

Separation Using Foaming Techniques

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Abstract

Separation of various chemical components from each other is often the most difficult step in analytical procedures. The problems attached to separation become further magnified when the species concentrations are extremely low. A group of techniques that has proven useful especially in dilute solutions for separating and concentrating metallic as well as nonmetallic ions and complexes, proteins, microorganisms, particulates, etc. is the adsorptive bubble separation techniques. Minerals have indeed been treated using some of these techniques for decades. The success of these processes is primarily dependent upon differences in the natural surface activity of various species or particulates in the system or in their tendency to associate with surfactants. The efficiency of the process is determined by such variables as solution pH, ionic strength, concentration of various activating and depressing agents, and temperature. A proper control of variables offers an opportunity to separate a variety of metallic and nonmetallic species and particulates. In this paper the principles governing various foam separation techniques, particularly froth flotation, are presented along with the recent results on the role of variables that can be controlled to achieve complete removal of species and particulates for analytical purposes.

INTRODUCTION

A variety of materials can be concentrated as well as separated from one another using foam separation techniques that make use of the tendency of surface-active components in a solution to preferentially concentrate at the solution/gas interface. Nonsurface active agents that are capable of associating with surface-active agents can also be separated using these

techniques. A comprehensive list of materials that have been treated using foam separation techniques is available in a recent publication (1). The list includes various anions such as alkylbenzyl sulfonate; chromate; cyanide and phenolate; cations of, for example, dodecylamine, mercury, lead, and strontium; proteins; microorganisms; and minerals. The attractive feature of this group of techniques is its effectiveness in the concentration range that is too dilute for the successful use of most other techniques. Furthermore, these techniques are ideally suitable for also treating materials that are too sensitive to changes in temperature. In this paper first principles that govern the separation will be briefly described and then the role of common variables that can be controlled for optimizing the separation will be examined with the help of typical examples.

Various foam separation methods studied in the past are listed in Table I on the basis of (a) the particle size of the materials and (b) the mechanism by which they are separated. Thus we have foam fractionation for separating surface-active species such as detergents from aqueous solution, and molecular and ion flotation for the separation of nonsurface-active species such as strontium, lead, and cyanides that can be made to associate with various surfactants. Nonsurface-active species that are separated in this manner are called colligends, and the surface-active agents used to separate them are called collectors. The separation of microscopic size organisms and proteins which are naturally surface active has been called foam flotation,

TABLE I
Various Adsorptive Bubble Separation Methods Classified on the Basis of
Mechanism of Separation and Size of the Material Separated (1)

Mechanism	Size range		
	Molecular	Microscopic	Macroscopic
	Foam fractionation; example, detergents from aqueous solutions		Froth flotation of nonpolar minerals; example, sulfur
Its association with surface active species	Ion flotation, molecular flotation; examples, Sr^{2+} , Ag^{2+} , Pb^{2+} , Hg^{2+} , cyanides, phosphates	Microflotation; examples, particulates in waste, microorganisms	Froth flotation; example, mineral: such as silica. Precipitate flotation (1st and 2nd kind); example, ferric hydroxide

and that of subsieve size particulates which are not surface active by themselves has been called microflotation. Froth flotation, used in the mineral beneficiation area for the last 60 years, refers to the separation of sieve-size particulates. It must be noted that, as opposed to all other foam separation techniques, froth flotation employs a relatively high gas flow-rate under turbulent conditions. Next to froth flotation, the most useful foam separation technique is precipitate flotation where the species to be separated is first precipitated, usually by a change of solution pH, and then floated with the help of surfactants which adsorb on the precipitates. In addition to the above techniques, there are also certain nonfoaming separation methods such as bubble fractionation (2) and solvent sublation (3) where adsorption at interfaces is again the basis for concentration, but the adsorbed material is collected for removal in another liquid that is immiscible with the bulk solution. All the above foaming and nonfoaming methods have been collectively called adsorptive bubble separation techniques (4).

METHODS

In practice, foam separation consists of aeration at a low flow-rate of the solution containing the species to be separated and a surfactant, if the species are not naturally surface active, and separation of the adsorbed components by simply removing the foam mechanically and breaking it using various chemical, thermal, or mechanical methods (5). Recovery or percent removal and the grade of the product is increased by using a stripping mode and an enriching mode, respectively. In the former mode the feed is introduced into the foam so that some amount of separation takes place while it is descending through the foam itself. In the enriching mode a certain amount of reflux for increasing the separation factor is achieved by feeding part of the foamate back to the top of the column. In a conventional froth flotation cell, a pulp of particles containing appropriate reagents is agitated using an impeller, and air is sucked in or sometimes fed into the cell. Those particles that are hydrophobic or that have acquired hydrophobicity adhere to air bubbles and thus rise to the cell top where they are removed by skimming. A flotation cell that is suitable for analytical purposes is the modified Hallimond cell (6) shown in Fig. 1. It consists mainly of two parts, a glass well with a fritted glass disk at the bottom connected to a gas reservoir and a bent top part with a stem just above the bend. Stirring can be accomplished either by means of a magnetic stirrer or by means of an impeller. Gas flow-rate is controlled

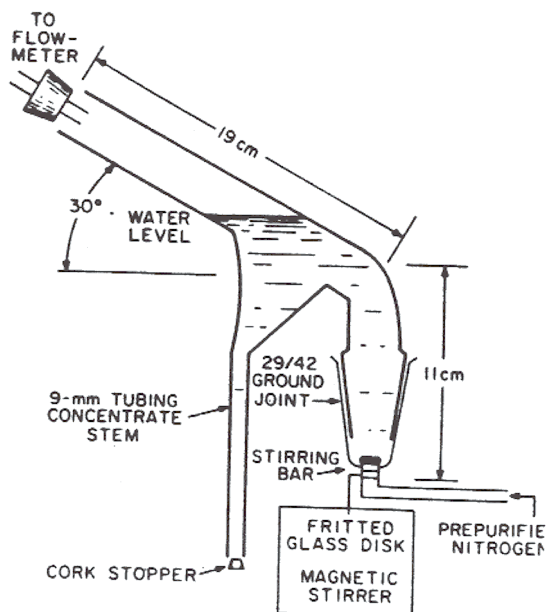


FIG. 1. Modified Hallimond cell for laboratory flotation (6).

by adjusting the pressure in the gas reservoir. Hydrophobic species will collect in the cell top and in the stem and can be separated from those in the well by decantation followed by rinsing of the cell top.

PRINCIPLES

Foam separation is based on the adsorption of surfactants at the liquid/air interface and the association of various chemical species and particulates with these surfactants. Surfactant adsorption at the liquid/air interface takes place because interaction energy between the nonpolar hydrocarbon chains of the surfactant and the polar water molecules is less than the interaction energy between water molecules themselves and therefore the presence of the organic molecules in bulk water is energetically less favorable than their presence out of the bulk water at the interface. As the size of the nonpolar chain increases, it becomes more and more energetically unfavorable for the chains to stay in the bulk water. An increase in chain length therefore causes an increase in its adsorption at the liquid/air interface (7) and therefore its percent removal by foaming. If the number

of polar groups or the number of double and triple bonds are increased, however, the adsorption and consequently the separation can be expected to be poorer.

It must be noted that the adsorption density of a surfactant will not increase by any significant amount on increasing its bulk concentration above its critical micelle concentration. The ratio of the surfactant concentration at the surface to that in the bulk, known as the distribution factor, which is actually a measure of the possible separation, will therefore decrease above the critical micelle concentration. Efficiency of separations can therefore be expected to be higher in dilute solutions than in concentrated solutions. Of course, there must be enough surfactant of one type or another to produce foams. Experimental results of Aenlle (8) for the distribution factor of a surfactant Aresket as well as of a uranyl species that was separated using Aresket did, in fact, show the factor to be largest in dilute Aresket solutions.

If the aim is to separate one surfactant from another or to purify a surfactant, it is most important to conduct the separation below the various critical micelle concentrations. Since micelles of a surfactant solubilize other surfactants and thereby reduce their adsorption at the liquid/gas interface, their distribution factor will be lower above the critical micelle concentration of any surfactant than below it. Foaming for purification has to be conducted, therefore, below the concentration at which micelle formation takes place.

The extent of separation of species is also dependent upon the removal of the bulk solution from the foams before the collection of the foams. The foam must therefore drain as much as possible without rupturing. This is dependent on various properties such as viscosity of the bulk liquid, electrical double-layer repulsion between the two surfaces of adjoining bubbles, and the elasticity and viscosity of the surface film. The role of these factors in foam separation techniques has been discussed by Lemlich et al. (9).

Foam separation of nonsurface-active materials is, as mentioned earlier, dependent upon their association with surface-active materials. This association can arise from chemical interaction between the two species, which often leads to the formation of complexes, or from physical interaction. Ion flotation, for example, is based on the association between the ions and the oppositely charged surfactant species due to electrostatic attraction.

Flotation of quartz using alkylamines is another example where electrostatic interaction is put to use for separation as well as concentration.

In this case quartz is negatively charged and hence adsorbs cationic aminium ions and thereby acquires hydrophobicity. Froth flotation of a large number of sulfide minerals, on the other hand, depends on the chemical reaction of the surfactant with the surface species of the mineral. Flotation of galena (PbS) using potassium xanthate is an example. Flotation based on the chemisorption of surfactants is employed for separation of several oxide and salt-type minerals in addition to sulfides. To enhance the adsorption of surfactants on desired minerals or to prevent the adsorption on others, a variety of reagents known as modifiers are used in practice (10). They include alkali or acid to adjust the pH; alkali sulfides, cyanides, and sulfites to depress the flotation of certain sulfide minerals; copper sulfate to activate the flotation of zinc sulfide; ferric chloride, calcium chloride, and cupric nitrate to activate the flotation of quartz; and polymeric reagents such as starch to depress the flotation of various salt-type minerals.

EFFECT OF VARIABLES

For the successful use of foam separation techniques as analytical tools, it is necessary to achieve, as much as possible, complete separation of the species of interest. Toward this goal, the effect of all relevant controllable variables on percent removal and selectivity by foam separation methods will be examined.

Chain Length of the Surfactant

For reasons given earlier, an increase in length of the nonpolar part of the surfactant should lead to an increase in its adsorption at interfaces and therefore its separation. Our results (7) for alkylammonium acetates have in fact shown that these reagents adsorb at the solution/air interface in increasing quantities as the chain length is increased. The length of the hydrocarbon chain of the surfactant was found to affect froth flotation of materials in a similar manner (11). Hallimond tube flotation of quartz with alkylammonium acetates of varying chain length is shown in Fig. 2 as a function of the surfactant concentration. It can be seen that the percent removal increases drastically on increasing the chain length of the surfactant. The chain length effect on flotation was ascribed to the tendency of the longer chains to associate into two dimensional aggregates called hemi-micelles at the solid-liquid interface (11, 12). The driving force for this association is the cohesive interaction between the chains and therefore is dependent on the chain length.

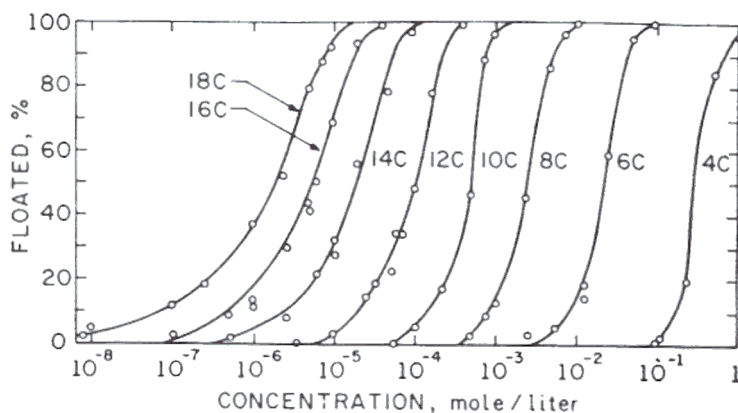


FIG. 2. The effect of hydrocarbon chain length on the flotation of quartz in alkylammonium acetate solutions (11).

Surfactant Concentration

It is also evident from Fig. 2 that the percent removal is strongly dependent on the concentration of the surfactant. This is not due to the dependence of physical properties or stability of foam since effects of such factors are eliminated in a Hallimond tube test. Rubín and co-workers (13), among others, have also observed dependence of collector concentration on the precipitate flotation of copper species. They found a collector to colligend ratio of one to be necessary in their case to get nearly complete removal of the copper. Concentration of the collector was found to be even more critical if ion flotation is used instead of precipitate flotation. Rubín and Lapp (14) have reported that while 100% removal of zinc species is possible using a collector to colligend ratio of 0.2 in the pH range of 8 to 11 where zinc hydroxide precipitates, almost no flotation is obtained at that ratio below pH 8 when zinc is present in dissolved ionic form. A larger quantity of collector was needed to remove the zinc completely under these conditions.

A great excess of collector has, however, been found to reduce the flotation of minerals (15), precipitates (16), and ions (17). In the case of particulate flotation, this is sometimes due to a reduction in the size of the bubbles to such a level that the bubbles could not levitate the large number of particles that collect on them (15). Adsorption of a second layer of collector at higher concentration with an orientation opposite to that of the first layer or adsorption of micelles can also cause a decrease in flota-

tion, but less likely to do so in most cases since only a small fraction of the surface needs to be hydrophobic for flotation to occur. The inhibitive effect of excess collector on ion flotation has been proposed by Davis and Sebba (17) to be mainly due to possible crowding of the bubble surface by the collector ions themselves and the formation of micelles with consequent adsorption of colligend ions on the nonfloatable micelles. Both for ion flotation and precipitate flotation, an optimum collector to colligend ratio is reported to exist (18-20). One technique reported by Grieves et al. (21, 22) for removing additional colligend from solution is by adding the collector in pulses instead of in one dose.

Solution pH

The role of pH in determining the form of the species present in solution and thereby its flotation as ions or precipitates is evident in the work of Rubin and Lapp (14) discussed earlier. The effect of pH on particulate separation is even more significant. In fact, it is primarily the proper choice of pH along with the type of collector that enables one to selectively float one type of particulate from another and thus obtain their separation. This effect of pH is illustrated in Fig. 3 where flotation of calcite with an anionic and a cationic collector is given as a function of pH at two con-

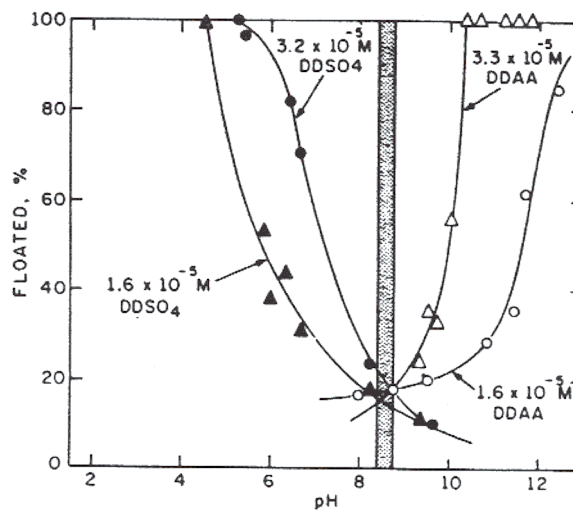


FIG. 3. The effect of pH on the anionic and cationic flotation of calcite (23).

centrations (23). The isoelectric point of calcite as measured by streaming potential is about pH 8 to 9.5 (23). It can be seen that significant flotation with an anionic collector is possible only below the isoelectric point where the particles are positively charged. Similarly flotation with a cationic collector is possible only above the isoelectric point where the particles are negatively charged. For analytical purposes, one is interested in determining how this material can be separated if it is mixed with another material, for example, quartz. The isoelectric point of quartz is near pH 2. Between pH 2 and 8 quartz is therefore negatively charged while calcite is positively charged. It is therefore possible to achieve a separation either by floating calcite with an anionic collector at, for example, pH 7 or by floating quartz with a cationic collector at that pH. It must be noted that this separation is likely to fail at much lower pH values since dissolved calcium species, for reasons given elsewhere, will activate the anionic flotation and depress the cationic flotation of quartz. Control of pH can be similarly used for separation purposes with other foam techniques. As an example, distribution factors obtained by Karger et al. (24) for mercury and iron in the presence of an amine are given in Fig. 4. These results suggest that the separation of mercury from iron can be obtained either by floating the former at higher pH values or the latter at lower pH values.

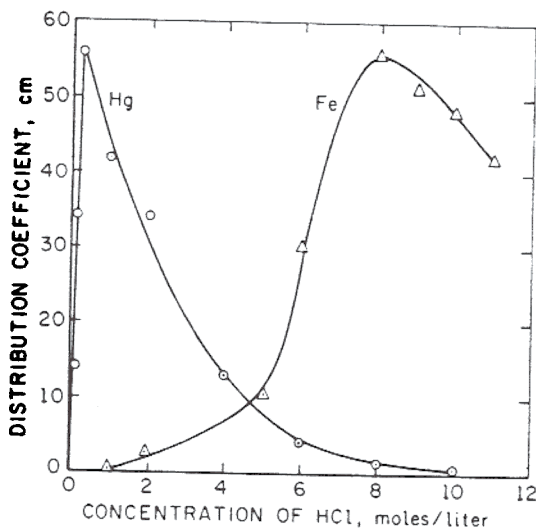


FIG. 4. Distribution coefficients for Fe and Hg as a function of HCl concentration in the presence of a cationic surfactant (24).

In addition to the above effects, pH also influences separation due to dependence of the collector hydrolysis on it. A typical example of this is the cationic flotation of quartz in basic solutions. Quartz is negatively charged above pH 2 and therefore it should be possible to float it with a cationic collector above this pH. In practice, however, one gets very little flotation of quartz with dodecylammonium acetate above pH 12 (25). Above pH 12, most of this collector is in its neutral molecular form and under such conditions it is apparently unable to adsorb on quartz and make it hydrophobic. Neutral molecules can, however, act as good collectors when present along with ionic surfactant species. Total adsorption of the surfactant at the solid/solution interface and hence flotation in a system containing both ionic and neutral surfactant species appears from the experimental results to be higher than when the same amount of surfactant is present totally in one or the other form. This is suggested to be due to the fact that, if some of the species adsorbed on the solid are neutral, they can actually screen the repulsion between the charged heads of the adsorbed ions. Based on the same principle, Fuerstenau and Yamada (26) were able to enhance flotation by adding long-chain alcohol along with the collector.

Ionic Strength

It is possible to float quartz with an amine collector above pH 2 because, as mentioned earlier, cationic aminium species adsorb electrostatically on the negatively charged quartz. Such electrostatic adsorption of aminium ions will take place in competition with other ions that are similarly charged. A significant increase in concentration of nonsurfactive cations will therefore decrease the adsorption of the cationic collector ions on the solid and hence also its flotation. Results obtained recently for the cationic flotation of quartz show this to be the case (see Fig. 5). Potassium nitrate thus acts as a depressant for the cationic flotation of quartz. Modi and Fuerstenau (28) have observed similar effects of sodium chloride on the anionic flotation of alumina. When sodium sulfate was added to the system instead of sodium chloride, the depression of flotation was even larger. This larger effect of sulfate over that of chloride results from the tendency of the bivalent sulfate to strongly adsorb and compete with dodecylsulfate more than the monovalent chloride. The above effect can also be used to enhance the flotation of a particle that has a charge opposite to that of the collector. Modi and Fuerstenau (28) were thus able to get complete flota-

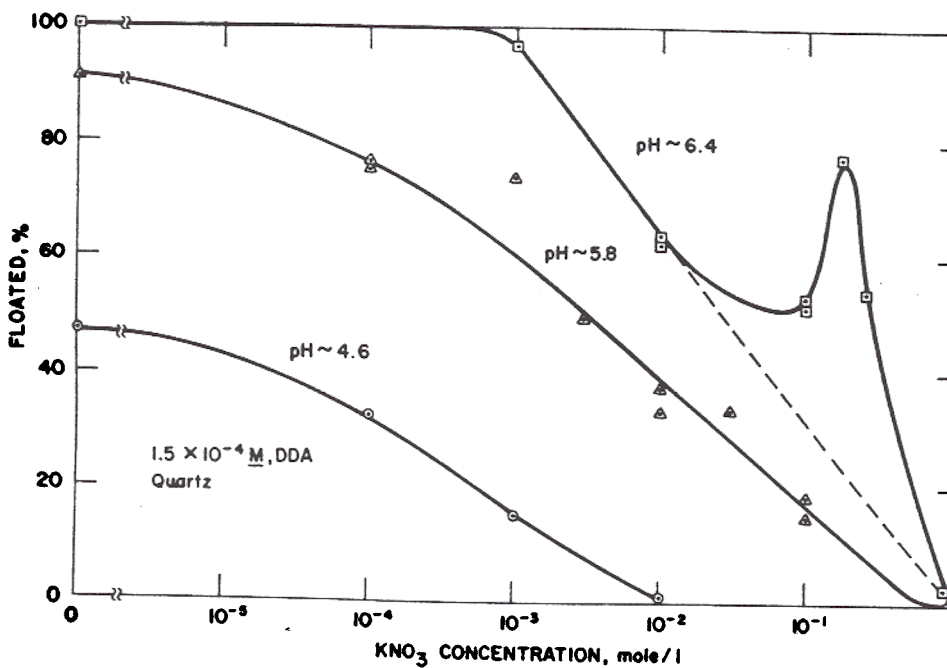


FIG. 5. Effect of ionic strength on the flotation of quartz with dodecylammonium acetate (DDA) (27).

tion of the positively charged alumina at pH 6 using a cationic surfactant by adding sufficient sodium sulfate to get a concentration of 10^{-2} mole/liter. Flotation of alumina occurs in the presence of bivalent sulfate ions because specifically adsorbing sulfate at such concentrations reverses the charge of the alumina particle to a negative sign and thus makes the adsorption of cationic surfactant possible. Similarly, negatively charged particles can be floated with anionic collectors if the particles are first modified by means of cations such as calcium and magnesium. These ions can often function most effectively in the pH range where they are in the hydrolyzed soluble form. Fuerstenau et al. (29) studied the role of iron, aluminum, lead, manganese, magnesium, and calcium in the anionic flotation of quartz as a function of pH and found that each cation began to function as an activator as the metal ions began to hydrolyze and ceased functioning in that manner when the solution pH corresponded to that at which the metal hydroxides begin to precipitate.

Concentration of Complexing Ions

Certain metallic species are first separated by complexing them with inorganic agents and then floating them with a collector. The concentration of the species used for complexing is found to be critical in several cases. Anionic flotation of copper hexacyanoferrate is reported to be impossible when the concentration of Cu^{2+} ions is below the point of stoichiometry equivalence (16). Shakir (30) also observed the concentration of the complexing anion to be critical for complete separation for the flotation of uranyl carbonate or uranyl bicarbonate anionic complex with cetyltrimethylammonium bromide. Whereas nearly 100% removal of the uranium could be obtained from 10^{-4} mole/liter uranyl solution in the presence of 0.01 M carbonate or bicarbonate, only 25% of it could be removed when the carbonate or bicarbonate concentration was 0.4 mole/liter. Evidently, control of the concentration of the complexing ions is important to get maximum recovery.

Flocculants and Polymers

In several cases, complete flotation can be obtained by adding auxiliary reagents, particularly flocculants. Flotation of *B. cereus* and illite with sodium lauryl sulfate was increased to almost 100% by Rubin et al. by adding alum (31, 32). Selective flocculation followed by flotation has proven to be a successful method for the separation of fine hematite from quartz (33). In such processes, the grade of the product will indeed suffer if the flocculant is not selective.

Separation by flotation is markedly affected by polymeric-type reagents such as starch. Figure 6 illustrates the effect of starch addition on the oleate flotation of calcite (34). It can be seen that small additions of starch decreases the flotation drastically. It is interesting to note that, unlike most other depressants, starch does not reduce flotation by inhibiting adsorption of surfactant on the colligend particles. In fact, adsorption of oleate on calcite was found to be higher in the presence of starch than in its absence. Thus even though the particles adsorbed more surfactant in the presence of starch, the particles are hydrophilic. This effect was ascribed to the peculiar helical structure that starch assumes in the presence of hydrophobic species or under alkaline conditions. The structure of helix is such that its interior is hydrophobic and its exterior is hydrophilic. Mutual enhancement of adsorption is possibly due to the formation of a helical starch-oleate clathrate with the hydrophobic oleate held inside

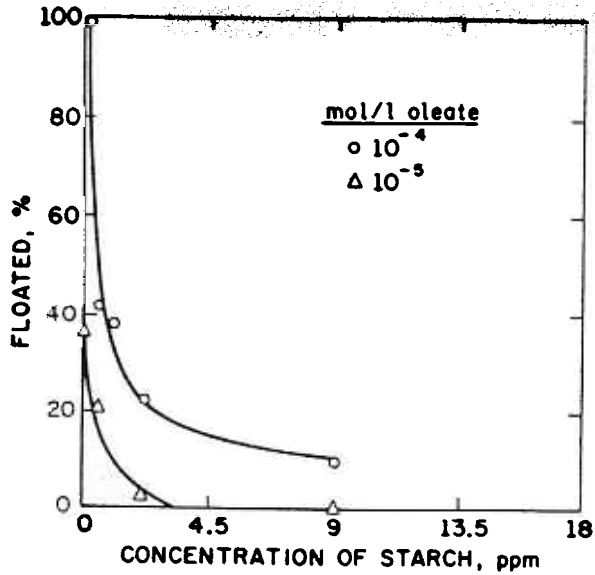


FIG. 6. Effect of addition of starch on the flotation of calcite using oleate (34).

the hydrophobic starch interior. The hydrophilic nature of calcite in the presence of starch and oleate results from the fact that the adsorbed oleate is obscured from solution by such wrapping by starch helices whose exterior is hydrophilic and also by simple overwhelming by massive starch species.

Physical Variables

Among the physical variables, flow rate of the gas, bubble size distribution, agitation, etc. do not produce any primary effects on the ultimate total flotation of materials, even though at extreme minimum and maximum levels some of these factors can influence the extent of removal. For example, excessive aeration could conceivably produce enough turbulence in the system to reduce the separation by molecular or ion flotation. The rate of removal of colligend is indeed dependent upon the levels of the above physical variables. One variable that has been found to be important, at least in froth flotation, is the temperature of the solution. In the case of flotation dependent on the physical adsorption of collector, the recovery

can be expected to decrease with increasing temperature, and in the case of that dependent on chemisorption, it can be expected to increase with it. There has been very little actual experimental work on temperature effects on froth flotation except to show that flotation of hematite with oleate increases with the temperature at which the material is reagentized. Our recent results (35) have however shown this to be true only at low ionic strength conditions. Above $2 \times 10^{-3} N$ ionic strength, flotation in our case is found to markedly decrease with increasing reagentizing temperature. The effect of temperature on foam separation has been reported by Rubin et al. (13) and Schoen and Mazzella (36) to be very little. Sheiham and Pinfold (20) noted an increase in the rate of removal of strontium carbonate precipitate on increasing the flotation temperature from 15 to 30°C. In the case of solvent sublimation of hexacyanoferrate, however, Spargo and Pinfold (37) noted a marked decrease in recovery on increasing the temperature. In the foam separation techniques, the effect of temperature on foam drainage and stability will also play a role in determining the separation efficiency.

EXAMPLES OF FOAM SEPARATED MATERIALS

A listing of typical materials separated by various foaming techniques is given below. For a more detailed list or the details of conditions of separation, a previous publication (1) or the original reference must be consulted.

Foam Fractionation. Alkylbenzenesulfonate (38, 39), amines (40), fatty acids (41), alcohols (41), detergents from waste waters (42), and surfactants from paper and pulp mill streams (43).

Ion Flotation. Ag (40), Au (44), Be (36), Co (45), Cu (46), Fe (36), Ra (36), cyanide (47), dichromate (48), and phenolate (48). See also *Ion Flotation* by Sebba (49).

Foam Flotation. Albumin (50), hemoglobin (51), catalase (52), algae (53), and methylcellulose (54).

Microflotation. Kaolinite (55), iron dust (56), deactivated carbon (55), *E. coli* (57), Ce (58), U (59), and trace elements in seawater (60).

Precipitate Flotation. Silver (61), chromium (62), copper (63), strontium (63), and zinc (64).

Froth Flotation. Sulfur (65), coal (66), calcium phosphate (67), feldspar (65), potassium chloride (68), and wastes (69). See also *Froth Flotation, 50th Anniversary Volume* (70).

CONCLUSIONS

The above discussion shows that complete removal of materials from solutions can be achieved by optimizing the levels of certain operating variables of foam separation techniques. In fact, these techniques should prove even more useful for analytical purposes than for the conventional industrial processes since in the former case it is possible to change pH, concentration of collector, etc. as much as necessary without any attention to the economic aspects of the processes. Furthermore, flotation times that are longer than that used in industrial operations can be employed in an analytical procedure in order to achieve complete recovery. Non-foaming adsorptive bubble separation techniques also appear promising for use as analytical separation tools. For example, solvent sublation, where the colligend is levitated by means of bubbles into a thin solvent layer above the solution, is reported to be capable of being more efficient than solvent extraction (71) since it is possible to attain colligend concentrations in the solvent above the equilibrium value with the former technique.

Because foam separation techniques can concentrate from solutions that are as dilute as 10^{-10} mole/liter, they will find applications as concentration techniques. However, their high degree of selectivity suggests that they can also be used for the separation of one material from another. Few other techniques can actually concentrate or separate from solutions containing parts per billion of the species as efficiently as the foam separation techniques.

REFERENCES

1. P. Somasundaran, "Foam Separation Methods," in *Separation and Purification Methods*, Vol. 1 (E. S. Perry and C. J. van Oss, eds.), Dekker, New York, 1972, p. 117.
 2. R. Lemlich, "Principles of Foam Fractionation," in *Progress in Separation and Purification*, Vol. 1 (E. S. Perry, ed.), Wiley-Interscience, New York, 1968, pp. 1-56. R. Lemlich, *Ind. Eng. Chem.*, **60**, 16 (1968). S. Bruin, J. E. Hudson, and A. I. Morgan, Jr., *Ind. Eng. Chem., Fundam.*, **11**, 175 (1972).
 3. B. L. Karger, T. A. Pinfeld, and S. E. Palmer, *Separ. Sci.*, **5**, 603 (1970).
 4. R. Lemlich, ed., *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972, p. 1.
 5. M. Goldberg and E. Rubin, *Ind. Eng. Chem., Process. Des. Develop.*, **6**, 195 (1967).
 6. D. W. Fuerstenau, P. H. Metzger, and G. D. Seele, *Eng. Mining J.*, **158**, 93 (1957).
 7. P. Somasundaran, *Trans. AIME*, **241**, 105 (1968).
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8. E. O. Aenlle, *An. Real Soc. Espan. Fis. Quim.*, **42**, 179 (1946); *Chem. Abstr.*, **41**, 4649i (1947).
9. R. A. Leonard and R. Lemlich, *Amer. Inst. Chem. Eng. J.*, **11**, 18 (1965). F. Shih and R. Lemlich, *Ibid.*, **13**, 751, (1967). R. Lemlich, "Principles of Foam Fractionation and Drainage," in Ref. 4, pp. 33-50.
10. A. M. Gaudin, *Flotation*, McGraw-Hill, New York, 1957, pp. 282-326
11. D. W. Fuerstenau, T. W. Healy, and P. Somasundaran, *Trans. AIME*, **229**, 321 (1964).
12. P. Somasundaran and D. W. Fuerstenau, *J. Phys. Chem.*, **70**, 90 (1966).
13. A. J. Rubin, J. D. Johnson, and J. C. Lamb, *Ind. Eng. Chem., Process Des. Develop.*, **5**, 368 (1966).
14. A. J. Rubin and W. L. Lapp, *Separ. Sci.*, **6**, 357 (1971).
15. P. Somasundaran and R. D. Kulkarni, *Trans. I.M.M.*, **82**, C164-167 (1973).
16. T. A. Pinfeld, in Ref. 4, p. 79.
17. B. M. Davis and F. Sebba, *J. Appl. Chem.*, **16**, 293 (1966).
18. M. W. Rose and F. Sebba, *Ibid.*, **19**, 185 (1969).
19. N. Aoki and T. Sasaki, *Bull. Chem. Soc. Japan*, **39**, 939 (1966).
20. I. Sheiham and T. A. Pinfeld, *J. Appl. Chem.*, **18**, 217 (1968).
21. R. B. Grieves and T. E. Wilson, *Nature*, **205**, 1066 (1965).
22. R. B. Grieves and D. Bhattacharya, *J. Appl. Chem.*, **19**, 115 (1969).
23. P. Somasundaran and G. E. Agar, *J. Colloid Interfac. Sci.*, **24**, 433 (1967).
24. P. L. Karger, R. P. Poncha, and M. W. Miller, *Anal. Lett.*, **1**, 437 (1968).
25. P. Somasundaran and D. W. Fuerstenau, *Trans. AIME*, **241**, 102 (1968).
26. D. W. Fuerstenau and B. J. Yamada, *Ibid.*, **223**, 50 (1962).
27. P. Somasundaran, *Ibid.*, **255**, 64 (1974).
28. H. J. Modi and D. W. Fuerstenau, *Ibid.*, **217**, 381 (1960).
29. M. C. Fuerstenau, C. C. Martin, and R. B. Bhappu, *Ibid.*, **226**, 449 (1963).
30. K. Shakir, *J. Appl. Chem. Biotechnol.*, **23**, 339 (1973).
31. A. J. Rubin, in Ref. 4, p. 216
32. A. J. Rubin and S. C. Lackey, *J. Amer. Water Works Assoc.*, **60**, 1156 (1968).
33. R. Sisselman, *Mining Eng.*, **25**, 45 (1973).
34. P. Somasundaran, *J. Colloid. Interfac. Sci.*, **31**, 557 (1969).
35. P. Somasundaran and R. D. Kulkarni, "Conditioning Temperature-Ionic Strength Interactions in Hematite Flotation," 103rd Annual AIME Meeting, Dallas, February 1974.
36. H. M. Schoen and G. Mazzella, *Ind. Water Wastes*, **6**, 71 (1961).
37. P. E. Spargo and T. A. Pinfeld, *Separ. Sci.*, **5**, 619 (1970).
38. C. A. Brunner and D. G. Stephan, *Ind. Eng. Chem.*, **57**, 40 (1965).
39. P. H. McGauhey and S. A. Klein, *Public Works*, **92**, 101 (May 1961).
40. C. Walling, E. E. Ruff, and J. L. Thorton, Jr., *J. Phys. Chem.*, **56**, 989 (1952).
41. E. Rubin and E. L. Gaden, Jr., in *New Chemical Engineering Techniques*, (H. M. Schoen, ed.), Wiley-Interscience, New York, 1962, pp. 319-385.
42. W. Krygielowa, J. Kucharski, and J. Wasowiczowa, *Chem. Abstr.*, **68**, 15871n (1968).
43. J. L. Rose and J. F. Sebald, *Tappi*, **51**, 314 (1968).
44. L. Dobresco and V. Dobresco, *Rev. Minelor (Bucharest)*, **19**, 231 (1968).
45. B. L. Karger and M. W. Miller, *Anal. Chim. Acta*, **48**, 273 (1969).
46. A. J. Rubin and J. D. Johnson, *Anal. Chem.*, **39**, 298 (1967).

47. R. B. Grieves and D. Bhattacharya, *Separ. Sci.*, **4**, 301 (1969).
48. R. B. Grieves, *Ibid.*, **1**, 395 (1966).
49. F. Sebba, *Ion Flotation*, Elsevier, New York, 1962.
50. W. W. Eckenfelder, Jr. and D. J. O'Connor, *Biological Waste Treatment*, Pergamon, New York, 1961.
51. F. Schutz, *Nature*, **139**, 629 (1937).
52. S. E. Charm, J. Morningstar, C. C. Matteo, and B. Paltiel, *Anal. Biochem.*, **15**, 498 (1966).
53. 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.
54. F. Schutz, *Trans. Faraday Soc.*, **38**, 85 (1942).
55. G. D. DeVivo and B. L. Karger, *Separ. Sci.*, **5**, 145 (1970).
56. D. Ellwood, *Chem. Eng.* **75**, 82 (1968).
57. A. M. Gaudin, in *Froth Flotation, 50th Anniversary Volume* (D.W. Fuerstenau, ed.), AIME, New York, 1962, p. 658.
58. F. Kepak and J. Kriva, *Separ. Sci.*, **7**, 433 (1972).
59. G. Leung, Y. S. Kim, and H. Zeitlin, *Anal. Chimi. Acta*, **60**, 229 (1972).
60. Y. S. Kim and H. Zeitlin, *Chem. Communi.*, 1971, 672. Y. S. Kim and H. Zeitlin, *Separ. Sci.*, **7**, 1 (1972). Matsuzaki and H. Zeitlin, *Ibid.*, **8**, 185 (1973).
61. E. J. Mahne and T. A. Pinfeld, *J. Appl. Chem.*, **19**, 57 (1969).
62. R. B. Grieves, *J. Water Pollution Control Fed.*, **42**, R336 (1970).
63. E. J. Mahne and T. A. Pinfeld, *Chem. Ind.*, 1966, 1299.
64. A. J. Rubin and W. L. Lapp, *Separ. Sci.*, **6**, 357 (1971).
65. A. F. Taggart, *Handbook of Mineral Dressing*, Wiley, New York, 1964, p. 12: 130.
66. *Ref. 10*, p. 539.
67. P. Somasundaran, *J. Colloid. Interfac. Sci.*, **27**, 659 (1968).
68. P. Somasundaran and G. O. Prickett, *Trans AIME*, **244**, 369 (1969).
69. R. Eliassen and H. B. Schulhoff, *Sewage Works J.*, **16**, 287 (1944).
70. D. W. Fuerstenau, ed., *Froth Flotation, 50th Anniversary Volume*, AIME, New York, 1962.
71. I. Sheiham and T. A. Pinfeld, *Separ. Sci.*, **7**, 43 (1972).

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SYMPOSIUM TO BE CONTINUED
