FOAM FLOTATION

Theory and Applications

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PREFACE

As the title indicates, this book does not propose to give complete coverage to the field of foam flotation. Complete coverage would require a book of unwieldy size which would duplicate the material covered in the excellent monograph on adsorptive bubble separations edited by Lemlich, the extensive treatment of all aspects of mineral flotation edited by M. C. Fuerstenau, and Sebba's book on ion flotation. Our objectives are (1) to provide those new to the field with a comprehensive guide to the literature; (2) to indicate some of the applications and possibilities of foam flotation techniques; (3) to give a rather detailed review of precipitate and adsorbing colloid flotation, which we believe to have considerable promise for resource recovery and industrial wastewater treatment; and (4) to provide mathematical analyses of a number of physical models used to gain insight into foam flotation phenomena.

Chapter 1 briefly describes the various adsorptive bubble separation methods, discusses some helpful general references, and mentions some present and potential applications. Chapter 2 gives a detailed review of lab scale work in precipitate, adsorbing colloid, and mineral flotation. In Chapter 3 we look into some fluid mechanical matters--viscous drag forces on particles attached to bubbles, and factors affecting floc particle-bubble encounters. Theoretical aspects at the microscopic level of particle flotation are discussed in Chapter 4. The macroscopic theory of flotation column operation and some experimental studies on continuous flow columns are presented in Chapter 5. Solvent sublation, which shows considerable promise for the removal and recovery of certain classes of organic compounds, is treated in Chapter 6. Chapter 7 points out some aspects of foam flotation which require additional work and includes our attempts at predicting some of the developments in this area which the next few years may bring. A general literature review and a review focusing on wastewater treatment and other large-scale applications are included as appendices.

We are indebted to Harry Zeitlin (University of Hawaii), Robert B. Grieves (University of Kentucky), Robert Lemlich (University of Cincinnati), and P. C. Somasundaran (Columbia University) for providing us with comprehensive collections of reprints on their work; Professor Zeitlin also helped to write Chapter 2. We are also most grateful to those students at Vanderbilt in chemistry and engineering who helped in sorting out the statistical mechanics of industrial waste treatment, who joined in our search for the perfect bubble, and who helped clean up when foam breaker motors burned out. Judy Kiefer helped with the writing of Chapter 5. We acknowledge with thanks a University Research Council grant from Vanderbilt that helped support the preparation of the book; and we are very much obliged to Judy Roy, Jewell Carter, and Connie Beasley, who typed the manuscript.

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CONTENTS

Chapter 1

INTRODUCTION

I. OVERVIEW

Adsorptive bubble separation techniques [1,2], with which this book is concerned, are based upon the differences in surface activity of the various substances which are present in a solution or suspension. These substances may be ionic or molecular, colloidal, crystalline, or cellular in nature, but in all cases they must be surface-active at the air-liquid interface--that is, they must selectively attach to the air-liquid interfaces of foams or of bubbles rising through a liquid pool. This permits their separation and concentration in a small volume of collapsed foam (foamate). Quite commonly a substance called the *colligend* [3], which is not intrinsically surface-active at the air-liquid interface, can be made so by adsorbing on its surface a *collector*, which is surface-active at both the colligend-liquid and the air-liquid interfaces, or by reacting it with (if it is an ion) a collector which converts it to a surface-active species. This extends adsorptive bubble separation techniques to a quite wide range of substances, including ions, neutral molecules, precipitates, active carbon, minerals, proteins, and bacteria.

The fundamental basis for all adsorptive bubble separations is the Gibbs equation [4], which, if a single solute is present and the dividing surface is chosen to make the surface excess of the solvent vanish, is given by

$$\Gamma = -\frac{a}{RT}\frac{d\gamma}{da} \tag{1}$$

where Γ is the surface excess of the solute, "a" is the activity of the solute, and γ is the surface tension, the free energy per unit area of the interface. For particulate material, Young's equation for contact equilibrium [5]

$$\gamma_{SA} - \gamma_{SB} = \gamma_{AB} \cos\theta \tag{2}$$

plays a crucial role. Here γ_{SA} is the surface free energy of the solid-gas interface, γ_{SB} is that of the solid-liquid interface, γ_{AB} is that of the gas-liquid interface, and θ is the contact angle between the solid-liquid interface and the gas-liquid interface.

Foam flotation devices can be run in a number of different modes: batch or continuous flow, with or without reflux of the collapsed foamate, with or without multiple staging, with feed to a pool at the bottom of the column, or with feed into the rising foam. Several illustrations of these modes of operation are shown in Fig. 1.1. Lemlich's book [6] discusses the advantages of these various modes.

Adsorptive bubble separation techniques have been classified according to whether or not a foam is employed, whether the solute being removed is or is not in a solid form, and, if solid, what the characteristics of the solid are. This classification and nomenclature, proposed some years ago by several of the leaders in the field [2], represents a reasonable compromise between evolved common terminology and logical systematization, and is employed by most workers. The classification is displayed in Fig. 1.2.

These techniques are first subdivided into foaming and nonfoaming separations. The latter are subdivided into bubble fractionation and solvent sublation. In bubble fractionation [8], surface-active material is transferred to the upper portion of a column of liquid by adsorption on rising bubbles followed by release at the top of the column as the bubbles burst. Solvent

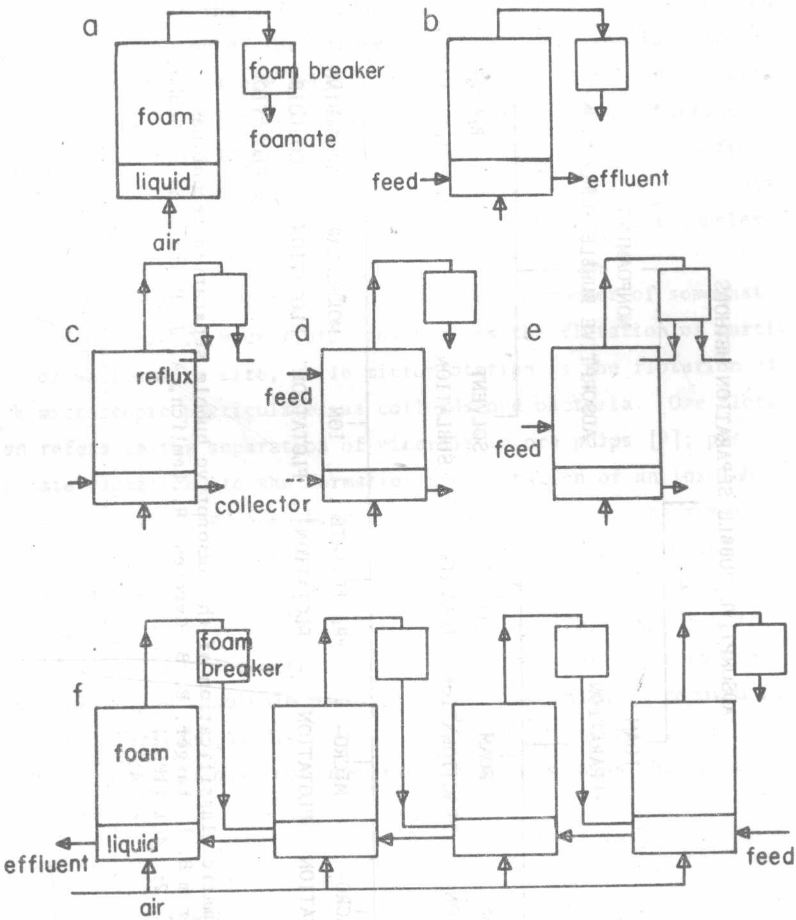

Fig. 1.1. Foam fractionation modes: (a) simple batch; (b) simple continuous flow; (c) continuous flow with enriching by reflux; (d) continuous flow stripping; (e) combined enriching and stripping; (f) staged operation (from Lemlich [6] and King [7]).

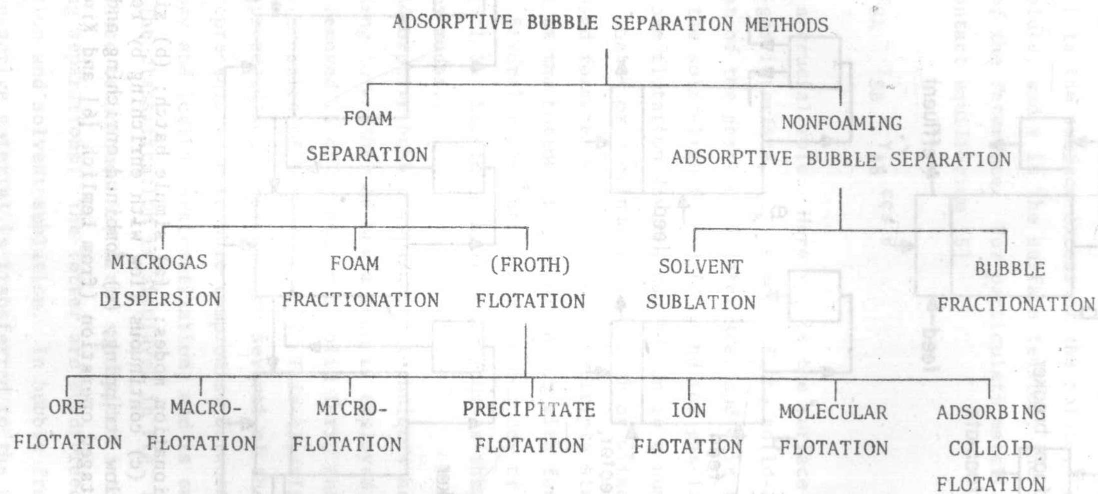

Fig. 1.2. Schematic classification of the adsorptive bubble separation techniques. Modified from B. L. Karger, R. B. Grieves, R. Lemlich, A. J. Rubin, and F. Sebba, *Separ. Sci. 2*: 401 (1967).

sublation [9] operates in much the same fashion except that the surface-active solute is transferred to an immiscible liquid layer floating on top of the liquid from which solute is being extracted. In this way remixing of the solute by axial dispersion is avoided.

Foam separations are subdivided into froth flotation, or simply flotation, in which particulates are removed; foam fractionation, in which soluble surface-active substances are removed from solution by adsorption at gas-solvent interfaces, and microgas dispersion, characterized by the extremely small size of the bubbles used.

Froth flotation is further divided into a number of somewhat overlapping areas. Macroflotation involves the flotation of particles of macroscopic size, while microflotation is the flotation of such microscopic particulates as colloids and bacteria. Ore flotation refers to the separation of minerals in ore pulps [9]; precipitate flotation, to the formation and flotation of an insoluble precipitate [10]; and adsorbing colloid flotation, to the removal of a solute by adsorption on (or perhaps coprecipitation with) a carrier floc which is then floated. Ion flotation [11] and molecular flotation involve the reaction of ions or molecules which are themselves not surface-active with a surfactant collector to yield a surface-active insoluble precipitate or scum which is removed in the foam. Lemlich [6] discusses a number of additional variations which, at present, have not been exploited as much as the above techniques have.

II. GENERAL REFERENCES

Here we present a listing of a number of general references on or relating to flotation separations for the convenience of the newcomer to the field. Our objective here is to provide more ready access to the basic literature on foam flotation than is given by the more detailed, specialized, and intimidatingly extensive reviews given in subsequent chapters and appendices.

A. Books

Adamson's text [4] provides an excellent introduction to the principles of surface chemistry necessary for an understanding of flotation separations. Topics of interest covered include: (a) an introduction to the structure, drainage, and stability of foams; (b) the theory of the electric double layer at charged interfaces, a matter of importance for the understanding of ionic surfactant systems; (c) contact angles and the solid-liquid interface; (d) adsorption of electrolytes and nonelectrolytes at solid-liquid interfaces; and (e) an introduction to ore flotation. The Gibbs equation and Young's equation are discussed.

Sebba's book, *Ion Flotation* [3], provides an introduction to ion flotation and solvent sublation, with asides on related areas. After five chapters covering the basics of surface chemistry and ionic solutions, the book presents a detailed and lucid discussion of the principles of ion flotation and the characteristics of sublate salts (ionic compounds of low solubility having an amphipathic cation and a metal complex anion). A discussion of the thermodynamics of ion flotation selectivity follows, with some comments on the problems which may arise in obtaining good selectivity if polynuclear complexes are present. A chapter on organic ion flotation focuses principally on organic dyes (particularly pH indicators), with briefer reference to picrate, gallate, tetraphenylboron, and alkaloids. A chapter on solvent sublation describes the method and discusses its use for the removal of sublate salts and the separations of cobalt from nickel and of methyl orange from bromphenol blue.

Four chapters describe a large number of potential applications of ion flotation and solvent sublation techniques. A summary of the possibilities of ion flotation separations is given which covers the entire Periodic Table. Areas of possible utility in analytical chemistry, in the treatment of wastewaters, in the recovery of metals from leach solutions, and in the recovery of metals from sea water are discussed. Despite the fact that as of this writing Sebba's book is eighteen years old, it still provides the reader with an ample supply of ideas for research and development in adsorptive bubble separations.

Bikerman's book on foams [12] provides detailed discussions of a number of foam characteristics of great interest in foam flotation separations; these include foam formation and structure, foam drainage, and foam stability. The book also contains an introduction to foam fractionation.

The areas of precipitate, adsorbing colloid, ion, molecular, and microflotation are relative newcomers to the field in comparison to ore flotation, which developed and matured to quite an extent during the period from 1915 to the late 1940's; see Gaudin's text on the subject [13]. A more recent book that gives a good idea of the scope and sophistication of the work in ore flotation was edited by Fuerstenau [14]. This book contains papers by the leading authorities on fundamental studies of the flotation of nonmetallic minerals (oxides, silicates, quartz, and salt-type minerals), on the flotation of sulfides (redox potentials are of importance in these systems), and on the thermodynamics of flotation processes. It also includes a wealth of material on industrial practice. No one involved in particulate flotation can afford to be unfamiliar with the ore flotation literature.

In 1972, Lemlich [6] edited a book on adsorptive bubble separations which provided introductions and literature reviews of all aspects of the subject. Topics covered by experts in the field included foam morphology; coalescence and drainage; principles of column operation; ion, precipitate, mineral, microflotation, and macroflotation; bubble fractionation and solvent sublation; more detailed articles on applications of these techniques to specific substances such as surfactants, phosphate, chromium, cyanide, hydrolyzable metals, activated carbon, and others; and waste treatment and other industrial applications. Several articles described work done in specific foreign countries--France, Israel, Italy, Japan, the Soviet Union. Work done at Radiation Applications, Inc. and Oak Ridge National Laboratory is also discussed. (Many of the original papers and reports summarized in these articles present problems of access to most readers.) The clear and authoritative presentations in this book make it well-adapted for student use, and also have helped people working in the field subsequently to note where additional research was needed. The present book was written to take up where Lemlich's book leaves off, and should not be regarded as replacing or superseding it.

Another collection of excellent articles on the flotation of particulate material was edited by Somasundaran and Grieves [15]. These articles include some on basic theory and many in which careful physico-chemical measurements were made on simple well-characterized systems. Most of the papers concern mineral flotation, but have a great deal of relevance to the flotation of all particulates. A smaller collection of articles on flotation was edited somewhat more recently by Li [16]; it includes work on ore, precipitate, and adsorbing colloid flotation and on foam fractionation.

B. General Review Articles

We next turn to review articles on foam flotation. Early reviews and articles by Cassidy [17], E. Rubin and Gaden [18], and Eldib [19] discuss foam separations in some detail. A dissertation by A. J. Rubin [20] contains a general discussion of methods and a lengthy bibliography through 1965. Grieves [21] in 1968 summarized his group's work on foam flotation methods in waste water purification. Karger and DeVivo's review [22] gives a detailed and systematic survey of principles and applications with 81 references through 1968; Lemlich [23] published a review at about the same time. Somasundaran published extensive reviews in 1972 [24] and 1975 [25]. Other general reviews include Ho, 1973 [26]; Grieves, 1975 [27]; Ahmed, 1975 [28]; Bahr and Hense, 1976 [29]; Panov, 1976 [30]; Richmond, 1977 [31]; Balcerzak, 1977 [32]; and Clarke and Wilson, 1978 [33]. Grieves has also published a recent (1982) review with 353 references [34].

C. Specialized Reviews

Grieves surveyed experimental work on the removal of oxyanions such as ClO_3^-, BrO_3^-, and $HCrO_4^-$ [35]. Izumi [36] reviewed the separation of heavy metals from aqueous solution with bubbles or foams, and Lemlich [37] discussed the removal of trace quantities of heavy metals from water by various adsorptive bubble techniques. Several review articles on wastewater treatment by flotation techniques have appeared [38-40]. Thomas and Winkler [41] reviewed the use of foam fractionation for the separation of enzymes and proteins in biological materials; and Loftus et al. [42] discussed the foam fractionation of cell components. Grieves (in Ref. 6) discussed the flotation of six species of microorganisms, as well as the foam separation of other particulates.

D. Ore Flotation Reviews

Although directed towards ore flotation principles and applications, most of the review articles in this section include information and insight important in some of the other techniques of flotation separation. Froth flotation of ores is the only separation-by-flotation process widely used at present on an industrial scale. Early work and developments relating to flotation of nonmetallic minerals were covered by Aplan and D. W. Fuerstenau [43] in 1962. In 1972, D. W. Fuerstenau and Healy [44] updated this review. The article by M. C. Fuerstenau and Palmer [45] reviews the flotation of oxides and silicates. Gurvich [46] in 1974 presented a brief review of the surfactants, collectors, and foaming agents used in the flotation of nonferrous, rare, and noble metal ores. The following year Jowett [47] discussed the basic principles of froth flotation and their applications to both minerals and coal. De Cuyper [48] devoted a review to the flotation of copper oxide ores. Finkelstein and Allison [49] devoted another to the flotation of zinc sulfide. Hanna and Somasundaran [50] wrote a lengthy review on the flotation of salt-type minerals; this included discussions of properties relevant to flotation, as well as separation problems and the role of organic and inorganic modifying agents.

Trahar and Warren [51] coauthored an extensive review on the relationship of particle size to removal efficiency; generally, ultrafine particles slow flotation rates. Somasundaran and Ananthapadmanabhan [52] have given a general description of flotation techniques, physico-chemical principles, and the effects of variables; they utilize data on naturally occurring minerals. Another review by Somasundaran [53] relates interfacial properties of the solid-liquid-gas system to flotation. It discusses the role and mechanism of adsorption as well as basic principles of froth flotation and their relationship to variations in ionic strength, pH, etc.

In 1976 D. W. Fuerstenau and Raghavan [54] reviewed several aspects of the thermodynamics of mineral flotation processes, including wetting, thin films, double-layer effects, collector adsorption considerations, etc. Amine collectors are quite important in the flotation of mineral impurities. Natarajan and Iwasaki [55] reviewed the literature on the mechanism of amine adsorption at metal, mineral, and charged surfaces and its relation to flotation. Ananthapadmanabhan, Somasundaran, and Healy [56] have reviewed the flotation chemistry of oleate and amine solutions, including interactions with mineral surfaces and dissolved species. Other discussions of mineral flotation which give particularly clear presentations of the physical chemical principles involved include Wakamatsu and D. W. Fuerstenau [57] and D. W. Fuerstenau and Healy [58]. Healy [59] has reviewed the flotation of minerals, stressing the importance of the electrochemical phenomena occurring at the particle surfaces.

III. APPLICATIONS AND POTENTIAL

One of the significant problems in the area of industrial waste treatment technology is that of removing low concentrations of toxic inorganics from aqueous systems. These contaminants can cause serious difficulties in biological waste treatment facilities, and are