for the separation of ethylhexadecyldimethylammonium bromide, but to have no effect in the cleaning of synthetic waters made up of distilled water, clay and salt using cationic surfactants(94). Ion flotation of cuprous ions using sodium laurylsulfate is reported by Rubin to be insensitive to temperature changes in the range 15 to 34°C(32). Schoen and Mazella(95) also found change in temperature to be of little effect in the foam fractionation of radioactive materials, provided the foam is not destroyed. However, precipitation flotation of both the "first kind and the second kind" is reported to improve with increase in temperature(28,30). For example, Mahne and Pinfold found the precipitate flotation of "second kind" of nickel with nioxime in the pH range 8 to 11 to improve when the temperature was increased from 21°C to 40°C(28). Precipitate flotation of the "first kind" of strontium with cationic collector was also found to improve with increase in temperature, possibly due to an increase in size of the precipitate. Flotation of palladium-nioxime precipitate was, however, an exception to the above effects in that it was without much sensitivity to temperature(29). It might be noted that the effect of temperature could be rather complex because of its influence on various other factors such as adsorption, surface elasticity and viscosity.

Gas Flow Rate

Low gas flow rate is in general beneficial for separation, even though the rate of separation will be lower at lower flow rates. Various workers, including Gaden et al(77), Lemlich et al(96,67), and Robertson and Vermeulen(78) have found that high enrichment and low foam density is obtained at low flow rates. There must, of course, be sufficient gas flow to maintain the foam height that is essential for good separation, the optimum flow rate being determined by the concentration of the surfactant and the transiency of the foam.

Feed Rate

Low feed rate is also found to be good for foam separation(76). Again, the amount of material to be separated in unit time will be lower at low feed rate and hence a compromise between the rate of removal and the extent of removal will have to be sought to determine the optimum feed rate.

Reflux Ratio

The degree of enrichment obtained by various workers(96,98,99) is, as expected, proportional to the reflux ratio. The ratio of the concentration of the surface active material or colligend in the overhead to that in the bottom increases with increase in reflux ratio unless and until the surface of the foams is saturated with surfactant.

Foam Height

As mentioned earlier, some foam height is needed to obtain good separations. If the foam is transient, foam height is particularly essential to obtain good enrichment and separation. Robertson and Vermeulen(78) noted, during their study of foam separation of rare earth elements using transient foaming, that the extraction rate decreases with increasing foam height up to 17 cm. of foam height and then stays constant. The initial decrease was attributed by the authors to the continuous loss of the surface containing the separated materials.

Pulsed Addition of Reagents

Pulsed addition of the reagent is usually more efficient than a single addition of it. During a study of foam separation of complexed cyanide using a cationic surfactant, Grieves and Bhattacharya(99) observed that they could remove 190% more of the complexed cyanide with one fifth less surfactant when the surfactant was added in three dosages as compared to when it was added in one dosage.

FOAMING DEVICES

The majority of the foaming devices are designed for operations without any significant agitation. Froth flotation devices, however, consist of tanks designed for high agitation of the pulp with impellers which also help to disperse the air and to keep the solid particles and the air in suspension. Air is introduced in one or more of the following different modes. In agitation cells, air is drawn in by the vortex created by the rotating impellers. In the subaeration cells, air is sucked through or blown to the base of the impeller, while in pneumatic cells it is introduced by simple direct blowing into the pulp. Also, air could be precipitated from the solution and entrapped by the tumbling action of the pulp under proper impeller speed and cell depth as in the case of the mechanical cells. Whenever the air precipitation is not enough low pressure air could easily be supplied. In some cases, the precipitation of air has been achieved by first dissolving the air under pressure and then releasing the pressure during the actual flotation. In practice, flotation cells are arranged in series so that the unfloated portion of one cell becomes the feed of the succeeding cell. Various cells used in plants are described in detail by Taggart in his "Handbook of Mineral Dressing"(100) and Gaudin in his book on flotation(101).

A special cell suitable for laboratory flotation research is the Hallimond Cell as modified by Fuerstenau(102). A sketch of the apparatus is given in Figure 19. The lower part of the cell consists of a glass with a fritted glass disk with a maximum pore size of 40 microns sealed to the bottom. This glass well is connected at the bottom to a supply of purified nitrogen to produce gas bubbles. The upper part consists of a bent glass tube with a stem just above the bend. A flowmeter is connected to the top of the tube to measure the gas flow. The Hallimond tube with a magnetic bar coated with polyethylene in it is placed on a magnetic stirrer and this enables controlled stirring of the quartz in the solution. The flow rate is controlled by adjusting the pressure in the gas reservoir which is read on a manometer connected to it.

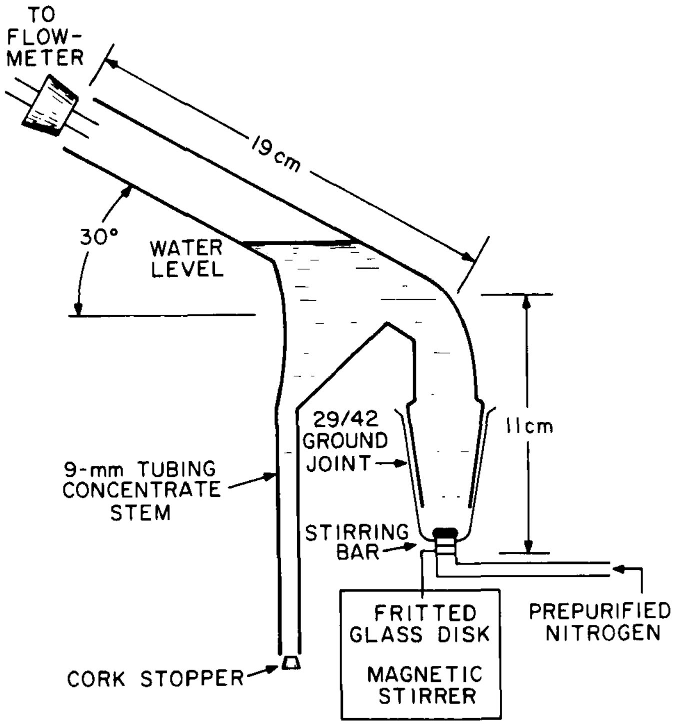

Figure 19. Modified Hallimond cell for laboratory froth flotation research(102).

Quantitative flotation experiments can be conducted by means of the modified Hallimond tube since important variables such as the flow rate of gas, stirring, pulp density, pH of the solution and time of flotation could easily be controled.

Devices used in other foam separation techniques consist essentially of a column with a maximum height of about 100 cm to 200 cm and a maximum diameter of 5 cm to 10 cm which contains the materials to be foam separated, a charger to introduce the gas in a dispersed form and a vessel to receive the foam. Various modes of operation have been discussed by Rubin and Gaden(10) and Lemlich(11) and been recently summarized by Robertson and Vermeulen(78). These include the simple mode (batch or continuous), the stripping mode, the enriching mode and the combined mode. In the stripping mode the feed is introduced into the foam above the pool level so that some amount of stripping by foam is achieved even before the liquid reaches the pool level. In the enriching mode, part of the foamate is fed back to the top of the column so that a certain amount of reflux can take place. Robertson and Vermeulen(78) have classified the devices into two categories called single-contact and multiple-contact devices. In single-contact devices, there is no coalescence between bubbles, whereas in multiple-contact coalescence and breakage occur and this causes a certain amount of internal refluxing, since some adsorbed material is always released into the foam during their breakage. Whether a device is single-contact or multiple-contact is determined mainly by the nature and concentration of the surfactants in the pool and by the viscosity of the bulk liquid that would control the foam drainage and the surface elasticity. The flow rate of the gas also has an influence on the type of contact that is obtained. A certain amount of multiple contact can be induced by column geometries which distort or stress the foam. Various modifications towards this purpose include Schutz's apparatus(103) containing a decreasing-diameter foam-drainage section which, in addition to stressing the foam, would also provide support for coalescing foam. Robertson and Vermeulen(78) increased the multiple-contact in their foam separation of rare earth elements by partial blocking of the foam with stacks of screens as well as with packings made out of plastic beads. They obtained improved separation with the above arrangements as a result of the internal reflux produced. In contrast to the decreasing-diameter drainage section, an expanded foam-drainage section has been tried in the separation of metal ions from nuclear process wastes. The purpose of this was to provide for better foam drainage and hence a greater volume reduction of the foamate. Horizontal foam-drainage sections have been used by Haas and Johnson(104) and by Shinoda and Mashio(105) to help the bubbles attain equilibrium faster and to prevent the entrainment of materials by the vertically rising foam bubbles.

The majority of the past studies has been with single stage apparatus, but some workers have used multistage systems also(10, 106-109). Column cascades, in which the residue from one column-bottom is refoamed in a second and third column, have been tried in the separation of metal ions from nuclear waste in order to achieve a high degree of decontamination of the waste. In the same area, a high degree of foam concentration was achieved by condensing and refoaming the foamate in a second column(108).

A recent noteworthy development in the area of foam separation devices is the use of electro-flotation(111). Here gas bubbles are produced by electrolysis and then separation is achieved by foam fractionation as well as by bubble fractionation. It might also be pointed out that Harper and Lemlich(112) obtained a high degree of separation by combining bubble fractionation in series with foam fractionation. In the case of bubble fractionation of dyes, Lemlich and co-workers(97) successfully used a photometer to follow the separation quantitatively. Others have used conductivity measurements between pairs of electrodes inserted at different places in the foam column to determine such parameters as foam density(113).

Finally, it is necessary to break the foam once it is separated from the main column. Foam breaking techniques tried by various workers include chemical methods(114) where sprays of foam inhibitors are used, thermal methods(105, 115-117) where sharp change in temperature is used to create a sudden change in viscosity, evaporation of solvent and sometimes a breakdown of chemicals, and mechanical methods using rotating stirring rods(119), whirling paddles(120), centrifuges(114,119), rotating disks(116,121) and extruders(122). These devices have been discussed in detail by Goldberg and Rubin(114). Rubin and Golt(121), while testing a high speed rotating disk for foam breaking, found that for foams impinging on a small area on top of a rotating disk, there is a critical speed above which all the foam would collapse. They report that a rotating disk, placed for the foam to fall on can serve as an effective foam breaker. Their preference for a foam-breaking device appears to be a high speed rotating disk with teflon walls around it. Strong liquid sprays also act as good foam breakers; but they are not as popular because of the dilution of the foam with the liquid. Other devices used include sonic vibrators(123), cyclone-type breakers(124) and combinations of various thermal and mechanical devices(116).

MODELLING OF FOAMING TECHNIQUES

Various mathematical models have been developed for froth flotation by several workers including Kelsall(125), Loveday and Woodburn(126,127), Harris and Chakravarti(128) and Fuerstenau et al(129,130). In foam separation mainly, Lemlich et al(11,131,132), Grieves et al(133), Haas and Johnson(104,122), and Rubin et al(134,135) are responsible for the successful models. Various models for froth flotation have been recently discussed by Harris and Chakravarti(128). Special mention might be made of their use of a "species distribution of rate" for a given - size particles of a given mineral. The frequent observation of the order of the kinetics of flotation different than 1 is attributed to the presence of such distribution. Of course, the fact that such an explanation is possible does not exclude with any degree of certainty the existence of non-zero order kinetics in the froth flotation of minerals. The mathematical models used in other foam separation techniques have been reviewed by Robertson and Vermeulen(78). Due to the large number of variables present in froth flotation and other foam separation techniques, much experimental and theoretical work remains to be done to obtain satisfactory working models of these operations. Optimization of a flotation operation with at least three factors varying at a time has been successfully attempted by Somasundaran and Prickett(136).

EXAMPLES OF FOAM SEPARATION

Foam separation techniques have been used for the separation of purification of minerals, surfactants, proteins, enzymes, microorganisms, and various metals. In 1962, Rubin and Gaden(10) presented a comprehensive review of the materials separated thus far by foam separation techniques. The following tables summarize most of the work published since then along with some of the salient works reviewed by Rubin and Gaden(10). It has been possible to give only a brief reference to the reported separations. For details the original publication must be consulted.

TABLE 2. EXAMPLES OF FOAM FRACTIONATION

Substance	Remarks	References
ANIONS		
Alkylbenzylsulfonate	Removed from waste water	79, 137, 139
Alkyl sulfate	Foam-separated during the study of factors in foam separation	Cited in ref. 10 page 361
Anionic surfactant Aerosol 22	Foam-separated from aqueous solutions	78
Dodecylsulfate	Selective removal from impurities	139
Fatty acid mixtures	From alkaline aqueous solutions	Cited in ref. 10, page 361
Hexadecanoate	Preferential removal of potassium hexadecanoate from solutions containing potassium tetradecanoate also	105
Lauryl sulfonic acid	from aqueous solutions	140
Methylene blue active surfactants	From paper and pulp waste waters	141
Monobutyl diphenyl sodium monophosphate (Aresket 300)	From Aresket in distilled water at 5×10^{-4} to 6×10^{-3} M/l initial concentration	96, 119
Myristic acid Nonylic acid	From aqueous solutions, results agree with Gibbs equation	Cited in Ref. 10 pages 361 and 362
Oleic acid	Alkali salts separated from aqueous solutions containing stearic and palmitic acids	Cited in ref. 10 pages 361 and 362

Substance	Remarks	References
ANIONS (Cont'd)		
Palmitic acid	From alkaline solutions; also in the presence of stearic and oleic acid	Cited from ref. 10 pages 361 and 362
Sodium laurate	From aqueous solutions, laurates concentrates in foam and hydrolyzes in it	Cited from Ref. 10 pages 361 and 362
Sodium oleate	Preferential separation from aqueous solution containing sodium laurate	142
Stearic acid	Alkali salts, from aqueous solutions and in the presence of oleic and palmitic acids	Cited from ref. 10 page 362
CATIONS		
Dodecylamine hydrochloride	From aqueous solutions	120
Dodecylpyridinium chloride	From very dilute solutions in the presence of various types of added electrolytes	82
Hexadecyltrimethylammonium chloride	From very dilute solutions in the presence of various types of added electrolytes	82
NONIONICS		
Amyl alcohol	From aqueous solutions; some concentration in the foam	Cited from ref. 10 pages 362 and 363
Isobutyl alcohol	A study of relation between concentration in foam and the residual liquid	
OP-7 and OP-10 (reaction product of dioctyl phenol with ethylene oxide containing 7 and 10 oxyethylene units resp.)	From waste water containing these nonionic surfactants and soaps	143, 144

Substance	Remarks	References
NONIONICS (Cont'd)		
Triton X-100 (tert. C_8H_{17} - Ø-(O$CH_2CH_2)_{9.7}$OH)	Foamed during the empirical test of theory for foam drainage and overflow in foam fractionation	132
	From 2.2 X 10^{-4} M/l aqueous solutions using foam and bubble fractionation combined	112
MISCELLANEOUS		
Acid mine water	From a mixture of it with municipal sewage	145
Bilirubine	From urine	Cited in ref. 10 page 362
Cellulose esters	From benzene solution	Cited in ref. 10 page 363
Detergents	From sewage	146
Dissolved or suspended organic materials	Along with nitrates and phosphates from aqueous sewage plant affluent	147
Methyl cellulose	From aqueous solution	148
Phenol	From a cationic surfactant solution at an optimum pH of 11.6	149
Surfactants	From pulp and paper mill waste	141
Sugar juice	An attempt on full scale purification of sugar juices by foaming	Cited from ref. 10 page 363
Synthetic surface active agents	From tannery waste waters	150
Urobiline	From urine	Cited from Ref. 10 page 363

TABLE 3. EXAMPLES OF MOLECULAR FLOTATION

Substance	Remarks	Reference
1-Chloromethyl naphtalene	From aqueous solutions using surfactants as nonyl phenyl polyethylene glycol ether	151
Phenol	Primarily as phenolate using ethylhexadecyldimethylammonium bromide	89

TABLE 4. EXAMPLES OF ION FLOTATION

ANIONS	Remarks	Reference
Aluminate	Aluminum separated from beryllium by floating oxalatoaluminate complexed with amines	152
Cerium-EDTA chelate	Using a cationic surfactant Hyamine 1622	78
Chromate	Soluble acid chromate separated at pH 4.2 using ethylhexadecyldimethylammonium bromide	76, 153
Cyanide	As soluble ferrocyanide at pH 7 using ethylhexadecyldimethylammonium bromide at a Fe/CN ratio of 10.21 mole: 1 mole	27, 76, 99, 154-156
	As polynucleated $FeFe(CN)_6^{2-}$, at pH 7 using ethylhexadecyldimethylammonium bromide	27, 76, 99, 154-156
Dichromate	Separated using ethylhexadecyldimethylammonium bromide	106, 159, 160
Gallate	Using a cationic surfactant	157, 158
Iodide	Using ethylhexadecyldimethylammonium bromide	153
1-Naphthoic acid 2-Naphthoic acid	Concentrated in foam from aqueous solution using surfactants as polyethoxyslearylmethylammonium chloride	151
Neodymium-EDTA chelate	Using the cationic surfactant Hyamine 1622	78
Orthophosphate	Using ethylhexadecyldimethylammonium bromide, optimum pH 8 to 9	89, 106, 161

ANIONS (Cont'd	Remarks	References
Phenolate	By diazo coupling	Cited in ref. 12
	Using cetyltrimethylammonium bromide	
	Using ethyhexadecyldimethylammonium bromide	106
Picrate	Using a cationic surfactant	157, 158
Samarium-EDTA Chelate	Using a cationic surfactant Hyamine 1622	78
Silicate	Using a cationic surfactant	157, 158
Thiosulfate	Complexes $Ag_2(S_2O_3)_2^=$, $Ag(S_2O_3)^-$ and $S_2O_3^=$ floated using ethylhexadecyldimethylammonium bromide	153
Zirconate	Floated as fluorozirconate with cationic surfactants	162
CATIONS		
Ag	From aqueous solutions using surfactants	163
	Using sodium dodecyl sulfate	164
	Thiosulfate complex with ethylhexadecyldimethylammonium bromide	153
Al	From dilute solutions using an anionic surfactant	165
	As oxalatoaluminate with amines	152
Au	From dilute solutions using anionic surfactants	165
Be	From aqueous solutions using coco oil acid laurate	95

CATIONS	Remarks	Reference
Ca	From aqueous solutions by anionic surfactants	158, 163
	From solutions of its salts using long chain alkyl sulfates and polyoxyethylene sulfates	166
Ce	Separated from aqueous solutions using Na dodecylbenzylsulfonate	167
	EDTA-chelate of cerium removed using cationic surfactant Hyamine 1622	78
Co	With Aresket 300	95, 158
	Its anionic chlorocomplex removed using hexadecyltrimethylammonium bromide	168
Cr	Using anionic surfactant from dilute solutions	165
	Removed as acid chromate using ethylhexadecyldimethylammonium bromide at pH 4.2	76, 153
Cs	From radioactive waste waters with soaps, and using electrolysis for producing foams	169
	From contaminated waters using detergents	170
	From aqueous solutions using sodium dodecyl benzylsulfonate	167
Cu	From aqueous solution using stearyl amine or sodium laurylsulfate, effect of pH examined	34
	From dilute aqueous solutions using sodium laurylsulfate and an auxiliary reagent N,N,N'N'-tetrakis (2 hydroxy propyl) ethylene diamine, NaCl improved separation	83
	Separated from solutions containing Zn by using increased pH	171

CATIONS (Cont'd	Remarks	Reference
	From aqueous solutions using anionic collectors	158,165
Fe	From aqueous solutions using toulene sulfonates	95
	From aqueous solutions using anionic detergents Nonionic detergents also tried, effect of pH studied, acid pH best	172
	Using stearyl amone or sodium laurylsulfate, effect of pH studied.	34
	From contaminated natural streams	173
	Using sodium dodecylsulfonate	164
	From aqueous solution containing 0.2 mM/l of Fe (III) using sodium laurylsulfate	3
	From aqueous solutions using long chain alkyl sulfates and polyoxyethylene sulfates	166
	As chlorocomplex using hexadecyltrimethylammonium bromide at pH 6-11	56, 168
	From dilute solutions using anionic collectors	165
Hg	$HgNO_3^-$ and HgCl complexes floated using hexadecyltrimethylammonium bromide	56, 168, 174
Mg	Using anionic collectors	163, 165
Mn	From aqueous solutions, some separations using long chain alkylsulfates and polyoxyethylenesulfates at pH 4 to 7	158, 166, 172
1-Naphthyl amine	Using sodium laurylsulfate	151
Ni	From dilute solutions using anionic collectors	165
	Using Aresket 300	169
Pb	From aqueous solution containing 10^{-4} M/l lead (II) using 2 X 10^{-3}M/l sodium laurylsulfate at pH 8.2 or below	3, 87
	From dilute solutions using anionic collectors	165

CATIONS (Cont'd)	Remarks	Reference
Radioruthenium	Using dodecylamine and gelatine at pH 5.6 to 8.5	175
Radium	From uranium mill waste waters using Aerosol 22	5,95
Sm	From aqueous solution using anionic surfactants	Cited in ref.10
	With polyaminopolycarboxylic acids	95
Sr	From solution containing 10^{-13} to 10^{-5} M/l Sr using sodium dodecylbenzylsulfonate	167
	From radioactive waste waters using soaps and electrolysis to produce foams	169
	From aqueous solutions with aromatic sulfonates and other surfactants, interference of Ca and Mg studied	77, 95, 158
U	Using Aresket 300	16
	From acid (HCl) solutions containing thorium salts with benzylthorium chloride	110
	From solutions containing vanadium and carbonates with benzylthorium chloride	176
V	From aqueous solutions	158
Th	From aqueous solutions	158
Zr	From aqueous solutions	158, 163

TABLE 5. EXAMPLES OF FOAM FLOTATION AND MICROFLOTATION

Substance	Remarks	Reference
ALGAE		
Chlamydomonas reinhardtii	Using collectors naturally produced by the organism	177
	Using stearyl amine as collector and ethanol as frother	57
Chlorella ellipsoidea	Using collectors naturally produced by organism	177
	Using stearyl amine as collector and ethanol as frother	57
General	Using commercial coagulants and collectors. Only promising reagents tested was arquad S, a quartenary amine compound, with bentonite and laurylammonium chloride. Optimum pH less than 4	178, 179
BACTERIA		
aer. aerogenes	Using collectors and coagulants	90
Bacillus anthracis	Floated using surfactants naturally produced by organisms	180
Bacillus cereus	Floated using surfactants such as cetyltrimethylammonium bromide, laurylamine, sodium laurysulfate or lauric acid; alum used as coagulant; pH effect studied	58
	Floated using surfactants naturally produced by the organism	180
Bacillus subtilis	Separated using dioctyl amine	181,182,183
	Floated using surfactants naturally produced by the organism	180

BACTERIA Cont'd	Remarks	Reference
Brucella suis	Partial flotation using surfactants naturally produced by the organism	180
Endamoeba hystolytica	Using a quartenary ammonium surfactants	184,185,186
Escherichia coli	Flotation from solution containing 3100 x 10^6 cells/cc with collectors in the presence of inorganic salts such as NaCl and Na Hydrogen phosphate; bovine albumin used as frother	183, 187,188
Mycobacterium tuberculosis var. hominis	Used flotation to concentrate the organism	189,190
Serratia marcescens	Removed by flotation from Bacillus subtil's var. niger	183
Miscellaneous	Removal of unidentified bacteria from sewage	191
COLLOIDS		
Al oxide sol		192,193
Carbon (active)	From synthetic waste water containing phenol and ethylhexadecyldimethylammonium bromide or dodecylsulfate or alkylphenoxy ethanol	194
Carbon (deactivated)		195,80
Clays	Separated at pH 2-12, both in the absence and presence of ferrous and ferric iron	196
Cr oxide sol		192,193

COLLOIDS (Cont'd	Remarks	Reference
Ferric oxide sol	Separated in colloidal form using ethylhexadecyldimethylammonium bromide best above pH 10.5 using Na dodecylsulfonate below pH 10.5	155, also 192 and 193
Illite	see clays	196
Iron dust	Oily dust floated using gas bubbles formed by electrolysis	197
Kaolinite	Using ethylhexadecyldimethylammonium bromide, see clays also	80, 196
Methyl cellulose	Foam fractionated according to molecular weight and methylation	148
Molybdenum	Collected from sea water by adsorbing on iron hydroxide precipitate and floating using Na dodecyl sulfate	198
Montmorillonite	Using ethylhexadecyldimethylammonium bromide, see clays also	80, 196
Stannic oxide sol		12
Wastes	Ink and pigments separated from scrap paper	199 (p. 89), 63 (p. 550)
	Solids removed from laundry wastes after adding ferric chloride to pH 6.7, 95% grease removal	200
	Removal of colloidal materials from sewage using pressure release flotation	191, 200
	Radioactive ions removed from waste waters by adsorbing on ferric hydroxide precipitate and floating	202

PROTEINS	Remarks	Reference
Acid prostatic phosphatase	Purified by foaming	200
Albumin	From aqueous solution; a limiting concentration above which the method failed	201
	From potato and beet juices	202
	From bovine serum solution	77
Albumoses	Concentrate in beer foam	Cited from ref. 10
Apple proteins	Proteins concentrated in foam	206
Beer proteins	Beer foam richer in proteins	Cited from ref. 10
Catalase	Purified by foaming from amalase	207
Cholic acid	From pure and impure aqueous *solutions; free crystalline acid* found in foam	208, 209
Cholinesterase	Purified by foaming horse serum	Cited from ref. 10
Dextrins	Concentrated in beer foams	
Diastaste	Diastaste concentrated in foam, lipase left in residue by pH control	
Fish scales	Partly hydrolyzed fish scales, different nitrogen concentrations in foam and bulk liquid	
γ- Globulin	From aqueous solution, a limiting concentration above which the method failed	204

PROTEINS (Cont'd	Remarks	Reference
Gonadotropic hormones	From urine	210
Hemoglobin	Strong salt drives hemoglobin into foam at pH 3	211
	From mixtures with serum	209
Hop resins	Concentrates in beer foams	Cited from ref. 10
Lactic dehydrogenase	Purified by foaming other proteins away	Cited in ref. 13
Lipase	Separated from diastase by foaming diatase away	Cited in ref. 10
Metaprotein	Accumulates in foam fractions from partly hydrolyzed soybean proteins	
Miscellaneous	Enzymes from fruit juices	
	Protein separated from artificial sea water	212
Pepsin	From solutions containing renin	213
Sugar beet proteins	From crude juice	214
Tyrosinase	Concentrates in the foam	215
Urease	Separated from catalase	216

TABLE 6. EXAMPLES OF PRECIPITATE FLOTATION

Substance	Remarks	Reference
Ag	Separated at 5 X 10^{-5} M/l concentration from ten-fold excess of Cr, Zn and Pb using α- nitroso β-naphthol or β-nitroso α-naphthol at pH 7 to 9	31
Au	Separated at 3 X 10^{-4} M/ l concentration from ten-fold excess of U using phenyl α-pyridyl ketoxime at pH 3 to 5	31
Co	Floated as ferrocyanide precipitate using gelatin	217
	Using α- nitroso β- naphthol at pH 2	91
Cr	Floated as ferrocyanide precipitate using gelatin	218
	Using sodium laurylsulfate at pH 8	76
	Using Na dodecylsulfate below pH 9 and above pH 4 and using ethylhexadecyldimethylammonium bromide above pH 10	154
Cs	Cs^{137} precipitated with $CuFe(CN)_6$ at pH 2 to 3 and floated best using Sapogen T (condensation product of chloroleic acid and methyl taurine) or cetyltrimethylammonium bromide	218
	Precipitated with Cu ferrocyanide and floated with Na dodecylsulfate	219
Cu	Floated as Cu ferrocyanide using gelatin	217
	Using Benzoinoxime at pH 8 to 9	91
	Using hydroxyquinoline at pH 6	91
	Using Na laurylsulfate at pH above 7	34

Substance	Remarks	Reference
	Nearly 100% removal above pH 8 using stearyl amine or sodium laurylsulfate	32, 34
Fe	Floated as ferrocyanide using gelatin	217
	Nearly 100% removal above pH 3 using Na laurylsulfate	32, 34
Mg	Floated as ferrocyanide complex using gelatin	217
Mn	Floated as ferrocyanide complex using gelatin	217
Ni	Separated at initial Ni concentration of 1.5 x 10^{-5} gm ion/l from hundred-fold excess of Co by precipitating with nioxime and floating at pH 4 to 12 and temperature 21 to 40°C	28, 91
	Using α-furildioxime at pH 10	91
	Floated as ferrocyanide precipitate using gelatin	217
Pd	Precipitated with nioxime and floated with no addition of collector at pH 1 to 2 from hundred-fold excess of Pt, Co or Fe, four hundred-fold excess of Ni and ten-fold excess of Au	91
	Using α-nitroso β-naphthol	91
Radioactive ions	Occluded in ferric hydroxide and floated with naphthalene sulfonic acid, gelatin and soap	217,219-221
Se	Precipitated at pH 2 using 3-3'-diamino benzidene and floated at pH 8 - 8.5, 35% recovery, slow precipitation	91
Sr	Separated at initial concentration of 10^{-3} M/l from Cs using dodecylpyridinium chloride	91,218
U	Floated as ferrocyanide precipitate using gelatin	217
	Separated at 10^{-4} M/l U (VI) concentration from ten-fold molar excess of Au and Fe, and hundred-fold excess of sulfate and Mn using phenyl-α-pyridyl ketoxime and benxoyl acetone	31

Substance	Remarks	Reference
	at pH 6 to 9	
Zn	Using 8-hydroxyquinoline at pH 6	91
	Floated as ferrocyanide precipitate using gelatin	217
	Nearly 100% removal above pH 8 using Na laurylsulfate	33

TABLE 7. FROTH FLOTATION WITHOUT ADDITION OF COLLECTOR

Substance	Remarks	Reference
Coal	Flotation depends on rank of coal-maximum at 89% carbon content; cresylic acid, pine oil or aliphatic alcohol etc. used as frothers	63 (p 539), 100 (p. 12:34 and p. 12:129)
Graphite	Easily floatable, pine oil is the preferred frother, might contaminate other materials easily and cause them to float, can be depressed using organic colloids	100 (12:129), 215, 63 (p.530)
Molybdenite	Natural flotation with or without the help of mineral oil, can be depressed using dextrin, starch, etc.	223
Rubber	Rubber recovered by flotation from milkweed plant after leaching, washing and ball milling	224
Sulfur	Floated using creosote as frother and Na silicate as a dispersant	100 (12:130), 62 (p. 529)
Talc	Naturally floatable, can be depressed using galactomannan, starch or glue	225, 100 (p 12:34)
Wastes	Paper and plastic materials from wastes	226, 227, 100 (p. 549-550)
Waxes	Easily floatable	63 (p 548)

TABLE 8. EXAMPLES OF FROTH FLOTATION USING COLLECTORS

Substance	Remarks	Reference
Anglesite ($PbSO_4$)	Floated at pH 9.5 to 11 using ethyl xanthate. NaH phosphate beneficial in small amounts	229 (p. 334)
	Responds to mercaptobenzothiazole in alkaline solution	228
Apatite ($(F.Cl.OH)Ca_5(PO_4)_3$)	Floated at pH 8 to 9 using fatty acids combination (fuel oil + tall oil + caustic soda)	223 (p. 238)
	Using dodecylammonium chloride above pH 6 and Na dodecylsulfonate below pH6	230
Barite ($BaSO_4$)	Floatable with fatty acid soaps and all anionic reagents such as sulfonates and sulfates in alkaline solutions (optimum pH with oleic acid 10-11)	231, 234 (p. 340), 100 (12:123)
Beryl ($Be_3Al_2(SiO_3)_6$)	Using fatty acids at pH 6 or petroleum sulfonates at pH 3 to 4	232
Bornite ($Cu_2SCuSFeS$)	Using ethyl xanthates, fatty acids, alkyl sulfates and sulfonates	35, 100 (12:109)
Calcite ($CaCO_3$)	Using fatty acid soaps at pH 8 to 9.5	231
	Using Na dodecylsulfate below pH 8 or dodecylammonium chloride at pH 10 to 12	100 (12:123)
Cement	Using oleic acid and Na silicate	223 (p. 341)
Cerrusite ($PbCO_3$)	Higher xanthates, sometimes with sodium sulfate	100 (p. 12:127)
Chalcocite (Cu_2S)	Readily floated by ethyl xanthates, fatty acids and long-chain sulfates and sulfonates	35, 100 (p.12:109)
Chalcopyrite ($CuFeS_2$)	Using ethyl xanthates, fatty acids and alkyl sulfates and sulfonates	35, 100 (p. 12:109)

Substance	Remarks	Reference
Cinnabar (HgS)	Conditioning with $CuSO_4$ at pH 8 and floating using higher xanthates and dithiophosphates	223, 100 (p. 12:108)
Corundum (Al_2O_3)	Floatable with soaps in acid pulp	100 (p. 12:126)
Feldspar ($KAlSi_3O_8 \cdot NaAlSi_3O_8 \cdot CaAl_2Si_2O_8$)	Conditioning by HF at pH 3 followed by floating with amine acetate, floatable with soap also	223 (p. 342), 100 (p. 12:126)
Fluorospar (CaF_2)	Using oleic acid and soap, optimum pH 8 to 9.5	233, 100 (p.12:123)
Galena (PbS)	Using ethyl xanthate as collector and oil as frother	35, 223 (p. 334)
	Using fatty acids and long-chain sulfonates and sulfates, activated by $CuSO_4$	100 (p 12:109)
Hematite (Fe_2O_3)	Using oleic acid at pH 7 to 7.4, Na hexametaphosphate and excess lead nitrate helpful	234
Ilmenite ($FeTiO_3$)	Using oleic acid along with corn oil and Na silicate, Isopolyacids helpful	100 (p 12:119)
Kyanite ($Al_2O_3 \cdot SiO_2$)	Floated using petroleum sulfonates and alcohol frothers at pH 3	223 (p. 344)
(Magnesite $MgCO_3$)	Floats readily with oleic acid	100 (p 12:124)
(Magnetite Fe_3O_4)	Using Na oleate and aux. reagents	100 (p 12:120)
Mica ($(H,K,Mg,F)_x Al_y(SiO_4)_3$)	Floatable with short chain alkyl amines or fatty acids, lead nitrate is an activator	235, 100 (p 12:127)
Psilomelane ($\sim H_4MnO_5$)	Floatable using a special process using tall oil, fuel oil and Oronite S wetting agent	223 (p. 335)

Substance	Remarks	Reference
Pyrite (FeS_2)	Using ethyl xanthates or fatty acids in acid solutions	35, 100 (p 12:109)
Pyrolusite (MnO_2)	Same as Psilomelane	
Pyrrohtite ($Fe_{11}S_{12}$)	Using ethyl xanthate below pH 6	35
Quartz (SiO_2)	Floatable with cationic collectors like dodecylammonium chloride or anionic collectors in presence of heavy metal ions	38, 100 (p 12:127)
Sphalerite (ZnS)	Using higher xanthates and dithiophosphates and frothers like cresylic acid or Aerofloat 15	223 (p. 338)
	Fatty acids in acid pulps	100 (p 12:111)
Spodumene ($LiAl(SiO_3)_2$)	Some floatable using oleic acid and frothers in slightly alkaline or neutral pulp	223 (p. 345)
	Floatable with soaps	100 (p 12:128)
Stibnite (Sb_2S_3)	Floatable with xanthate in presence of $CuSO_4$	100 (p 12:112)
	Floatable with thiocarbanilid as Aerofloat in presence of lead	100 (p 12:112)
Sylvite (KCl)	KCl can be floated away from NaCl using amines	136,236,237, 237
Textile fibers	With or without a frother, vinyon and wool float well at all pH without any reagent, rayon does not float at any pH, silk, casein and nylon float in acid pH	239
Vegetable and seed products	Peas cleaned by dropping in aerated emulsion of hydrocarbon in dil. Na lauryl sulfate and floating contaminants and damaged peas	237

Substance	Remarks	Reference
	Germinating seeds separated from non-germinating	238
Wastes	Solids removed from laundry waste after adding ferric chloride to pH 6.7, alum also effective	200
	Sewage floated, dodecyl amine removed 95-99% of solids	191

ACKNOWLEDGMENT

The author wishes to thank Mr. B. M. Moudgil for help with the literature search.

REFERENCES

1. B.L. Karger, R.B. Grieves, R. Lemlich, A.J. Rubin and F. Sebba, Separ. Sc., 2, 401 (1967).
2. "Adsorptive Bubble Separation Techniques", R. Lemlich, ed., Academic Press, New York, 1972.
3. T.A. Pinfold, Separ. Sc., 5, 379 (1970).
4. A.J. Rubin, J. Am. Water Works Assoc., 60, 832 (1968).
5. H.M. Schoen, E. Rubin, and D. Ghosh, J. Water Pollution Control Federation, 34, 1026 (1962).
6. P. Somasundaran, Trans. AIME, 241, 105 (1968).
7. J.T. Davies and E.K. Rideal, "Interfacial Phenomena", Academic Press, N.Y., 1963.
8. Nilsson, J. Phys. Chem. 61, 1135 (1957).
9. E. Matijevic and B.A. Pethica, Trans. Faraday Soc., 54, 1382 (1958); Croatica Chemica Acta, 29, 431 (1957).
10. E. Rubin and E.L. Gaden, Jr., in "New Chemical Engineering Techniques", H.M. Schoen, ed., Interscience, New York, 1962, p. 319-385.
11. R. Lemlich, in "Progress in Separation and Purification" Vol. 1, E.S. Perry, ed., Interscience, New York, 1968, p. 1-56.
12. R. Lemlich, I and EC, 60, 16 (1968).
13. B.L. Karger and D.G. DeVivo, Separ. Sc., 3, 393 (1968).
14. D.K. Chattoraj, J. Coll. Interf. Sci., 26, 379 (1968); J. Phys. Chem., 70, 2687 (1966).
15. P.H. Elworthy and K.J. Mysels, J. Coll. Interf. Sci., 21, 331 (1966); M. Abuhamidiyyah and K.J. Mysels, J. Phys. Chem., 71, 418 (1967).
16. E. Rubin, Ph. D. Dissertation, Columbia University, 1962.
17. Radiations Applications Inc., Long Island City, N.Y. Eng. Mining J., Aug. 1960.

18. I.J. Lin and P. Somasundaran, J. Coll. Interf. Science, 37, 371 (1971).

19. A.P. Brady and A.G. Brown, in "Monomolecular Layers", Sobotka H, ed., Amer. Assoc. Adv. Science, Washington, D.C., 1954, p. 42.

20. E. Rubin and J. Jorne, I and EC Fundamentals, 8, 474 (1969).

21. P. Somasundaran and D.W. Fuerstenau, J. Phys. Chem., 70, 90 (1966).

22. F. Sebba, "Ion Flotation", Elsevier, New York, 1962.

23. Rubin, et, al, U.S. Public Health Service AWTR-5, Report No. 999-LP-5, 1963.

24. E. Rubin and J. Jorne, J. Coll. Interf. Sc., 33, 208 (1970).

25. D. Bhattacharyya, J.A. Carlton and R.B. Grieves, AIChE Journal, 17, 419 (1971).

26. R.B. Grieves, and R.W. Lee, I and EC Process Des. Develop., 10, 390 (1971).

27. R.B. Grieves and D. Bhattacharyya, Separ. Sc., 4, 301 (1969).

28. E.J. Mahne and T.A. Pinfold, J. Appl. Chem., 18, 52 (1968).

29. E.J. Mahne and T.A. Pinfold, J. Appl. Chem., 18, 140 (1968).

30. I. Sheiham and T.A. Pinfold, J. Appl. Chem., 18, 217 (1968).

31. E.J. Mahne and T.A. Pinfold, J. Appl. Chem., 19, 57 (1969).

32. A. J. Rubin, J.D. Johnson, and J.C. Lamb III, I and EC Process Des. Develop., 5, 368 (1966).

33. A.J. Rubin, and W.L. Lapp, Separ. Sc., 6, 357 (1971).

34. A.J. Rubin and J.D. Johnson, Anal. Chem. 39, 298 (1967).

35. J. Rogers, in "Froth Flotation, 50th Anniversary Volume", D.W. Fuerstenau, ed., AIME, N.Y. 1962, pp. 139-169.

36. D.W. Fuerstenau, and B.J. Yamada, Trans. AIME, 223, 30 (1962).

37. P. Somasundaran and D.W. Fuerstenau, Trans. AIME, 241, 102 (1968).

38. D.W. Fuerstenau, T.W. Healy and P. Somasundaran, Trans. AIME 229, 321 (1964).

39. P. Somasundaran, T.W. Healy and D.W. Fuerstenau, J. Phys. Chem., 68, 3562 (1966).

40. P. Somasundaran and D.W. Fuerstenau, J. Phys. Chem., 70, 90 (1966).

41. D.W. Fuerstenau, Pure and Applied Chemistry, 24, 135 (1970)

42. J.M.W. Mackenzie, Minerals Science and Engineering, 3, 25 (1971).

43. P. Somasundaran and G.E. Agar, J. Coll. Interf. Sc., 24, 433 (1967).

44. P. Somasundaran, in "Clean Surfaces: Their Preparation and Characterization for Interfacial Studies", G. Goldfinger, ed., Marcel Dekker, New York, 1970, p. 285.

45. H.J. Modi, and D.W. Fuerstenau, Trans. AIME, 217, 381 (1960).

46. M.C. Fuerstenau, C.C. Martin, and R.B. Bhappu, Trans. AIME, 226, 449 (1963).

47. M.C. Fuerstenau, D.A. Rice, P. Somasundaran, and D.W. Fuerstenau, Trans. IMM, 73, 381 (1965).

48. M.C. Fuerstenau, and D.A. Rice, Trans. AIME, 241, 453 (1968).

49. P. Somasundaran, J. Coll. Interf. Sc., 31, 557 (1969).

50. K. Freudenberg, E. Schaaf, G. Dumpert, and T. Plotez, Naturwiss., 27, 850 (1939).

51. P. Somasundaran, and D.W. Fuerstenau, "The Heat and Entropy of Adsorption and Association of Long Chain Surfactants at the Alumina-Aqueous Solution Interface", accepted for publication in Trans. AIME, 1972.

52. P. Somasundaran, T.W. Healy and D.W. Fuerstenau, J. Coll. Interf. Sc., 22, 599 (1966).

53. E. B. Johnson and C. Bjorne, in "Milling Methods in Americas", N. Arbiter, ed., Gordon and Brearch, N.Y. 1964. p. 161.

54. C. Bjorne and J. Keeley, Mining Engineering, June 1964, p. 65.

55. A.C. Dorenfeld, in "Froth Flotation--50th Anniversary Volume", D.W. Fuerstenau, ed., AIME, New York, 1962, p. 373.

56. B.L. Karger, R.P. Poncha and M.W. Miller, Analytical Letters, 1, 437 (1968).

57. A.J. Rubin, E.A. Cassel, O. Henderson, J.D. Johnson, and J.C. Lamb III, Biotech. Eng., 8, 135 (1966).

58. A.J. Rubin and S.C. Lackey, J. Am. Water Works Assoc. 60, 1156 (1968).

59. D.E. Garrett, "Phosphate Removal by Foam Fractionation", presented to the 3rd meeting of the AIChE--IMIQ meeting, Denver, Colo., Aug. 30-Sept. 2, 1970.

60. G.N. Shah and R. Lemlich, I and EC Fundamentals, 9, 350 (1970)

61. T.J.N. Grainger-Allen, Trans. IMM (London), 79, C15 (1970).

62. V. Bjerknes, "Vorlesungen Uber Hydrodynamische Fernkrafte Nach C.A. Wagner Theorie", Leipzig: J.A. Barth, 1902, Vol. 1,p.388; Vol. 2, p. 316.

63. A.M. Gaudin, "Flotation", 2nd. ed., New York, 1957, pp. 157-162.

64. K.L. Sutherland and I.W. Wark, "Principles of Flotation", Aust. Inst. Min. and Met., Melbourne, 1955, pp. 357-374.

65. T.M. Morris, Trans. AIME, 187, 91 (1950).

66. C.W. Nutt, Chem. Eng. Sci., 12, 133 (1960).

67. A. Sheludko, Koll. Zeit. Polymere, 191, 52 (1963).

68. A.S. Joy and A.J. Robinson, in "Recent Progress in Surface Science", Vol. 2, J.F. Danielli, K.G.A. Pankhurst, and A.C. Riddiford, ed., Academic Press, New York, p. 169.

69. C.C. Harris and V. Lepetic, Mining Engineering, 67, (1966); N. Arbiter, C.C. Harris, and R.F. Yap, Trans. AIME, 244, 134 (1969).

70. W.L. Haberman and R.K. Morton "An experimental investigation of the drag and shape of air bubbles rising in various liquids", Model Basin Report No. 802 (1953).

71. J.A. Kitchener, in "Recent Progress in Surface Science" Vol. 1, J.F. Danielli, K.G.A. Pankhurst, and A.C. Riddiford, ed., Academic Press, N.Y., 1964, pp. 51-93.

72. S. Ross, I and EC, 61, 48 (1969).

73. K.J. Mysels, K. Shinoda, and S. Frankels "Soap films", Pergamon, London, 1959.

74. J.A. Kitchener, and C.F. Cooper, Chem. Soc. London Quart. Rev. 13, 71 (1959)

75. E.O. Aenlle, Anales Fis. Y. Quim. (Madrid), 42, 179 (1946); C. A. 41, 4649i (1947).

76. R.B. Grieves, J. Water Pollution Control Federation, 42, R336 (1970).

77. R.W. Schnef, E.L. Gaden, E. Mirocnik, and E. Schonfeld, Chem Eng. Prog. 55, 42 (1959).

78. G.H. Robertson and T. Vermeulen, "Foam Fractionation of rare-earth elements", Lawrence Radiation Laboratory Report, UCRL-19525, December 1969.

79. C.A. Brunner, and D.G. Stephan, I and EC, 57, 40 (1965).

80. G.D. DeVivo and B.L. Karger, Separ. Sc., 5, 145 (1970)

81. R.B. Grieves and S.M. Schwartz, J. Am. Water Works Assoc., 58, 1129 (1966).

82. I. Sheiham and T.A. Pinfold, "Some Parameters affecting the Flotation of cationic surfactants", to be published.

83. W.L. Dick and F.D. Talbot, I and EC Fundamentals, 10, 309 (1971).

84. A.M. Gaudin, and A. Rizo-Patron, Trans. AIME, 153, 462 (1943); R. Schuhmann and B. Prakash: Trans. AIME, 187, 591 (1950).

85. I.W. Wark, "Principles of Flotation", Aust. Inst. Min. and Met., Melbourne, 1938, p. 187.

86. F.F. Aplan and D.W. Fuerstenau, in "Froth Flotation, 50th anniversary volume", ed., by D.W. Fuerstenau, AIME, New York, 1962, p. 170.

87. A.J. Rubin and W.L. Lapp, Anal. Chem., 41, 1133 (1969)

88. R.B. Grieves and D. Bhattacharyya, Nature, 204, 441 (1964)

89. R.B. Grieves, Foam Fractionation of surfactants and of orthophosphate and phenol, in reference 2.

90. A.J. Rubin, Biotech. Eng., 10, 89 (1968)

91. E.J. Mahne and T.A. Pinfold, Chemistry and Industry, 1299 (1966).

92. F. Schutz, Brit. Patent 498,643, Jan. 11, 1939.

93. S.I. Mitrofanov, in "Progress in Mineral Dressing," Almquist and Wiksell, Stockholm, 1957, p. 461.

94. R.B. Grieves and R.K. Wood, J. Am. Inst. Chem. Engrs., 10, 456 (1964); R.B. Grieves and D. Bhattacharya. J. Am. Oil. Chem, 42, 174 (1965); R.B. Grieves and D. Bhattacharya, J. Water Pollution Control Fed., 37, 980 (1965).

95. H.M. Schoen and G. Mazella, Ind. Water Wastes, 6, 71 (1961).

96. R. Lemlich, and E. Lavi, Science, 134, 191 (1961).

97. D.O. Harper and R. Lemlich, AIChE Journal, 12, 1220 (1966).

98. E. Schonfeld, and A.H. Kibbey, Nucl. Appl. 3, 353 (1967).

99. R.B. Grieves and D. Bhattacharya, J. Appl. Chem. (London), 19, 115 (1969).

100. A.F. Taggart, "Handbook of Mineral Dressing", John Wiley and Sons, New York, 1964, pp. 12:55 to 12:78.

101. Reference 63, pages 414-428.

102. D.W. Fuerstenau, P.H. Metzger and G.D. Seele, Engineering and Mining J., 158, 93 (1957).

103. F. Schutz, Trans. Faraday Soc., 41, 437 (1946).

104. P.A. Haas and H.F. Johnson, I and EC Fundamentals, 6, 235 (1967).

105. K. Shinoda and K. Mashio, J. Phys. Chem., 64, 54 (1960)

106. R.B. Grieves, Separation Science, 1, 395 (1966).

107. P.F. Wale, P.J. Alder, and D.L. Banfield, Chemical Engineering Process Symposium series, 65 (91), 19 (1969).

108. M. Arbitat, Chim. Anal., 39, 217 (1957).

109. M. Arbitat, U.S. Pat. 2,313,007, March 2, 1943.

110. C. Jacobelli-Turi, S. Terenzi and M. Palmera, I and EC Process Design Dev., 6, 162 (1967).

111. V.P. Shvedov, and M.F. Yakushev, Radiokhimiya, 12, 871 (1970).

112. D.O. Harper and R. Lemlich, I and EC Process Des. Dev. 4, 13 (1965).

113. S. Fanlo and R. Lemlich, AIChE-Chem. E. Symposium series No. 9, 75 (1965).

114. M. Goldberg and E. Rubin, I and EC Process Des. Dev. 6, 195 (1967).

115. E. Gastrock and J.D. Reid, Ind. Eng. Chem., Anal. Ed., 10, 440 (1938).

116. B.L. Karger, R.P. Poncha and M.M. Miller, Anal. Chem., 38, 764 (1966).

117. H. Kishimoto, Kolloid-Z, 192, 66 (1963).

118. R.P. Poncha, and B.L. Karger, Anal. Chem., 37, 442 (1965).

119. C.A. Brunner and R. Lemlich, I and EC Fundamentals, 2, 297 (1963).

120. C. Walling, E.E. Ruff, and J.L. Thorton, Jr., J. Phys. Chem., 56, 989 (1952)

121. E. Rubin and M. Golt, I and EC Process Des. Dev., 9, 341 (1970)

122. P.A. Hass and H.F. Johnson, AIChE Journal, 11, 319 (1965).

123. R.M.G. Boucher and A.L. Weiner, Food Processing, 23, 85 (1962).

124. P.A. Haas, Ph.D. Thesis, University of Tennessee, 1965.

125. D.F. Kelsall, Trans. IMM (London), 70, 191 (1960-61).

126. B.K. Loveday, Trans. IMM, 75, C219 (1966).

127. E.T. Woodburn and B.K. Loveday, J. South African Min. and Met., 65, 612 (1965).

128. C.C. Harris and A. Chakravarti, Trans. AIME, 247, 162 (1970).

129. K.V.S. Sastry and D.W. Fuerstenau, Trans. AIME, 247, 46 (1970)

130. B. Ball, P.C. Kapur, and D.W. Fuerstenau, Trans. AIME, 247, 263 (1970).

131. R. A. Leonard and R. Lemlich, AIChE Journal 11, 18 (1965).

132. F. Shih, and R. Lemlich, AIChE. Journal, 13, 751 (1967).

133. R.B. Grieves, S. Kelman, W.R. Obermann, and R.K. Wood, Can. J. Chem. Eng. 41, 252 (1963).

134. E. Rubin, C.R. Lamantia, and E.L. Gaden, Jr., C.E.S., 22, 1117 (1967).

135. E. Rubin, and M.S. Hoffer, I and EC Fundamentals 8, 483 (1969).

136. P. Somasundaran and G.O. Prickett, Trans. AIME, 244, 369 (1969).

137. P.H. McGauhey and S.A. Klein, Public Works, 92, 101 (May 1961).

138. E. Rubin, R. Everett, J.J. Weinstock and H.M. Schoen, U.S. Public Health Publ. AWTR-5, Cincinatti, 1963.

139. L. Shedlovsky, J. Ross and C.W. Jakob, J. Colloid. Sci., 4, 25 (1949).

140. A.P. Brady, J. Phys. Colloid. Chem., 53, 56 (1949).

141. J.L. Rose and J.F. Sebald, Tappi, 51, 314 (1968)

142. R. Dubrisay, Compt. Rend., 194, 1076 (1932).

143. B.N. Khrustalev, V.V. Pushkarev, and E.N. Mikheev, Zh. Prikl. Khim. (Leningrad), 41, 2463 (1968), C.A. 70, 48886r (1969).

144. V.V. Pushkarev, V.L. Zolotavin, and B.N. Khrustalev, Ochistka Povtorne Ispol'z. Stochnykh Vod. Urale, 2, 59 (1967), C.A., 71, 87373a (1969).

145. D.C. McLean, item No. 5.0966 in "Water Resources Research Catalog", Vol. 2, U.S. Dept. Interior, Nov. 1966.

146. W. Krygielowa, J. Kucharski, and J. Wasowiczowa, Zesz-Nauk. Politech. Slask. Chem. No. 34, 103 (1966), C.A., 68, 15871n, (1968).

147. D.E. Garrett, U.S. Patent 3,448,044, June 1969.

148. F. Schutz, Trans. Faraday Soc., 38, 85 (1942).

149. R.B. Grieves and R.C. Aronica, Intern. J. Air Water Pollution, 10, 31 (1966).

150. V. Kondratavicius, Kozh. Obuv. Prom., 11, 15 (1969), C.A., 70, 108994m (1969).

151. B.L. Karger and L.B. Rogers, Anal. Chem., 33, 1165 (1961).

152. J.A. Lusher and F. Sebba, J. Appl. Chem., 15, 577 (1965).

153. R.B. Grieves and D. Bhattacharya, "Foam Separation of Anions: Stoichiometry", to be published.

154. R.B. Grieves and D. Bhattacharya, "Ion, Colloid, and Precipitate Flotation of Inorganic Anions", in reference 2.

155. R.B. Grieves, D. Bhattacharya, and W.L. Conger, CEP. Symp. Ser., 65, 29 (1969).

156. R.B. Grieves, and D. Bhattacharya, Separ. Sci. 3, 185 (1968).

157. F. Sebba, Nature, 188, 736 (1960)

158. F. Sebba, Nature, 184, 1062 (1959).

159. R.B. Grieves and S.M. Schwartz, AIChE Journal, 12, 746 (1966).

160. R.B. Grieves, E. Wilson and K.Y. Shih, AIChE Journal, 11, 820 (1965).

161. R.B. Grieves and D. Bhattacharya, Separ. Sc. 1, 81 (1966).

162. H.W. Rice and F. Sebba, J. Appl. Chem., 15, 105 (1965).

163. C. Walling, E.E. Ruff, and J.L. Thornton, J. Phys. Chem., 61, 486 (1957).

164. N. Aoki and T. Sasaki, Bull. Chem. Soc. Japan, 39, 939 (1966).

165. L. Dobresco, and V. Dobrescu, Rev. Minelor. (Bucharest), 19, 231 (1968).

166. J.J. Bikerman, U.S. Office Saline Water, Res. Dev. Progr. Rep. 1970, No. 510.

167. D.L. Banfield, I.H. Newson, and P.J. Alder, Proc. AIChE-I Chem. E. Joint Meet. London, 1965, page 3.

168. B.L. Karger and M.W. Miller, Anal. Chim. Acta, 48, 273 (1969).

169. V.P. Shvedov and M.F. Yakushev, Radiokhimiya, 12, 871 (1970), C.A., 74, 130160n (1971).

170. L. Argiero, and A. Paggi, Health Phys., 14, 531 (1968).

171. C. Jacobelli-Turi, M. Palmera, and A. Margani, Ric. Sci., 36, 1198 (1966).

172. J.J. Bikerman, U.S. Office Saline Water, Res. Dev. Progr. Rep. 1969, No. 382.

173. D.C. McLean, item No. 5.0965 in "Water Resources Research Catalog", Vol. 2, U.S. Dept. Interior, Nov. 1966.

174. M.W. Miller and G.L. Sullivan, Separ. Sci., 6, 553 (1971).

175. F. Kepak and J. Kriva, Separ. Sci., 5, 385 (1970).

176. C. Jacobelli-Turi, A. Barocas, and S. Terenzi, I and EC Process Des. Dev., 6, 161 (1967)

177. G.V. Levin, J.R. Clendenning, A. Gibor, and F.D. Bogar, Appl. Microbiol., 10, 169 (1962).

178. H.B. Gotaas, and C.G. Golueke, "Recovery of Algae from Waste Stabilization Ponds", Algae Research Project, Sanitary Engineering Research Laboratory, issue No. 7, IER Series 44, University of California, 1957.

179. L.R.J. van Vuuren, P.G.J. Meiring, M.R. Henzen, and F.F. Kolbe, Intern. J. Air Water Pollution, 9, 823 (1965).

180. W.A. Boyles and R.E. Lincoln, Appl. Microbiol., 6, 327 (1959).

181. A.M. Gaudin, A.L. Mular, and R.F. O'Connor, Appl. Microbiol., 8, 91 (1960).

182. A.M. Gaudin, A.L. Mular, and R.F. O'Connor, Appl. Microbiol., 8, 84 (1960).

183. A.M. Gaudin, in "Froth Flotation, 50th Anniversary Volume, D.W. Fuerstenau, ed., AIME, N.Y., 1962, p. 658.

184. S.H. Hopper and M.C. McCowen, J. Am. Water Works Assoc., 44, 719 (1952)

185. S.H. Hopper, J. Am. Water Works Assoc., 37, 302 (1945).

186. S.H. Hopper, Am. Soc. Tropical Medicine and Hygiene Meeting, 1955.

187. A. M. Gaudin, N.S. Davis, and S.E. Bangs, Biotechnol. Eng., 4, 223 (1962).

188. A.M. Gaudin, N.S. Davis, and S.E. Bangs, Biotechnol. Eng., 4, 211 (1962).

189. A. Dognon, Rev. Sci., 79, 613 (1941).

190. A. Dognon, Bull. Soc. Chim. Biol. 23, 249 (1941).

191. C.A. Hansen and H.B. Gotaas, Sew. Works J., 15, 242 (1943).

192. B.R. Clanton, Textile Res., 8, 301 (1938).
193. J.E. Magoffin and B.R. Clanton, Textile Res., 8, 357 (1938).
194. R.B. Grieves and E.F. Chouinard, J. Appl. Chem. (London), 19, 60 (1969).
195. E.F. Chouinard, "Removal of deactivated carbon by foam separation", IIT Thesis, 1968.
196. C.J. Grandall and R.B. Grieves, Water Research, 2, 817 (1968).
197. D. Ellwood, Chem. Eng. 75, 82 (1968).
198. Y.S. Kim and H. Zeitlin, Separ. Sc., 6, 505 (1971).
199. C.W. Merill and J.W. Pennington, in "Froth Flotation--50th Anniversary Volume", D.W. Fuerstenau, ed., AIME, N.Y. 1962, p. 55.
200. R. Eliassen and H.B. Schulhoff, Sewage Works J., 16, 287 (1944).
201 W.W. Eckenfelder, Jr., and D.J. O'Connor, "Biological Waste Treatment", Pergamon Press, New York, N.Y. 1961.
202. S.A. Voznesenskii, G.A. Sereda, L.I. Baskv, E.V. Tkachenko, and V.F. Bagretsov, Kernenergie, 4, 316 (1961), C.A., 62, 2610e (1961).
203. M. London and P.B. Hudson, Arch. Biochem. and Biophys., 46, 141 (1953).
204. J. Spurny and B. Jakoubek, Tenside, 5, 1 (1968).
205. W. Ostwald and A. Siehr, Kolloid-Z, 79, 11 (1937).
206. S.G. Davis, C.R. Fellers, and W.B. Esseler, Food Research, 14, 417 (1949).
207. S.E. Charm, J. Morningstar, C.C. Matteo, and B. Paltiel, Anal. Biochem., 15, 498 (1966).
208. R. Bader and F. Schutz, Trans. Faraday Soc., 42, 571 (1946).
209. F. Schutz, Nature, 139, 629 (1937).
210. R. Courier, and A. Dognon, Compt. Rend., 209, 242 (1939).

211. A. Dognon and L. Gougerot, Bull. Soc. Chim. Biol., 29, 702 (1947).

212. G.T. Wallace, Jr., and D.F. Wilson, U.S. Clearing House Fed. Sci. Tech. Inform., AD 1969, AD 1969, AD-697924, C. A . 72, p. 223 (1970).

213. G. Andrews and F. Schutz, Biochem. J. (London), 39, li (1945).

214. o. Spengler and W. Dorfeldt, Z. Wirtschaftsgruppe Zuckerind, 92, 279 (1942); C. A., 37, 6923 (1943).

215. A. Dognon and H. Dumontet, Compt. Rend. Soc. Biol., 135, 884 (1941).

216. M. London, M. Cohen, and P.B. Hudson, Biochem. et Biophys. Acta, 13, 111 (1954).

217. V.V. Pushkarev, Y.V. Egorov, E. Tkachenko, and V. Zolatavin, Atom Energ., 16, 48 (1964).

218. J. Oglaza and A. Siemaszko, Nukleonika, 14, 275 (1969), C.A. 72. 8440z (1970).

219. S. Voznesenskii, G. Serada, L. Baskov, E. Tkachenko, and U Bagretsov, Kernenergie, 4, 316 (1961), C.A., 62, 2610e (1965).

220. V.V. Pushkarev, V.F. Bagretsov, and V.D. Pizako, Radiokihimiya, 6, 120 (1964).

221. V.V. Pushkarev, 8, 431 (1966); C.A., 65, 14477b (1966).

222. D.J. Brown, in "Froth Flotation, 50th Anniversary Volume", by D.W. Fuerstenau, ed., AIME, N.Y., 1962, p. 518.

223. C. Thom, in "Froth Flotation, 50th Anniversary Volume", D.W Fuerstenau, ed., AIME, N.Y., 1962, p. 343.

224. W.T. Turall, J. Klassen and H. Smedley, Can. J. Research, 21B, 195 (1943).

225. F.M. Lewis and T.M. Morris, in "Froth Flotation, 50th Anniversary Volume", D.W. Fuerstenau, ed., AIME, N.Y. page 465.

226. R. Eliassen and B.S. Henry, Water Works and Sewage, 90, 418 (1943).

227. R. Elliassen and B.S. Henry, Sewage Works, J., 16, 287 (1949).

228. I.W. Wark and A.B. Cox, Trans. AIME, 134, 64 (1939).

229. I.W. Wark and A.B. Cox, Trans. AIME, 134, 10 (1939).

230. P. Somasundaran, J. Coll. Interf. Sc., 27, 659 (1968).

231. O. Lee, RI 2744, USBM, 1926.

232. K.E. Baarson, C.L. Ray, and H.B. Treweek, in "Froth Flotation, 50th Anniversaty Volume", D.W. Fuerstenau, ed., AIME, N.Y., 1962, p. 427.

233. M.A. Cook and A.W. Last, Utah Engr. Expt. Sta. Bull., 47, 1950.

234. W.E. Keck, G.C. Eggleston and W.W. Lowry, Trans. AIME, 134 102 (1939).

235. E.H. Crabtree and J.D. Vincent, in "Froth Flotation, 50th Anniversary Volume, D.W. Fuerstenau, ed., AIME, N.Y., p.51.

236. G.E. Atwood and D.J. Bourne, Trans. AIME, 196, 1099 (1953).

237. A.M. Neubert, Food Inds., 19, 769 and 890 and 892 (1947).

238. T. Earle, U.S. Patent 2,155,219 (1939).

239. J.M. Preston and S. Saha, J. Textile Inst., 40, T381 (1949).

240 Paper presented at the Symposium on "Colloid and Surface Chemical Methods of Separation" held at the 162nd ACS national meeting, Washington D.C.