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SEPARATION BY FLOTATION

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I. INTRODUCTION

There has been much recent activity in the theory and application of separation by flotation, both in the United States and abroad. This review primarily addresses new developments in foam flotation, colloid flotation and precipitate flotation. The work in ore flotation represents a major effort and would itself require a lengthy article. Work from ore flotation which significantly impacts on the areas of interest listed above is included here, however. Foam separation of biological materials and the microflotation of bacteria are not routinely discussed in this review. A few recent review articles on these areas are included at the end of the Review Articles and Books Section to afford the interested reader a start on that literature. The development and use of flotation separation techniques for waste treatment and water reuse over the last few years are included in this article.

The review will be divided into the following topics:

- Review Articles and Books
- Theory and Models
- Removal of Metals
- Removal of Anions and Organic Compounds
- Additional Laboratory Studies
- Applied and Large Scale Studies
- Miscellaneous Studies

There is some overlap when an article significantly contributes to two or more of the categories. Reference is made wherever applicable.

The basis of all foam flotation methods is the Gibbs equation, which relates the rate of change of surface tension with bulk solute activity to the surface excess of solute. Adamson's book[1] discussed the Gibbs equation in some detail, and Karger and DeVivo made clear its application in their excellent discussion of the general theory of adsorptive bubble separations.[2] Newson[3] has shown that for the simple removal of surfactant by foaming the Gibbs equation is valid, indicating close approach to equilibrium in the foaming process. Karger et al.[4] and subsequently Pinfold[5] have discussed and systematized the nomenclature in the field.

Ion flotation and foam fractionation involve the removal from solution of dissolved ions by the addition of a surface active collector, followed by foaming. In the first technique, ion and surfactant form an insoluble precipitate or scum on the air-water interface; in the second, no solid phase is formed. In precipitate flotation the ion is reacted with a non-surfactant to form a precipitate which is then removed by flotation with a surfactant. In adsorbing colloid flotation the dissolved material is removed by adsorption or coprecipitation onto colloidal particles which are then removed by flotation. Froth flotation is the technique commonly employed in the mining industry (extractive metallurgy). Particulates are first conditioned with necessary reagents. Then the system is agitated and air introduced; the air bubbles collide with the particles and attach if the particle surface is hydrophobic. Thus combined, the particles-bubble system rises to the top and is skimmed off.

II. REVIEW ARTICLES AND BOOKS

A. <u>General Reviews</u>

Sebba's book[6] gave a particularly detailed discussion, and Cassidy published a review in 1957.[7] Articles by E. Rubin and Gaden[8] and by Eldib[9] discussed foam separations in some detail, and

Grieves[10] published an article in 1968 summarizing his work on foam flotation methods in waste water purification. A. J. Rubin's dissertation[11] contained a discussion of general methods and a lengthy bibliography through 1965. Karger and DeVivo's review[2] gave a detailed and systematic survey of principles and applications, with 81 references through 1968. Lemlich[12] published a review at about the same time, and has more recently edited an excellent book giving broad coverage of the subject.[13] Bikerman's book gives a very clear discussion of foam flotation principles and practice.[14] Somasundaran published an extensive review in 1972,[15] and another in 1975.[16] Grieves also published a review in 1975,[17] as did Ahmed.[18] Other general reviews include: Ho, 1973;[19] Bahr and Hense, 1976;[20] Panou, 1976;[21] Richmond, 1977;[22] and Balcerzak, 1977.[23]

B. Specialized Reviews

Fuerstenau and Palmer review the flotation of oxides and silicates.[24] Grieves surveys the experimental studies of the removal of oxyanions such as ClO_3^-, BrO_3^- and $HCrO_4^-$.[25] Similar articles have been written to survey the state of the art of removing metals from solution by flotation methods. The metal can be removed either as the cation or in a complex, depending upon conditions and requirements. Izumi[26] reviews the separation of heavy metals from aqueous solution employing bubbles or foam, and Lemlich[27] presents various "adsubble" (adsorptive bubble) techniques and their use in removing trace heavy metals from water.

Trahar and Warren[28] coauthored a long review on the effect of particle size on removal efficiency in extractive metallurgy. Generally, ultrafine particles slow flotation rates. Critical assessments of various proposed theories are also included.

In 1977 at least three review articles were published which assessed the use of flotation techniques in (waste) water treatment in the United States and abroad. Ecklund and Andersson[29] coauthored one such review; Hyde, Miller, Packham and Richards[30] a second; and Marks and Thurston[31] third.

Amine collectors comprise an important group of surfactants in the flotation of mineral impurities. Natarajan and Iwasaki[32] reviewed the literature which elucidated the mechanism (with regard to flotation chemistry) of amine adsorption at metal, mineral and charged surfaces.

Fuerstenau and Raghavan[33] in 1976 reviewed several aspects of the thermodynamics of flotation processes. This included wetting; thin films; various collector-adsorption considerations; double layer effects, etc. This work pertained principally to minerals.

Thomas and Winkler[34] in 1977 reviewed the use of foam fractionation in the separation of enzymes and proteins in biological materials. Grieves[35] discussed in his chapter on the flotation of particulates six species of bacteria treated by batch foam separation experiments. Bacteria possess colloid characteristics and have a net negative charge at neutral pH. The differences in foaming behavior between the species are discussed. These include experimental conditions, removal efficiency, foam volumes and effect of ion strength variations. Loftus et al.[36] studied the foam fractionation of major cell components. They found that both liquid and protein distribution coefficients decreased with pH.

C. Ore Flotation Reviews

Although filled with ore flotation terminology and applications, many of the more extensive review articles listed here include findings common and important to 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 the flotation of nonmetallic minerals were covered by Aplan and Fuerstenau in 1962[37] in a review commemorating the 50th anniversary of froth flotation. In 1972 Fuerstenau and Healy[38] updated this commentary. In 1974 Gurvich[39] presented a brief review of the surfactants, collectors and foaming agents used in the flotation of nonferrous, rare, and noble metal ores. In 1975 Jowett[40] reviewed the basic principles of froth flotation and their applications to both minerals and coal. DeCuyper devoted a review to the flotation of copper oxide ores.[41] Finkelstein and Allison[42] devoted another to the flotation of zinc sulfide. There is also a Russian series on flotation with a chapter on technology by Abramov.[43] Somasundaran and Ananthapadmanabhan have an excellent chapter on flotation,[44] in which they present a general description of flotation techniques; overall physical-chemical principles; and the effects of variables. Their examples are taken predominantly from data on naturally occurring minerals.

They and Healy[45] have written another review covering the chemistry of oleate and amine solutions in flotation. Oleic acid and dodecylamine are two widely used collectors. Results in the literature indicate that collector species interact with mineral surfaces and dissolved species. This is a significant determinant of interfacial properties which, in turn, affect adsorption and flotation. Hanna and Somasundaran[46] in 1976 wrote a lengthy review on flotation of salt-type minerals. It included discussions of properties relevant to flotation as well as separation problems and the role of organic and inorganic modifying agents. Another review by Somasundaran[47] related interfacial properties of the solid-liquid-gas system to flotation. It discussed the role and mechanism of adsorption as well as basic principles of froth flotation and their relationship to variations in ionic strength, pH, etc.

The Smithsonian Science Information Exchange[48] compiles sets of titles and abstracts of current research projects; one such set is "Flotation Processes". This listing in February, 1978, contained over 50 entries describing current research on flotation both in the U.S. and abroad; most of these deal with minerals flotation.

III. THEORY AND MODELS

We first review the literature concerning the theory and modeling of column operation. Next we will consider recent theory and models at the scale of the individual bubble and/or particle. Then we will step down to the microscopic theory of foam flotation - i.e. adsorption isotherms, localized equilibria, etc.

A. Column Operation

The analysis of the operation of foam stripping columns has been studied by a number of workers;[3,49,50,51,52,53] the earlier work is reviewed by Goldberg and E. Rubin,[53] who also referenced a number of papers on foam drainage, which has a profound effect on the efficiency of foam separations. Recently Wang and his coworkers have worked out a theory for continuous bubble fractionation columns; their approach required an assumption of local equilibrium between surface and bulk phases.[54,55,56] Goldberg and Rubin have analyzed stripping columns without solute transfer in the countercurrent region.[53] Cannon and Lemlich have given a detailed analysis based on the assumption of linear isotherms,[57] and Lee has given a somewhat similar treatment.[58] Sastry and Fuerstenau carried out an analysis of the differential equations modeling a countercurrent froth flotation column, by means of which they obtained formulas for column efficiency in some limiting cases.[59] Wilson et al. have analyzed stripping column operation with axial diffusion, non-linear isotherms, and finite rate of solute transport between surface and bulk liquid phases;[60] they solved the differential equations describing mass transport by iterative use of quasi-linearization method. Earlier E. Rubin and Gaden derived the operating equation for single-stage foam columns.[8] Grieves and his coworkers have developed a model which enables them to use batch foam fractionation rate data from one system to predict the performance of both batch and continuous systems.[61]

Lemlich in 1977[62,63] developed a theory to predict the changes in bubble size distribution in a foam with time. Initial size distributions were taken from published data. The theory predicts a reduction in the number of bubbles coupled with a shift towards larger bubble sizes. These trends are in agreement with experimental observations. Results show that the percent decrease in surface area is much less than the percent decrease in bubble population. This result is important to processes which, like foam fractionation, are surface area intensive.

B. Particle Attachment to Bubbles

An article by Petrakova et al.[64] deals with the mechanism of interaction of gas bubbles with mineral particles, and Abramov[65] has also worked on the physicochemical modeling of flotation systems. Reay and Ratcliff[66] gave a theoretical treatment to quantify the benefits (increased contacting efficiency) of using smaller bubbles or larger particle sizes in dispersed air flotation systems. Results indicated that larger particles are collected preferentially. When particles are sufficiently large not to be affected by Brownian motion, flotation rate increases with increasing particle diameter.

The attachment of a spherical particle to a planar liquid surface after contact is made is elegantly analyzed by Scheludko et al.[67] in terms of capillarity. The minimum size particle ($\sim 10^{-4}$ cm) for which flotation can occur is calculated as well as the maximum size particle which can remain attached. The maximum size is a function of contact angle. Particle detachment can be caused by gravity or the kinetic energy of collision with a bubble, the former permitting the larger radius values, so the latter collision radius determines the upper limit of flotability for a given system. The maximum radius calculated for a representative system is 2.7×10^{-2} to 5.5×10^{-2} cm for gravity detachment but only 2.6×10^{-3} for collision detachment. This smaller size corresponds to those particles observed in practice to be removed by flotation. The minimum contact time required for attachment is also estimated. Agreement was found between experimental and theoretical values for the particle sizes and contact angles. Deryagin et al.[68] also studied the criteria for bubble attachment. He employed the theory of heterocoagulation. In the same year, 1977, Bleier et al.[69] published a paper on adsorption and critical flotation conditions also using heterocoagulation. They maintain that surface tension data show a large charge density at the surface of a bubble during flotation. Heterocoagulation suggests that the oppositely charged double layer of a system reacts to produce a large potential energy of attraction. These electrostatic forces lead to the rupture of the aqueous film around the particles, and then these electrostatic forces decrease. This results in the desorption of the ionic species in the gas/liquid interface. The parameter which determines whether a particle and bubble will heterocoalesce is the relative hydrophobicity of the particle surface. The examples used were quartz-amine collector systems.

C. Microscopic Theory

Early work on adsorption on the quartz-amine system was done by Petrov et al.[70] They also performed theoretical analyses employing a modified Langmuir equation. They studied adsorption at liquid-solid interfaces in solutions of various pH. Experimental results corroborated their theoretical findings. They maintained, having confirmed the hypothesis of interaction between adjacent liquid and solid surfaces, that when the liquid film burst the adsorption layer is not destroyed, but lies on the solid surface.

Panaiotov and Platikanov in 1972-73[71] performed an interesting study in which they compared various equations of state for adsorbed layers. The state equations included those of Frisch, Frumkin, Gaustalla, Helfand, Langmuir and Lebowitz. They experimentally determined the 'E-values' (surface compressibility modulus) for the soluble adsorbed layers (at the air-solution interface) of caproic and lauric acids. The E-value is related to the equations of state via the surface tension and surface concentration. The best agreement was found employing the Gaustalla equation. The same method, using E-values, can be used to study adsorption kinetics. Various other studies have been made of adsorption kinetics at gas/liquid interfaces. Kretzchmar[72] presented a discussion of the different models described in the literature. He also determined dynamic adsorption using a Langmuir-type equation of state and presented experimental studies using a nonionic surfactant. Katz[73] discussed the various methods for the calculation of the free energy of adsorption of nonionic surfactants at the air/water interface using surface tension data. He stated that changes in the polar groups of the nonionic surfactant do not greatly affect the value of the adsorption energy; the hydrophobic end of the molecule is more important. He employed Syskowski's equation for the surface pressure, and Langmuir's expression for ΔG°, the standard free energy of adsorption. Surfactant series (with varying polar portions) studies included: polyoxyethylene t-octylphenols and octylethers.

Next let us consider some articles on the particles themselves. These surface studies were performed in connection with ore flotation technology. Additional theoretical work and experimental measurements will be included in latter sections.

Koretskii[74] recently determined the thermodynamic work, W, required to wet a particle's surface by a liquid; this quantity is then used in a theoretical description of flotation processes.

Lai and Fuerstenau[75] proposed a model for the surface charge distribution of a metal oxide and the resultant flotation response. In water an oxide surface will exhibit, simultaneously, positive, negative, and electrically neutral sites, due to the interaction of H^+ and OH^- with the surface. Equations representing the distribution of these sites were developed as functions of hydrogen ion activity, and the point of zero charge was determined. Experiments were performed using various oxides (minerals) and collectors which adsorbed either physically or chemically. It was anticipated that flotation efficiency would reflect surface site distributions since flotation had been shown to correlate with adsorption phenomena. Moreover it seemed reasonable to assume that at low collector concentrations a physically adsorbing cationic collector, for example, would adsorb over a negative site; an anionic collector, over a positive site. In all cases the flotation response correlated with the site distribution model allowing for, in some cases, secondary effects of pH variation such as concomitant ionization of neutral flotation collectors and surface sites.

Jorne' and E. Rubin have used the Gouy-Chapman model of the diffuse double layer to explain how the ionic charges and sizes of species present determine the selectivity of surface adsorption of counterions in foam fractionation.[76] A streaming potential phenomenon predicted by Wilson and Wilson[77] was observed by Clarke.[78] Floc foam flotation isotherms and local rate effects were investigated by Wilson and his coworkers by means of a modified Gouy-Chapman model in which the binding force between particles and the air/water interface is due to coulombic attraction between the negatively (positively) charged air/water interface and the positively (negatively) charged particles. The charge on the air/water interface is assumed due to the formation of hemi-micelles of ionic surfactant on it, and the coulombic interaction is modified by the ionic atmospheres in the vicinities of the two surface charge densities.[79,80,60] This group has extended the statistical mechanical treatment of floc adsorption isotherms to include the effects of non-ideal flocs and salts,[81] the electrical repulsions between floc particles,[82] and the occurrence of cooperative phenomena in the surfactant films.[83] More recently, they have examined a model used by Fuerstenau, Somasundaran, Healy, and others for some time in interpreting the results of ore flotation experiments (84,85,86,87,88,89, 90,91, for example). In this model, it is assumed that the particle surface is made hydrophobic by the adsorption of the ionic heads of the surfactant ions in the primary adsorption layer of the particle, leaving the hydrocarbon tails presented to the water. Van der Waals interaction between the hydrocarbon tails makes the occurrence of a surface condensation phenomenon possible; particles with surfaces densely occupied by surfactant are hydrophobic, with non-zero air/water contact angles; this results in bubble attachment. Wilson's group investigated the statistical mechanics of this phase change;[83] the effects of specific adsorption of foreign ions on displacement of surfactant from the floc and on floc zeta potential;[92,93] and the calculation of adsorption isotherms for this non-coulombic model for the attachment of floc particles to the air/water interface.[94] They also examined the magnitude of the viscous drag forces tending to detach floc particles from the air/water interface.[92,94] Much of this theoretical work and a number of experimental studies were recently summarized.[95,96,97]

IV. REMOVAL OF METALS

In this section we shall primarily address the removal of metals from solution by ion, foam, colloid and precipitate flotation techniques. Removal of the metals may be achieved in various forms; as cation, complex ion (positive or negative), precipitate, etc. Removal studies have been performed on metals individually; on laboratory mixtures; on sea water; and on industrial wastes. We will then briefly review the scope of heavy metal removal developed in conjunction with the extractive metallurgic industry.

A. General and Analytical

Early work on metals removal by foaming techniques includes studies by Walling and his associates,[98] by Sebba,[99] and by Schnepf and his coworkers.[100] Banfield and his collaborators[101] noted a fall-off of the distribution coefficient (reduced removal) with increasing surfactant concentration above the critical micelle concentration; Karger and DeVivo make this observation, too,[2] as have others.[102,103]

A. J. Rubin and his coworkers have published papers on the foam separation of Pb(II),[104] of Zn(II),[105] and of Cu(II) and Fe(II)[106] with sodium lauryl sulfate. Stearylamine was also used with Cu(II) and Fe(III). Effects of pH and ionic strength were studied, and conditions yielding foam fractionation and precipitate flotation were employed. Earlier, A. J. Rubin, Johnson, and Lamb made a study in which the effects of a number of variables on the two processes were investigated.[107] More recently Rubin and Haberkost reported on the coagulation and flotation of titanium dioxide and an ethanol frother.[108] They found that sodium lauryl sulfate is a quite satisfactory surfactant for this, and that the process is extremely efficient if run in the pH range of minimum solubility of $Al(OH)_3$.

Karger and Miller studied the foam fractionation of chloro complexes of Fe(III) and Hg(II) and Co(II) with a cationic surfactant, and demonstrated that these could be separated by control of chloride concentration.[109,110]

Talbot in 1971[111] investigated the foam flotation of Cu(II) with sodium lauryl sulfate. Other studies on the removal of copper include a 1973 study by Takechi[112] in which he tested five surfactants. Removal was greater than 90% from solutions initially containing 10 ppm Cu. Mori et al.[113] removed Cu(II) by batch foaming with N-(β-hydroxyhexadecyl)diethylenetriamine in equimolar proportions. Valdes-Krieg et al.[114] have patented a foam removal technique for reduction of copper in effluent blowdown from evaporation desalination plants. Huang and Wilson used CuS and hexadecyltrimethylammonium bromide to remove cadmium and mercury;[115] Robertson et al. developed techniques for the removal of lead and zinc with hydroxides and sodium lauryl sulfate;[116] and Chatman et al. obtained excellent copper removals with ferric hydroxide and sodium lauryl sulfate.[117]

Miller and Sullivan[118] have studied the foam fractionation of Hg(II) nitro complexes. A more recent study by Yoshida et al.[119] deals with the removal of organomercury compounds by flotation with a collector, guanylthiourea, and a foaming agent such as Na laurylbenzenesulfonate. The concentration of methylmercuric chloride under such conditions was reduced by 99% (initial concentration = 1 ppm) in 20 minutes; changes in ionic strength did not affect the results. Nozaki et al.[120] reported on the ion flotation of Hg(II) in NaCl solution using cationic surfactants such as cetyltrimethylammonium chloride or cetylpyridinium chloride. The species removed were confirmed to be $HgCl_3^-$ and $HgCl_4^{-2}$.

Schonfeld and his coworkers have observed that surfactants which can act as chelates as well as simple exchange sites are unusually effective.[121] Following this up, Okamoto and Chou published on the selectivity of separations of Hg and Cd with a chelating surfactant.[122] Lemlich and others have carried out studies demonstrating the utility of refluxing in foam separations.[9,110,123,124,125] Schonfeld and Kibbey[126] constructed an excellent foam fractionation apparatus with which they obtained concentration factors of greater than 10^3 in removing radioactive strontium. Shakir has reported on the foam separation of U(VI) from sulfate media.[127] Bikerman[128] has studied the foam fractionation of calcium, iron, and manganese with alkyl sulfates and poly (oxyethylene) sulfates, and noted that nonionic surfactants were ineffective. Dziomoko and Sidenko[129] carried out ion flotation of dichromate using N,N,N',N'-tetramethyl-N,N'-dicodecylhexamethylenediammonium dibromide. Charewicz and Niemiec[130] investigated the flotation of perrhenates (ReO_4^-) with cationic surfactants (amine salts), and Podeuk and his coworkers[131] patented a method for ion flotation of tungsten and molybdenum with amines in acid solution. Sebba and coworkers[132] found that cationic surfactants yielded good separation of chloroaurate. Moroi and Matuura[133] investigated the removal of Cs(I) and a number of Co(III) complexes with sodium dodecyl sulfate. Kepak and Kriva[134] used dodecylamine or gelatin to separate ionic and colloidal forms of Ru(IV) chlorides and Ru(III) nitrates. Stachurski[135] developed a stochastic mathematical model for flotation processes which he checked against data on molybdenum. E. Rubin and Jorne'[136] investigated surface hydrolysis effects in foam separations involving anionic surfactants. Rabrenovic[137] has carried out ionic flotation of uranium from dilute solution. Kim and Zeitlin[138,139,140] have used adsorbing colloid flotation (with ferric hydroxide collector and sodium dodecyl sulfate) to recover traces of molybdate and uranyl carbonate; they have used ferric hydroxide and dodecylamine to recover trace amounts of zine and copper.

More recently, Zeitlin and his coworkers have published what promises to be extremely useful work on the foam separation with various surfactants of many of the coprecipitating collectors commonly used in trace analyses in oceanographic work and have developed a number of analytical methods.[141,142,143] In 1976 Rothstein and Zeitlin[144] reported the separation of silver from sea water by adsorbing colloid flotation. The system employed a lead sulfide collector, a stearyl amine surfactant and nitrogen gas. Mean recovery from aqueous solution was 91.8% with an 8.1% relative standard deviation. The dissolved ionic species are assumed to be $AgCl_2^-$ and $AgCl_3^{-2}$. In the same year Hagadone and Zeitlin[145] discussed the use of adsorbing colloid flotation for the removal of vanadium. pH is critical, with optimum results at 5.0. $FeCl_3$ was employed as the collector and Na dodecylsulfate as the surfactant. Recovery was 86.1 ± 3.7%. Problems of reproducibility with unspiked sea water samples were caused by complexation of vanadium and relatively low atomic adsorption spectroscopy sensitivity. Other work on sea water includes Valdes-Krieg et al.,[146] who studied foam and bubble fractionation for removal of trace metal ions from water in a continuous feed system. Ninety-nine percent of the Cu(II) was removed from solution containing 1.0 ppm Cu(II) as $CuSO_4$ with a feed containing 41.6 ppm Neodal at a 2.20 gpm/ft^2 feed rate. Zhorov et al.[147] investigated the adsorbing colloid flotation of Cu, Mo and U from sea water. Hydrated iron oxide was used as the sorbent; stearic acid and indolebutyric acid as the collectors and Stearox 6 as the foaming agent. Wallace et al.[148] investigated the concentration of particulate trace metals and particulate organic carbon in marine surface waters by bubble flotation. The transport to the surface by bubbles of these particulates was studied in an effort to obtain an order of magnitude estimate of bubble transport in open-ocean conditions. The trace metals studied included: Al, Mn, Fe, V, Cu, Zn, Ni, Pb, Cr and Cd. Recoveries were greater than 50%. The ratio of the concentration of a given metal brought to the surface by bubble transport to the concentration of that metal brought to the surface by atmospheric deposition was evaluated. Although the values for these mechanisms varied over three orders of magnitude among the various metals, the ratios for the various metals varied only over one order of magnitude. This could suggest some coupling of the two mechanisms.

Ferguson and Wilson developed methods for the removal of lead and cadmium from industrial wastes by precipitate flotation and by adsorbing colloid flotation.[149] Skrylev et al.[150] studied the removal of zinc and cadmium by flotation with potassium caproate. They found the process improved by small additions of electrolyte, e.g., NaCl, $MgCl_2$ and $CaCl_2$. Kubota[151] also investigated the removal of cadmium from wastewaters in which the surfactant was already present. Izumi[152] studied the removal of combinations of heavy metals such as found in the wastewater of a plating plant or nonferrous mining industry. He employed froth flotation agents such as fatty acid amides, amines, or alkylpolyamines, and treated water containing 10 ppm each of Cu, Zn, Cd, and Pb. He reported that by aerating at various pH's it was possible to recover the metals individually. Selecki and Kawalec-Pietrenke[153] studied the ionic and precipitate flotation of chromium complexes. Grieves and Bhattacharyya[154] in a chapter in reference 13 discussed the flotation of Cr(VI) in batch and continuous modes. Techniques include: ion flotation; dissolved air-ion flotation; and precipitate flotation. Skrylev et al.[155] also investigated the flotation separation of chromium as chromate and dichromate ions. Rosin amine acetate was used. Seifullina et al.[156] reported on the flotation separation of germanium(IV) as the trihydroxyfluoronate complex with rosin amine acetates.

In 1974 Charewicz and Grieves[157] described the selective foam separation of the oxyanions of vanadium, chromium, molybdenum, tungsten and rhenium from multi-component systems. Each oxyanion was present in 10^{-6}M concentration, and hexadecyldimethylbenzylammonium chloride was the cationic surfactant. Studies on the effect of H^+ and Cl^- competition were performed, as were separation studies on the relative selectivity of oxyanion removal. In 1976 Walkowiak, Bhattacharyya and Grieves[158] described the selective foam fractionation of the chloride complexes of zinc, cadmium, mercury and gold. The surfactant was hexadecyltrimethylammonium chloride. The effect of Cl^- concentration was studied for single metals and mixtures.

Gold can be efficiently separated from the other three metals at a Cl^- concentration of 0.01M, gold and mercury at 0.5M Cl^-. Also in 1976, Walkowiak and Grieves[159] discussed the foam fractionation of the cyanide anion complexes of zinc, cadmium, mercury and gold. The surfactant again was hexadecyltrimethylammonium chloride. One hundred percent flotation was achieved for each metal. The effects of CN^- concentration as well as NO_3^-, $SO_4^=$, and halides (Cl^-, Br^-) were studied. The interference to metal flotation by the anions increased as follows: $SO_4^{-2} < Cl^- < CN^- < Br^- < NO_3^-$. A selectivity sequence, for single metal and mixed metal solution was established as follows: $Au(CN)_4^- > Hg(CN)_4^{-2} > Cd(CN)_4^{-2} > Zn(CN)_4^{-2}$. Walowiak and Rudkin[160] determined selectivity coefficients for $Ag(CN)_2^-$ and $Au(CN)_2^-$ in foam fractionation experiments with hexadecyltrimethylammonium iodide.

B. Extractive Metallurgical Applications

Even after sixty-plus years of flotation techniques in the mining industry, economic incentives encourage vigorous research. The literature is filled with studies to remove various metals from mining ores, residuals and wastewaters. The metals under investigation span the periodic table. A brief survey of recent papers include flotation studies of the following metals: beryllium;[161] nickel;[162,163,164] cobalt;[162,163] copper;[163,164] the lanthanide series;[165] zinc;[166] iron;[166] manganese;[166] silver;[167] platinum;[167] molybdenum;[168,169,170] mercury;[171] tungsten;[172] vanadium;[173] ruthenium;[174] and germanium.[175]

V. THE REMOVAL OF ANIONS AND ORGANIC COMPOUNDS

Generally there appears to be less in the literature on the use of flotation techniques to remove or separate anions or organic compounds from solutions than there is on cations. Here removal of an anion refers to a species considered a contaminant in its own right - creation of negatively charged complexes of metals to facilitate removal was reviewed in the previous section. There are ambiguous areas open to interpretation, circumstance, etc., such as chromium/chromate or arsenic/arsenate. Also included in this section will be studies on the removal of nonionic inorganic substances by flotation.

A. Anions

Grieves, Bhattacharyya and their coworkers have applied flotation techniques to a number of waste treatment problems: flotation of dichromate,[176,177] phosphate,[178,179] phenolate[179,180] (and chromic hydroxide[181]), and cyanide complexes with Fe(II).[159,182] They recently investigated the stoichiometry of the separation of the anions I^-, $HCrO_4^-$, $S_2O_3^=$, and $Ag(S_2O_3)^{-3}$ with ethylhexadecyldimethylammonium bromide.[183] Earlier work concerned the foam separation of active carbon;[184] the flotation of dichromate with ethylhexadecyldimethylammonium ion;[185] the effect of colloidal particulates on foam fractionation;[186] the foam fractionation of colloid-surfactant systems;[187] and foam separation processes for removing inorganic and organic ions with surfactants.[188] An interesting practical application studied by these workers is the precipitate coflotation of calcium sulfite and calcium carbonate which may be of use in treating wet scrubber slurries resulting from sulfur dioxide removal from stack gases.[189] More recently Grieves with Charewicz and The[190] continued studying the selective flotation of anions. Ethylhexadecyldimethylammonium bromide was found to be selective for SCN^- > I^- > ClO_3 > Br > NO_2^- in this order. Hexadecyldimethylbenzylammonium chloride was selective for the oxyanion of five metals as follows: Re(VII) > Mo(VI) > Cr(VI) > W(VI) > V(V). A later paper by Grieves et al.[191] continued his work on chromate ions and discussed the removal of thiosulfate ($S_2O_3^{-2}$) from solution with ethylhexadecyldimethylammonium bromide.

Phillips and his coworkers have made a rather detailed study of equilibria and mass transfer rates in the continuous foam fractionation of phosphate and other anions.[192,193,194] Ervin and Danner investigated the effects of a number of parameters, including reflux ratio, on the continuous foam fractionation of phenol.[195] Skrylev and Boresov studied the flotation of arsenate[196] and tungstate[197] ions using rosin amine acetate and hydrochlorides, respectively. Recovery of arsenic was 87% in 30 minutes. Clarke and Wilson demonstrated the feasibility of floc foam flotation of fluoride with aluminum hydroxide and sodium lauryl sulfate both in synthetic mixtures and in scrubber wastes from aluminum manufacture.[198]

Grigor'ev and coworkers[199] studied the sorption of arsenite by ferrous sulfide. The sorbed complex is reported as $Fe_2S_2O_3(AsO_2)_2$. The process is exothermic. An increase in temperature should therefore shift the reaction equilibrium to the left, decreasing the adsorption. However, the extent of the adsorption actually increased due to an increased number of adsorption sites, a result of increased sulfide oxidation at the higher temperature.

The kinetics of the foam flotation of sulfur-35 (as $SO_4^=$) were studied by Berezyak et al.[200] The rate of entry of the sulfur and surfactant into the foam layer depended on ionic strength. At neutral pH the surfactant had minimum entry into the foam while the sulfur had maximum entry. The kinetics of flotation were first order.

B. Hydrophobic Solids, Clays

The recent literature contains three articles pertaining to the flotation of naturally occurring nonionic, inorganic (with one exception) substances. Work in 1975 by Chander, Wie and Fuerstenau[201] deals with the flotation of naturally hydrophobic solids: graphite, talc, sulfur, stibnite, paraffin, etc. The authors concluded on the basis of available data that the crystal structure, nature of charged surface (hydrophilic) sites and anisotropic behavior play important roles in determining the specific properties of inherently hydrophobic substances. In 1976 Glebov and Kon'shin[202] discussed the effect of organic materials found in sea water on the flotation of naturally occurring sulfur. By performing replicate experiments using distilled water, purified sea water and natural sea water, they determined that the natural hydration of sulfur is most reduced in the natural sea water. They concluded that the dissolved organic material in the sea water caused the additional hydrophobicity which in turn increases flotability. Skrylev et al.[203] used primary alkyl amines and rosin amine acetates to remove silicon from natural waters.

Other studies were performed on natural systems. DeVivo and Karger[204] studied the effects of aggregation in the flotation of colloidal particulates - kaolin and montmorillonite were floated with ethylhexadecyldimethylammonium bromide, and zeta potential, cation concentrations, pH, and ratio of surfactant to initial particulate concentration were varied.

C. Oils

Interesting work has recently been done by Skrylev and coworkers[205,206,207,208] on the flotation removal of emulsified oils at low concentrations. Vegetable oils such as sunflower, corn, coconut and cottonseed were removed in 20 minutes with a gelatin collector and a mixed cationic surfactant, viz - C_{10-14} primary amines, rosin amine acetate and polyethylene polyamine. Best removal occurred at pH 2-3; worst at pH 10-11. The removal of oils from wastewaters was accomplished using 30-70 mg/l $FeSO_4$ and 1-5 mg/l alkyl pyridinium chloride. Residual oil concentrations ranged from 10-30 mg/l. Removal kinetics were first order. Studies on rape seed oil fatty acids - their structure vs removal with various nonionic and anionic surfactants - were conducted by Zwierzykowski and Ledochowska.[209]

VI. ADDITIONAL LABORATORY STUDIES

This section reviews recent articles not directly describing a method of removing a species from solution. For example, the subjects of foams, thin films, double layers, laboratory (cf. theoretical) experiments on adsorption kinetics, among several other topics, will be addressed.

A. Foam Stability and Prevention

Foam stability is important in the effective removal of substances by foaming techniques. One of the factors affecting foam stability is bubble size,[210] which is itself affected by a number of factors. Ivanov et al.[211] reported in 1974 that temperature variation (11-21°C) does not affect bubble size in a foam. Similarly the dimension of a bubble does not depend upon depth in the liquid at which the bubble is formed but their lifetimes do depend on this depth. A study that same year by Kubritskaya and Kheison showed that foam stability is a function of gas density and pH.[212] They reported that the foam destruction rate was affected by a viscosity change resulting from a pH increase. Pustovalov[213] reported that foam stability depends upon the concentration of electrolyte in solution.

Bilkun and Chistyakov[214] reported that the addition of water soluble polymers stabilized foams in aqueous solutions of anionic and nonionic surfactants. They also investigated common polyelectrolytes. Volkov and Maloteev[215] qualitatively and quantitatively studied the physical properties of foams mechanically produced using air. Grishna and Mitriskov[216] dealt with the effect of surfactants on the structure of a dynamic foam, and Sviridov and Skrylev[217] suggested that the stability of foams be used as an index of relative flotation separation efficiency.

In 1975 a symposium on foams was held in Stockholm, at which a lot of work on foam behavior and stability was presented and later published in the proceedings.[218] Friberg and Saito[219] studied the effect of a liquid crystal phase on foam stability, finding that, while the substance forming liquid crystals did not form foam itself, when it was present in an aqueous medium it enhanced foam stability. Prins[220] presented a mechanism explaining foam stability in terms of formation history and surface dilatational viscosity.

We next deal with foam breakers and foam prevention. Roberts et al.[221] reported a mechanism for foam prevention. It was suggested that the presence of emulsified drops is necessary for foam prevention. Koretskaya[222] in 1977 attributed the prevention of foam formation to the dehydration and separation of surfactant molecules. In another paper Koretskaya with Kruglyakov[223] discussed the mechanism of heterogeneous foam quenching. The degree of stability was ascribed to the ability of a quenching agent to displace adsorbed foaming agents on the boundary layers. For the collapse of foams in larger-scale continuous flow apparatuses, our experience has been that the high-speed spinning disc technique described some years ago by E. Rubin and his coworkers[224,225] is a very effective method.

B. Properties of Thin Films

The study of the properties of individual bubbles relates to the formation of foams and their use in separations. Collins et al.[226] developed a method of measuring the charge on small gas bubbles. This permits the determination of electromobilities or zeta potentials of bubbles which can be important in flotation techniques. Dedek and Barcal[227] studied the effect of surface tension variation on the adhesion of air bubbles to a solid surface; they used various alcohols to change the surface tension. A decrease in surface tension (as compared to pure water) increased the induction period for the bubble and reduced the total sticking time. Other factors involved in bubble adhesion include the bubble's velocity at the time of impact and the properties of the solid surface. The ramifications of bubble adhesion in flotation are obvious. While adhesion is not routinely monitored during system operation, gross parameters (such as input air flow rate) can be varied with resultant changes in efficiency, reflecting changes in bubble adhesion. The capture-efficiency of small petroleum emulsion droplets by air bubbles during flotation was investigated by Rulev et al.[228] Although the capture efficiency can be simply defined as a ratio of the squares of the diameters of the particle and bubble, in reality surface interactions must also be taken into account.

Skrylev and coworkers[229] studied the adsorption of surfactants on the movable surface of a solution/gas interface. Conclusions drawn included: the adsorption equilibrium at the bubble/surfactant (solution) interface is instantaneous; equilibrium between the bubble and colloidal surfactant/dispersion requires time; the Gibbs equation correctly predicts the limiting adsorption for a surfactant solution; the colloidal surfactants adsorb irregularly.

Ingram[230] reviewed the literature concerning the intermolecular forces in surfactant films which contribute to foam stability and he presented some original studies in this area. Buscall et al.[231] worked on the equilibrium properties of foam films formed from nonionic surface-active agents (decylmethyl sulfoxide and decyldimethyl phosphene oxide). Film thickness depended on the nature and concentration of the anion in solution. The surfactant dedecyldimethylamine oxide behaved like a cationic species at a pH < 7 and nonionically at pH's > 7. Interactions in surfactant-coated foam lamellae include electric double-layer repulsion and Van de Waals attractive forces (Vrij et al.[232]). Another recent study on thin films examined the effect of surface diffusion on the rate of thinning (Manev et al.[233]). Another hydrodynamic study of films was performed by Ivanov et al.[234] This concerned the expansion rate of the perimeter during three phase contact as a function of various parameters. (See ref. 67 for an example of the relation of this work to foam flotation.) Lemlich[235] analyzed the limiting conductivity of low density polyhedral foams.

C. Effects of pH, Additives, and Impurities

Other laboratory investigations assessed the effects of changing operating conditions on removal efficiency. These cover an extremely broad range of parameters. Much work has been done to assess the impact of pH on removal efficiency. Skrylev and coworkers[236] reported that as the length of the hydrocarbon part of an amine collector increases, the optimum pH for a given flotation system shifts towards more acidic values. In earlier work Skrylev[237] assessed the effect of pH on the flotation of various alkaline earth metal ions. Fuerstenau and Wakamatsu[238] explain the effect of pH (and concentration) on adsorption isotherms. Sodium dodecanesulfonate/alumina/water interface was the system investigated. Adsorption significantly occurred only at pH's less than 9, the zero charge point of alumina. At low concentrations surfactant ions were adsorbed individually in the double layer. When adsorption in the Stern layer reaches a critical value the surfactant associates via the hydrocarbon chains, forming hemimicelles. This occurrence changed the slope of the isotherm.

Another area of wide interest is the effect of additives and/or impurities on a flotation system. Skrylev and coworkers[239,240] investigated the effect of impurities on the flotation of surfactants. Small amounts of C_{3-5} alkanols increase flotation but larger amounts reduce it. Small amounts of chloride salts increase flotation, but again larger amounts reduce it. The increase of surfactant flotation with increasing ionic strength of the solution is probably due to the reduction in coulombic repulsion of the surfactant ionic heads for each other as the more dense double layer is able to screen more effectively. Additional studies were conducted using $SO_4^{=}$ and CN^- salts and gelatin as additives in four different surfactant systems. Resultant effects depended on the nature of surfactant and additive employed. Effectiveness of flotation was found to increase when the surface active agent, formed by the surfactant and additive, had low solubility. Kazakov et al.[241] also studied the effect of aliphatic alcohols on foam formation. They reported an initial increase, then fall off, of foam stability with increasing length of alkyl radical.

Maiofis et al.[242] studied the effects of inorganic electrolytes on the foaming capacity of surfactants by varying the concentration of NaCl; a concentration of NaCl > 2.5 M changes the surface tension isotherm. Berezyuk et al.[243] also studied the effect of various chloride salts on the rate and extent of passage into a foam of Na dodecylbenzene sulfate. They reported that the effect is a function of the radius of the hydrated cation and the flocculation ability of the salt. The resultant order is $LiCl < NaCl < AlCl_3 < CaCl_2$. $AlCl_3$ solutions yielded the highest percent passage of the surfactant into the foam phase. A $CaCl_2$ solution (at 0.1 M and pH 12.9) produced the fastest rate of passage. The kinetics are first order. Khentov et al.[244] reported that the addition of the Na salts of salicyclic and 2,4-dihydroxy benzoic acids decreases the efficiency of chloride (Cl^-) separation from sulfate ($SO_4^{=}$) using foam fractionation. They suggest that the salts decrease the surface energy of the chloride and sulfate ions. This in turn causes their even distribution on the surface of the foam bubble. Substitution by additional Na depresses the $Cl^-/SO_4^=$ separation even further. Sheiham and Pinfold[245] have studied the effects of added electrolytes on the flotation of hexadecyltrimethylammonium chloride and of dodecylpyridinium chloride. Maas[246] has shown that addition of organic vapors to the air stream generating the bubbles may markedly speed up some foam separations.

Skrylev et al.[247] found that the removal of various dilute emulsions was increased by the addition of small amounts of quaternary pyridine or quinoline salts with alkyl substituted nitrogen. Surfactants with heterocyclic amine groups had the same effect, extent of which depends upon the size of the alkyl group or heterocyclic radical. Skrylev and Ososkov[248] also report the use of C_8-C_{12} primary and secondary aliphatic amines to float petroleum products to be optimum. This is based on cost considerations and the fact that dosage requirements are not critical.

Another area of interest is the effect of molecular weight of nonionic surfactants on their removal from solution. Zwierzykowski et al.[249,250] stated that the lower molecular weight surfactants gave the best foaming, and found an inverse relationship between the degree of oxyethylation of a surfactant and the quality of foaming (i.e. removal). However, this last was true only when the compounds dissolved well in water. Poor foams resulted from surfactants which were not readily soluble. This occurs for less than 7 oxyethyl groups.

Grieves and coworkers[251] studied the effect of particle size of the surfactant-colligend precipitate on the extent of ion flotation. Generally particle size and flotation increase with increasing temperature. They also reported that the optimum chain length in the surfactant (quaternary ammonium sulfate) increased with increasing temperature, and that increasing the surfactant to contaminant concentration ratio increased the removal up to a limiting value. This limit is a function of the surfactant's chain length.

Another aspect of flotation of current interest is adsorption kinetics. Kulkarni and Somasundarun[252] wrote an extensive article on the kinetics of oleate adsorption at the liquid-air interface and the role of kinetics in hematite flotation. Kato et al.[253] studied the adsorption rate of surfactant ions in continuous flow foam separation techniques. They found that adsorption rate increases with decreasing bubble diameter (cf. ref. 66) and increases when electrolytes were present, due presumably to the reduction of surfactant-surfactant repulsions by the more compact double layer.

Collins and Jameson[254] studied the effect of the double layer in the flotation of fine particles. Flotation rates decrease as the potential across the column is increased. Reay and Rateliff[255] tested the hydrodynamic collision of fine particles using very small bubbles during flotation. Flotation rate vs size (using glass beads) agrees well with predictions from simple models. Results from experiments using latex particles did not agree as well with model results. The simple models do not take into account electric forces such as those associated with the zeta potential.

Valdes-Krieg et al.[256] developed a method to determine surface equilibria and mass transfer rates in concurrent-flow bubble columns. Surface concentrations in equilibrium with the bulk liquid are measured by surfactant or counter-ion depletion in the bulk liquid phase, which is followed by sampling along the column height. The equilibrium is determined by a mass balance equation. By successive operation at constant flow conditions and various collector and counter-ion concentrations the adsorption isotherms can be determined. The effect of counter-ions on surfactant distribution can also be studied. These data should aid in the proper design of devices for bubble and foam fractionation separations.

D. Column Alignment

Another interesting paper by Valdes-Krieg and coworkers[257] dealt with the effect of vertical alignment of the column on the performance of bubble or foam fractionation columns. They report that a misalignment of 1° introduced pronounced effects on the surfactant concentration distribution along the length of the column. The surfactant concentration in both the foam and liquid effluents was higher with misalignment. The foam had a lower liquid volume fraction and lower air hold-up. Back circulation of bubbles occurred on the lower side, and channeling was also present. The axial concentration gradient was less steep in the misaligned column. Consequently it appears that precise alignment of the column in a vertical position is essential for efficient and reproducible flotation separations.

The first Valdes-Krieg paper appeared in the proceedings of a 1975 AIChE Symposium Series on Advances in interfacial phenomena of particulate/solution/gas systems; applications to flotation research. The symposium consisted of twenty-four papers ranging from basic principles of interface and solution phenomena[258] to ore beneficiation[259,260] to research papers on adsorption[261] and electrokinetics.[262]

VII. LARGE SCALE APPLICATIONS

Besides the wide use of froth flotation in the mining industry, other flotation techniques are being upgraded from laboratory investigations to the pilot and full scale levels. This mode of treatment offers a variety of attractive aspects such as low energy requirements; high removal efficiency; reasonable capital investments; and a comparatively low level of maintenance and operational requirements. Also there is the possibility of recovery and reuse of the separated substances. However, an article by Barskii and Reizlen[263] discussed some of the inherent problems of transferring laboratory scale experiments directly to industrial conditions. A major conclusion was that determination of optimal conditions for industrially scaled processes must be made on a statistical basis resulting from many test runs. Below we present some recent developments in the application of flotation technology to industrial and environmental problems.

A. Industrial Waste Treatment

One of the most promising areas for the utilization of full scale flotation removal systems is in the treatment of industrial wastewaters. The scaling-up process in foam flotation studies is illustrated in the application of theory and experimental principles by Wilson and coworkers (described earlier 117, 149, 198) to the construction and operation of a foam flotation pilot plant. The unit was used both in the laboratory and on-site to test the removal of lead and other metals from industrial wastewaters.[97] Rettenberger recently wrote a general paper on the use of flotation in industrial wastewater treatment.[264] A review article on the advantages of flotation techniques in the treatment of textile wastewater was prepared by Alavedra Ribot.[265]

Another field well-suited to the use of flotation in wastewater treatment is the laundry industry or facility. The literature contains many references to its current and potential use. For example, Grieves and Bewley[266] assessed the feasibility of recovery of surfactants from laundry discharge by foaming techniques. This treatment is especially important when dealing with effluents from mobile military encampments, field hospitals, etc.

Still, the main potential for the general use of flotation lies in the treatment of metal-containing wastewaters with recovery of valuable metals. Pearson and McPhater[267] describe a general precipitate flotation process adaptable to effluents from various processes. Initially any complexing ions are destroyed and then the metal is precipitated by an alkaline reagent. The precipitate-containing effluent travels to a flotation tank and up through the froth layer. The froth layer is skimmed and the skimmate filtered or otherwise reclaimed.

A more specific application is the foam fractionation of Zn(II) and Cr(VI) by Okiawa and coworkers.[268] Their system was successfully tested on non-ferrous mining waters and wastewaters from the wood preservation and synthetic textile fiber industries. Another study, on the removal of Cd^{+2} from wastewaters, was performed by Takahoski and Tabuchi.[269] Skrylev et al.[270] investigated various collectors for use in the flotation of dichromate ion from industrial wastes. Best removal was 88% using dodecylamine.

It would appear, in view of federal legislation,[271] that a new and important application of flotation technology may be opening up - the removal of toxic organic compounds from industrial discharges. In this connection Bishop[272] successfully removed 100% of the powdered activated carbon added to water by single stage continuous flow foam flotation using ethylhexadecyldimethylammonium bromide. Surfactant concentrations as low as 30 mg/l and hydraulic loading rates < 1 gal/min ft^2 were used.

B. Domestic Sewage

Foam flotation can be successfully employed in the treatment of domestic sewage, also. Early work by E. Rubin et al.[273] discussed contaminant removal from sewage treatment plant effluent by foaming. This is especially important in the removal of refractory (non-biodegradable) constituents in effluent from secondary (biological) treatment. Up to 45% of this residual chemical oxygen demand was removed after foaming. The total dissolved solids and chloride ion concentrations were not affected by foaming. Zwierzykowski and Medrzicka[274] investigated foaming as a means of removing detergents and mineral oils from water and sewage. Foam generation in aeration basins is a problem, as is the coating of the microorganisms or biological floc with oil. In another paper[275] they assessed, on a laboratory scale, single and multistage removal of various detergents by foaming. Dissolved air flotation (DAF) is frequently used to remove solids in waste treatment processes; its widest application is in the treatment of industrial wastes.[276] DAF requires air either under reduced or increased pressures.

C. Other Applications

Flotation techniques are also being investigated as a means of removing contaminants from sea water. Skrylev and Ososkov[277] assessed the feasibility of removing emulsified petroleum from sea water by flotation. On a different tack, Valdes-Krieg et al.[278] studied the recovery of anionic surfactant from sea water desalination blow down brine. Surfactants are added to desalination systems to improve evaporation rates. Work at the laboratory and pilot plant scales indicates that 95-97% surfactant recovery is feasible.

Another field employing flotation technology (but not with regard to wastewater treatment) is the coal industry.[279,280] A recent review article on coal flotation was written by Aplan.[281]

An indication of the far-ranging application of flotation treatment technology is shown by the work of Grieves et al.,[189] who conducted experimental studies on the precipitate flotation of $CaSO_3$ and $CaCO_3$ and mixtures in slurries. This was in conjunction with treating the purge stream from an SO_2 - limestone wet scrubber, an air pollution control device used in coal-burning power plants. Excellent results were obtained by floating at a neutral pH - 95% of the sulfite and 97% of the carbonate were removed using Na dodecylbenzene sulfonate.

VIII. MISCELLANEOUS STUDIES

The final section contains a few papers relating to flotation separations but which do not come under the previous headings.

Talmon and E. Rubin[282] developed a chromatographic method based upon liquid foam separation techniques. The sorption bed is the foam moving in a tall, vertical column. The foam exhibits a large surface area for adsorption. The foam is eluted from the top down, counter-current to the rising foam. The mechanism for the separation of mixtures is differential adsorbance to the bubble surface; solutes with greater affinity for the gas liquid interface are washed down more slowly. The technique can be used in a pulse or continuous mode. The possibility of recovery of solutes from the foamate is under investigation.

Another interesting study by Skrylev and coworkers[283,284] investigated the effect of a magnetic field on ion flotation. They reported that static, alternating and mixed magnetic fields have a marked effect on the separation of Ni, Co and Cu ions. The extent of the effect is a function of the ion and the field - the mixed field having the greatest effect. Field effect was found not to be a function of pH (pH ≤ 11).

The creation of micelles is undesirable during flotation, since they reduce the attraction of the floatable substance towards the collector-coated air-water interface (see figure). The critical micelle concentrations (CMC's) of various straight chain ionic surfactants were compared with the CMC's of alkyl sulfates of the same

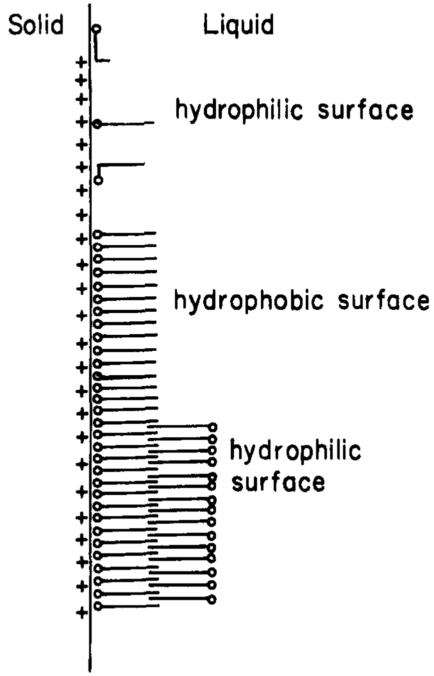

FIGURE 1

Surfactant film structures at various concentrations of surfactant in the bulk solution. Bulk surfactant concentrations increase as one goes from top to bottom. Only the middle structure would produce bubble attachment.

chain length, for the same ionic strength and temperature. For the five different hydrophilic groups studied the CMC was higher when the ionic charge on the head group was closer to the α-carbon atom in the alkyl chain. This correlation was noted and explained by Strigter[285] as follows: there is an increase in electrostatic self-potential of the surfactant ion when during micellization the head group moved from the bulk solution into the vicinity of the nonpolar micelle core. Grebnev[286] studied the rate of disintegration of micelles in solution. Dilution of a concentrated (above CMC) solution to a value in the concentration range where flotation can be efficiently employed caused a micelle of C_{16}-C_{18} saturated collectors to disintegrate in 15-30 minutes. Collectors having unsaturated hydrocarbon chains required only 2-3 minutes to break up.

IX. CONCLUSION

We observe that flotation separations appear well-adapted to the recovery of valuable trace metals and other substances, and to the removal of toxic ionic substances from wastewaters, both areas which can be expected to be increasingly important in the future. Those of us working in the field still have quite a bit of unfinished business with which to deal. If large installations are to be efficient, we must stabilize the plug flow of foams in large columns at high hydraulic loading rates. We need more information on the effects of interfering solutes and how to prevent these interferences by pretreatment, choice of surfactant, and operating conditions. Economics will dictate more work on the recovery and recycling of surfactants from collapsed foamates and sludges, and on the properties of these sludges. And further work on the use of foam flotation techniques for the removal of trace organics from water is surely indicated.

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