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FOAM FLOTATION TREATMENT OF HEAVY METALS AND FLUORIDE-BEARING INDUSTRIAL WASTEWATERS

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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FOAM FLOTATION TREATMENT OF HEAVY METALS AND FLUORIDE-BEARING INDUSTRIAL WASTEWATERS

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet needs both efficiently and economically.

This report is a product of the above efforts. These studies were undertaken to perform a laboratory-scale investigation of floc foam separation techniques to remove toxic heavy metals and fluoride from wastewaters produced at primary aluminum smelters, secondary lead smelters, and copper and brass mills. Simulated and real industrial wastewaters were studied. Floc foam separation techniques combine the attractive features of simplicity, economy, low energy usage, potential for recovery, and effective removal of pollutants from diluted wastewaters to concentrations well below the standards established or anticipated by the regulatory agencies.

Such information will be of value both to EPA and to the industry itself. Within EPA's R&D program the information will be used as part of the continuing program to develop and evaluate improved and less costly technology to minimize industrial waste discharges. Besides its direct application to effluents from non-ferrous metals industry, this technology may find application to treat metal-containing wastes generated by a host of other industries.

For further information concerning this subject the Industrial Pollution Control Division should be contacted.

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ABSTRACT

Laboratory studies demonstrated that floc foam flotation techniques are capable of reducing lead, cadmium, mercury, copper, zinc, arsenic, and fluoride in dilute aqueous systems to very low levels. Simulated as well as real industrial wastes were studied. Copper, lead, and arsenic are readily removed with $Fe(OH)_3$ and sodium lauryl sulfate; fluoride and zinc, with $Al(OH)_3$ and sodium lauryl sulfate; cadmium and mercury, with CuS and hexadecyltrimethylammonium bromide. Batch flotation techniques as well as continuous flow systems were studied. Continuous flow systems proved to be more efficient than the batch techniques. Floc foam flotation techniques are not effective for treatment of wastes containing high concentrations (>10 g/ℓ) of dissolved salts. Adequate control of pH is essential in most of the separations, and proper design and placement of the influent dispersion head and baffles are necessary to permit maximum column loading. The calculation of the isotherms for floc adsorption on surfactant films was carried out by means of statistical mechanics, and the results were found to be in good agreement with the experiment. Computations of column performance in the steady state were made by means of a mathematical model, and the dependence of column performance on the parameters of the model were investigated.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

a	-- cell dimension
a_i	-- number of sites containing i particles
a_1	-- first Langmuir adsorption isotherm parameter, also effective thickness of ionic atmosphere
a_2	-- second Langmuir adsorption isotherm parameter
c	-- solute or floc particle number density, cm^{-3}
C	-- concentration of 1-1 electrolyte, moles/cm^3
c_{feed}	-- concentration of solute in column effluent
c^i	-- liquid solute concentration in compartment i
c^i_j	-- first element of eigenvector
c_{max}	-- maximum number density of floc particles, cm^{-3}
D	-- dielectric constant of water, approximately 78
D_ℓ	-- effective diffusion constant in the liquid phase
D_S	-- effective diffusion constant in the surface phase
e	-- |electronic charge|, 4.77×10^{-10}esu
F	-- column separation parameter
g/ℓ	-- grams/liter
HTA	-- hexadecyltrimethylammonium bromide
ID	-- inside diameter
k	-- Boltzmann's constant
K	-- equilibrium adsorption isotherm
k_1	-- rate constant governing solute transport between the surface and liquid phases
K_S	-- solubility product
ℓ	-- liter(s) or column length
LS^-	-- lauryl sulfate ion
m	-- number of cells in a surface adsorption site
min	-- minute(s)

ABBREVIATIONS (continued)

m/ℓ	-- moles/liter
N	-- normal
NLS	--sodium lauryl sulfate
N_o	-- Avogadro's number, 6.023×10^{23}
OD	-- outside diameter
$Pf(j_i)$	-- one-particle partition function for a particle in cell j_i
pK_s	-- $-\log_{10} K_s$
ppm	-- parts per million (in water, numerically equal to mg/ℓ)
q	-- electric charge of floc particle
q(s)	-- site partition function
Q(N,M,T)	-- canonical ensemble partition function for M sites, N particles
S	-- specific foam area
$\bar{s}$	-- average number of floc particles per site
S_{excess}	-- surface excess of floc particles
T	-- absolute temperature
V	-- volume of liquid contained in 1 cm^3 of foam
V'	-- flow rate of column effluent/v_ℓ
V(i)	-- potential energy of a floc particle in the ith cell
v_ℓ	-- velocity of liquid downward
v_s	-- velocity of surface upward
x	-- distance from air-solution interface, or distance from base of column
x_i	-- position of the boundary between compartments i and i+1
α_j^i	-- integration constant
β	-- 1/kT
Γ	-- surface concentration of solute
Γ_i	-- surface solute concentration in compartment i
Γ_j^i	-- second element of eigenvector
δ	-- film thickness of drained film
$\varepsilon j(s)$	-- energy of site when occupied by s particles in cells $j_1, j_2, \ldots j_s$

ABBREVIATIONS (continued)

λ	-- absolute activity
λ_j^i	-- eigenvalue
μ	-- chemical potential
μ_{config}	-- configurational free energy per floc particle
μmhos	-- micro-ohms^{-1}, micromhos
ξ_i	-- position of the midpoint of the ith compartment
Ξ	-- grand partition function
π	-- product symbol
σ	-- reduced floc density, c/c_{max}
Σ	-- summation symbol
ψ	-- electric potential
ψ_o	-- surface potential
!	-- factorial symbol

SYMBOLS

Al	-- aluminum	Hg	-- mercury
As	-- arsenic	Mn	-- manganese
C	-- carbon	N	-- nitrogen
Ca	-- calcium	Na	-- sodium
Cd	-- cadmium	O	-- oxygen
Cl	-- chlorine	P	-- phosphorus
Cu	-- copper	Pb	-- lead
F	-- fluorine	S	-- sulfur
Fe	-- iron	Zn	-- zinc
H	-- hydrogen		

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SECTION I

CONCLUSIONS

Floc foam flotation techniques were investigated on the laboratory scale, and demonstrated to be capable of reducing lead, cadmium, mercury, copper, zinc, arsenic, and fluoride in dilute aqueous solutions to very low levels. Simulated as well as real industrial wastes were studied.

Copper, lead, and arsenic are readily removed with $Fe(OH)_3$ and sodium lauryl sulfate (NLS). The reagents are stable and low in both cost and toxicity. These separations are rapid in the batch mode, and the red-brown color of $Fe(OH)_3$ makes it possible to follow the progress of the separation visually in a glass or lucite column. The separations of lead arsenate and copper were also carried out successfully by the continuous flow technique in a 4.8 cm-ID column; lead was also separated in a 10.2 cm-ID continuous flow column at flow rates of the order of one ℓ/min.

Zinc and fluoride are removed with $Al(OH)_3$ and sodium lauryl sulfate (NLS). Both reagents are stable and low in cost and toxicity. Fluoride has been separated by the continuous flow method as well as the batch technique. It was found that use of a small amount of $Fe(OH)_3$ in the fluoride separation, to act as a visual tracer, did not interfere with the ability of the $Al(OH)_3$-NLS system to remove fluoride by the continuous flow technique.

Cadmium and mercury are removed with CuS and HTA (hexadecyltrimethylammonium bromide); cadmium is also removed with FeS and HTA. Attempts to obtain adequate foam flotation separation with ferric or aluminum hydroxides and NLS were not successful, although a combination precipitation-foam flotation method using $Fe(OH)_3$-HTA at a pH of 12 was able to reduce cadmium levels to 0.01 ppm. We note that sulfide ion and H_2S, present in small amounts at the initial stage of the process are both toxic. Copper salts, sodium sulfide, and HTA are all relatively expensive compared to alum or ferric chloride and NLS. The black color of the sulfides, however, does facilitate following the separation visually when transparent columns are used.

It was found that pH must be closely controlled. With continuous flow systems it was also necessary to design and place the influent dispersion head and associated foam baffles carefully to maximize the feasible influent flow rate.

The method is not effective for separations from wastes containing high concentrations (>10 g/ℓ) of dissolved salts.

The dependence of separation efficiency on dissolved salt concentration, temperature, floc electric charge, surfactant concentration, and floc concentration in the influent has been calculated by means of statistical mechanics from a Gouy-Chapman type model. The results are quite consistent with the experimental data. Increasing salt concentrations decrease floc adsorption isotherms markedly; temperature has relatively little effect; increasing floc electric charge or surfactant concentration below the critical micelle concentration increases the adsorption isotherm; increasing influent floc concentration decreases separation efficiency drastically above a certain critical range.

Column performance was simulated mathematically by means of two simultaneous differential equations and their associated boundary conditions; these were solved by a quasi-linearization method in which the adsorption isotherms mentioned above were used. The dependence of column performance on such parameters as liquid and gas flow rate, bubble size, isotherm parameters, diffusion and mixing constants, and rate constant for floc transport between the liquid and the film surface was studied. This computer model should prove highly useful in continuous flow column design.

SECTION II

RECOMMENDATIONS

The results obtained in these studies justify a recommendation that pilot plant studies be initiated on the following separations: (1) lead with $Fe(OH)_3$ and sodium lauryl sulfate (NLS); (2) copper with $Fe(OH)_3$ and NLS; (3) fluoride with $Al(OH)_3$ and NLS; (4) zinc with $Al(OH)_3$ and NLS; (5) cadmium with FeS and hexadecyltrimethylammonium bromide (HTA); and (6) mercury with CuS and HTA. The apparatus should be constructed to be readily portable by truck, so that it could be transported conveniently to the various industrial plants when wastewaters are to be treated. The characteristics of the various wastes such as concentration of toxic substance(s), conductivity, total dissolved solids should be determined and related to optimum separation parameters such as pH, flocculent and surfactant concentrations, and influent and air flow rates. The performance of various types of influent dispersion heads and foam stabilizing baffles should be studied to develop designs permitting maximum column throughput. The recycling of surfactant should be investigated as a means of reducing the cost of these separations, and efforts should be made to minimize surfactant loss. Finally, experience gained at the pilot plant level should permit cost estimates of the various separations.

In the course of the pilot plant studies, efforts should be made to relate actual column performance to the parameters used in a mathematical model simulating column operation. Reliable parameters would facilitate optimal column design and operation.

Ore processing and smelting wastewaters should be screened for the presence of arsenic; those found to contain it should be studied on a bench scale to determine the feasibility of removing arsenic by means of floc foam flotation with $Fe(OH)_3$ and NLS.

The possibility of developing floc foam separations for nickel, antimony, chromate, chromium(III), selenium, dyes, fibers, and phenols should be investigated by means of batch studies on a bench scale.

When dealing with more concentrated wastewaters, the compatibility of precipitation pretreatment [such as with Na_2CO_3, $Ca(OH)_2$, Na_2S, or other precipitating agents] and the above floc foam flotation treatments should be ascertained.

Synthetic and actual wastewaters containing mixtures of metal ions should be studied by means of batch floc foam flotation techniques to determine whether the removal of several components at once is feasible. The possibility of selective removal of single species should also be explored, since this

would facilitate recycling of the material back to the process or recovery for use elsewhere.

SECTION III

INTRODUCTION

One of the current problems in the area of advanced methods of waste treatment is that of removing low concentrations of toxic metals. These can cause serious difficulties in secondary sewage treatment plants and are not effectively removed by such treatment. Neither are they removed by conventional methods of drinking water treatment. Recent studies, particularly the very extensive work on mercury, and to a lesser extent the work on cadmium and lead, have focused concern on the impact of trace amounts of these substances upon man. The maximum recommended levels of these metals in drinking water are quite low (0.005 ppm for lead, and 0.01 ppm for cadmium), and industries are under heavy pressure to reduce the discharge of these elements to the lowest possible level.

A number of techniques exist to remove metal ions from aqueous solution: (1) chemical precipitation as an insoluble salt, hydroxide, or oxide; (2) ion exchange; (3) distillation; (4) freezing; (5) reverse osmosis; (6) electro-osmosis; (7) solvent extraction; and (8) foam flotation methods. Of these techniques, foam flotation appears to possess some distinct advantages when one is dealing with large volumes of solutions that are quite dilute in the ions to be removed. This method for the removal of trace contaminant heavy metals in (1) rapid; (2) cheap in terms of labor, equipment, energy and chemicals; (3) capable of application in small, intermediate, and large scales; (4) productive of quite small volumes of liquid or solids highly enriched in the contaminants; (5) capable of reducing the levels of these contaminants to concentrations well below the standards established or anticipated by the regulatory agencies. Data published in the literature and our own results described herein indicate that adsorbing colloid foam flotation techniques show considerable promise of meeting these criteria.

Substantial volumes of dilute industrial wastes containing toxic metals or fluoride are of common occurrence in the United States. Several examples are listed:

1. Wastewaters from copper and brass mills and casting operations and from copper smelters and refineries are a significant pollution problem. There are about 100 rolling and drawing mills and over 500 plants involved in the casting of copper and brass in the U.S.; and there are about 30 copper smelting and refining plants, with a total annual production of some 1.3 million tons. Rinsewater and acid bath dumps are the major pollution problems at the mills and foundries; acid baths are usually 5% to 10% sulfuric acid, and are often followed by 3% to 8% sodium dichromate bath which may contain hydrofluoric acid. The major contaminants in these wateswaters are copper, zinc, chromium, and acid, together with smaller amounts of fluoride and nickel. Copper smelter waste may contain on the order of 0.6 mg/l of cadmium, 7 mg/l of copper, 7 mg/l of lead, and 7 mg/l of zinc. Electrolytic refinery waste may contain 50 to 100 mg/l of copper, 1 mg/l of lead, and 10 to 20 mg/l of nickel. It was noted in a recent report on the nonferrous metals industry that "most pressing needs...were related to smelter-refinery-type wastewaters which were generally acid and contained metals or metalloids in the range <1 to 100 ppm." (1)

2. A large amount of fluoride wastewater results from the use of wet scrubbers in aluminum refining. The primary aluminum smelting industry carries out the reduction of purified alumina to produce aluminum metal. This is done electrolytically in electrolytic cells or pots connected in series in a potline. Some 30 such reduction plants in the U.S. have a total annual capacity of about 5 million tons of aluminum. The electrolysis of alumina in a salt bath of alumina and cryolote results in offgases containing oxygen, CO, CO_2, fluoride, particulate material, and other constituents. Water from wet scrubbers used for air pollution control in the potline is a major source of wastewater in the primary aluminum industry; these scrubber waters generally contain up to several hundred ppm of fluoride, depending upon recycle and/or treatment.

3. Wastewaters from secondary lead smelters are a serious pollution problem. About 40 smelters in the U.S. account for over 50% of domestically produced lead; input includes principally used storage batteries and telephone cables, and the smelted lead is used primarily in storage battery manufacture. Major pollutants in wastewaters from these operations are lead (several hundred mg/l) and antimony (up to 50 mg/l); sulfuric acid is also present.

The heavy metals and fluoride present in these wastes are toxic pollutants that can affect man, animals, and aquatic life, and can completely disrupt secondary sewage treatment facilities if discharged to sanitary sewers.

SECTION IV

LITERATURE REVIEW

This review is restricted to ion foam fractionation, colloid flotation, and precipitate flotation; work on ore flotation, microflotation of bacteria and algae, foam separation of biological materials, and other applications has been excluded. Non-foaming adsorptive bubble separations are excluded also, since it is felt that these are unlikely to lead to satisfactory application in the area of interest.

The earlier work is already covered by review; Sebba's book (2) gives a particularly detailed discussion, and Cassidy (3) published a review in 1957. Articles by E. Rubin and Gaden (4) and by Eldib (5) discuss foam separations in some detail, and Grieves (6) published an article in 1968 summarizing his work on foam flotation methods in waste water purification. A. J. Rubin's dissertation (7) contains a discussion of general methods and a lengthy bibliography through 1965. Karger and DeVivo's review (8) gives a detailed and systematic survey of principles and applications, with 81 references through 1968. Lemlich (9) published a review at about the same time, and has more recently edited a book on the subject (10). Somasundaran (11) published an extensive review in 1972.

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 (12) discusses the Gibbs equation in some detail, and Karger and DeVivo make clear its application in their excellent discussion of the general theory of adsorptive bubble separations (8). Newson (13) 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. Grieves and his coworkers have developed a model which enables them to use batch foam fractionation rate data from one system to predict the performances of both batch and continuous systems (14). Karger et al. (15) and subsequently Pinfold (16) have discussed and systematized the nomenclature in the field. The analysis of the operation of a foam stripping column has been attacked by a number of workers (13, 17, 18, 19, 20, 21); the earlier work is reviewed by Goldberg and E. Rubin (21), who also reference a number of papers on foam drainage, which has a profound effect on the efficiency of foam separations. 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 of foam fractionation (22). E. Rubin and Gaden derived the operating equation for single-stage foam columns (4).

Ion flotation and foam fractionation involve the removal from solution of dissolved ions by the addition of surface active collector followed by foaming. In the first technique, ion and surfactant form an insoluble precipitate or scum on the foam surface; 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 onto colloidal particles which are then removed by flotation. We next review representative recent experimental work in these areas.

A. J. Rubin and his coworkers have published papers on the foam separation of Pb(II) (23), of Zn(II) (24), and of Cu(II) and Fe(II) (25) 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 (26). Recently Rubin and Haberkost reported on the coagulation and flotation of titanium dioxide with aluminum hydroxide and an ethanol frother (27). They found that sodium lauryl sulfate was a quite satisfactory surfactant for this, and that the process was extremely efficient if run in the pH range of minimum solubility of $Al(OH)_3$.

Early work includes studies by Walling and his associates (28), by Sebba (29), and by Schnepf and his coworkers (30). Banfield and his collaborators (31) noted a fall-off of distribution coefficient with increasing surfactant concentration above the critical micelle concentration; Karger and DeVivo make this observation, too (8), as have others (13, 32).

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 (33, 34). Karger, Poncha, and Miller showed that use of reflux could yield extremely good separations from highly dilute solutions recovering methyl orange from 0.17 ppm solution (35). DeVivo and Karger (36) 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 concentrations were varied.

Talbot (37) has investigated the foam flotation of Cu(II) with sodium lauryl sulfate, and Miller and Sullivan (38) have studied the foam fractionation of Hg(II) nitro complexes. Schonfeld and his coworkers have observed that surfactants which can act as chelates as well as simple exchange sites are unusually effective (39). Lemlich and others have carried out studies demonstrating the utility of refluxing in foam separations (5, 18, 35, 40, 43). Schonfeld and Kibbey (42) 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 (43). Sheiham and Pinfold (44) have studied the effects of added electrolytes on the flotation of hexadecyltrimethylammonium chloride and of dodecylpyridinium chloride. Maas (45) has shown that addition of organic vapors to the air stream generating the bubbles may markedly speed up some foam separations. Bikerman (46) has studied the foam fractionation of calcium, iron, and manganese with alkyl sulfates and poly(oxyethylene) sulfates, and noted that non-ionic surfactants were ineffective. Dziomko and Sidenko (47) carried out ion flotation of dichromate using N,N,N',N'-tetramethyl-N,N'-didodecylhexamethylenediammonium dibromide. Charewicz and Niemiec (48) investigated the flotation of perrhenates with cationic surfactants (amine salts), and Podneuk (49) patented a method for ion flotation of tungsten and molybdenum with amines in acid solution. Sebba (50) patented a method for the precipitate flotation of metal hydroxides (Fe, Cu, Zn) from dilute solution. Charwicz and Niemiec (51) found that cationic surfactants yielded good separation of chloroaurate. Moroi and Matuura (52) investigated the removal of Cs(I) and a number of Co(III) complexes with sodium dodecyl sulfate. Kepak and Kriva (53) used dodecylamine or gelatine to separate ionic and colloidal forms of Ru(IV) chlorides and RuNO(III) nitrate. Stachurski (54) developed a stochastic mathematical model for flotation processes which he checked against data on molybdenum. E. Rubin and Jorne' (55) investigated surface hydrolysis effects in foam separations involving anionic surfactants. Rabrenovic (56) has carried out ionic flotation of uranium from dilute solution. Kim and Zeitlin (57, 58, 59) 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 zinc and copper. More recently, Matsuzaki and Zeitlin 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 (60).

Grieves, Bhattacharyya and their coworkers have devoted much effort to applying flotation techniques to waste treatment problems. They have studied flotation of dichromate (61, 62), phosphate (63), phenolate (64), chromic hydroxide (65), and cyanide complexed with Fe(II) (66). 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 (67). Earlier work concerned the foam separation of active carbon (68), the flotation of dichromate with ethylhexadecyldimethylammonium ion (69), the effect of colloidal particulates on foam fractionation (70), the foam fractionation of colloid-surfactant systems (71), and foam separation processes for removing inorganic and organic ions with surfactants (72).

Ferguson and Wilson have recently developed methods for the removal of lead and cadmium from industrial wastes by precipitate flotation and by

adsorbing colloid flotation (73). Nguyen and Phillips have made a rather detailed study of equilibria and mass transfer rates in the continuous foam fractionation of phosphate (74). Ervin and Danner investigated the effects of a number of parameters, including reflux ratio, on the continuous foam fractionation of phenol (75). Clarke and Wilson have demonstrated the feasibility of floc foam flotation of fluoride with $Al(OH)_3$ and sodium lauryl bromide to remove cadmium and mercury (77).

A streaming potential phenomenon predicted recently by Wilson and Wilson (78) was observed by Clarke (79). Floc foam flotation isotherms and local rate effects were investigated by means of a modified Gouy-Chapman model (80, 81, 82, 83). Recently Wang and his coworkers have worked out a theory for continuous bubble fractionation columns; their approach requires an assumption of local equilibrium between surface and bulk phases (84, 85, 86). Goldberg and Rubin have reviewed a number of models for foam flotation column operation and analyzed stripping columns without solute transfer in the countercurrent region (21). Cannon and Lemlich have given a detailed analysis based on the assumption of linear isotherms (87), and Lee has given a somewhat similar treatment (88). Wilson et al. have analyzed stripping column operation with axial diffusion, nonlinear isotherms, and finite rate of solute transport between suface and bulk liquid phases (82).

SECTION V

OBJECTIVES OF THE RESEARCH PROGRAM

The objective of our work was to carry out bench scale studies using adsorbing colloid flotation techniques to remove copper, lead, cadmium, and fluoride from actual and simulated industrial wastewaters, in order to lay the groundwork for the development of economic and simple methods to concentrate these toxic substances from industrial wastes. Time permitted us to study techniques for the removal of mercury, arsenic, and zinc, as well. The apparatus is rather simple, consisting of an air compressor, foaming column and sparger, metering equipment for introducing the collector surfactant and the reagents which form the adsorbing colloid, a foam breaker, and (if it is desired to reclaim the surfactant) a filter or centrifuge for recovering the surfactant solution from the collapsed foamate.

We desired to determine the lowest concentration levels to which these toxic substances could be feasibly reduced by adsorbing colloid foam flotation, and what variables significantly affect the speed of removal and the ultimate concentration of contaminant in the column effluent. Although continuous flow studies were not originally within the scope of this project, time and manpower permitted us to undertake some continuous flow studies and to construct a column simulator computer program.

Availability of a computer program simulating column operation would greatly facilitate the design of continuous flow columns for industrial use. We developed the theory of adsorption isotherms and rate effects, and constructed a column simulator computer program which takes into account axial mixing, finite rate of solute transport between the surface and bulk phases, and realistic adsorption isotherms. We also made use of the Gouy-Chapman model and the Smoluchowski equation to determine the magnitude of the rate of solute transport to the surface phase due to driven diffusion. We were also able to use the Gouy-Chapman model, modified to take into account the finite volume of the floc particles, and the methods of statistical mechanics to calculate improved adsorption isotherms for charged flocs on interfaces occupied by ionic surfactant molecules. This theoretical work gives us a clear understanding of (1) the various factors governing adsorption of flocs on surfaces of films, and (2) the factors governing continuous flow stripping column performance.

The possibility of recycling surface active agent was also established.

SECTION VI

BATCH TECHNIQUE LABORATORY STUDIES

The bulk of the experimental work described in this report was carried out in three essentially identical batch type apparatuses, one of which is diagrammed in Figure 1. The column was made of glass, 3.8 cm outside diameter (OD) by 90 cm in length. A 2.6 cm-OD side arm 3.5 cm from the top of the column permitted discharge of foam to a container; a 1.0 cm-OD side arm with a standard taper joint 12 cm from the bottom of the column provided a port for insertion of a miniature combination electrode for measuring pH. The bottom of the column was closed with a rubber-stopper through which were inserted a stopcock for sampling, a "fine" glass gas dispersion tube for introduction of air, a drain, and a small tube to a 10 cm^3 hypodermic syringe for introduction of reagents during the course of a run. House air was used to generate the bubbles; it was passed through ascarite, water (for rehumidification) and glass wool. A sulfuric acid scrubber and silica gel used in some of the work were found to be unnecessary. Airflow was controlled with a small needle valve and measured with a soap film flowmeter and a stopwatch.

Laboratory grade sodium lauryl sulfate (NLS) was used as the anionic surface active agent; hexadecyltrimethylammonium bromide (HTA) was used as the cationic surfactant. Reagent grade chemicals were used throughout, except for chemicals present in the industrial wastewater samples.

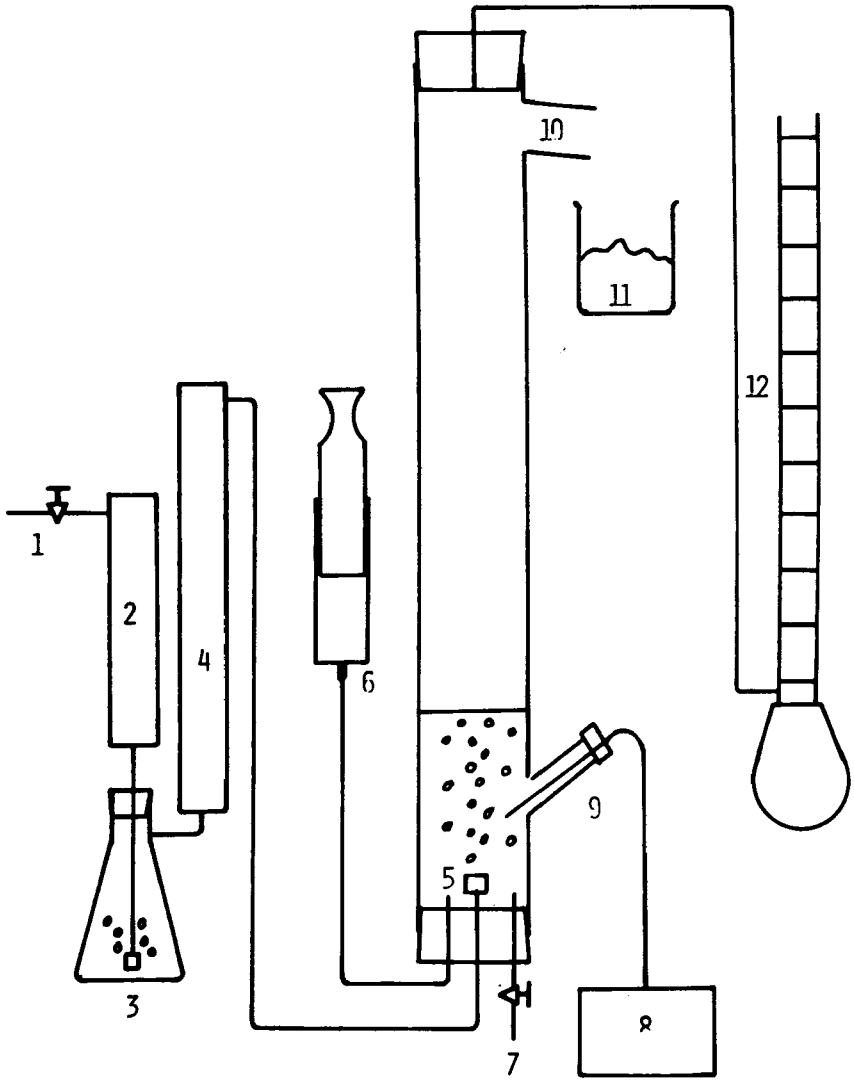
The basic procedure was essentially the same for all the batch separations on synthetic samples. Stock solutions (1.000 g/ℓ of the metal ions, fluoride, and surfactant) were mixed in the desired amounts and diluted to nearly 200 ml with deionized water, sodium nitrate was added if desired to increase the ionic strength, the pH was adjusted to the desired level by addition of 1.0 M NaOH and 0.10 M HNO_3, and the solution diluted to 200 ml. The solution was then added to the column and the airflow rate measured several times with the soap film flowmeter. The pH was monitored during the course of the run, and approximately 7 ml samples were withdrawn from the bottom of the column at 5-minute intervals. The samples were analyzed by atomic absorption spectrophotometry (lead, cadmium, mercury, copper, and zinc) or by colorimetric methods (fluoride by the SPADNS method, arsenic by ammonium molybdate-stannous chloride).

FOAM SEPARATION OF LEAD(II) BY BATCH TECHNIQUES

Previous work by Ferguson (74) has demonstrated the feasibility of removing lead from dilute solutions by means of floc foam flotation with ferrous sulfide and HTA. The relatively high cost of HTA compared to NLS and the

Figure 1. The batch apparatus.

1- air needle value
2- ascarite for CO_2 removal
3- humidifier
4- glass wool column
5- fritted glass sparger
6- reagent syringe
7- drain
8- pH meter
9- pH electrode port
10- foam discharge port
11- discharged foam
12- soap film flowmeter



deterioration and toxicity problems inherent in the use of sulfides led us to seek alternative methods employing NLS and flocs other than sulfides. Two systems which have yielded rather good results with lead are $Fe(OH)_3$-NLS and $Al(OH)_3$-NLS. Ferric chloride, alum, and technical grade sodium hydroxide are all readily available in quantity at relatively low cost, and NLS is one of the cheapest of the commercially available surfactants.

Floc foam flotation separations are often markedly dependent on pH and on ionic strength, for reasons discussed in Section VIII and Appendix A. We therefore systematically varied these parameters for both the $Fe(OH)_3$-NLS and the $Al(OH)_3$-NLS systems. The results for $Al(OH)_3$-NLS are summarized in Table 1; those for $Fe(OH)_3$-NLS, in Table 2.

TABLE 1. FLOC FOAM FLOTATION OF LEAD WITH $Al(OH)_3$ AND NLS*

pH	Residual lead (ppm)				
	At 0 M $NaNO_3$	At .025 M $NaNO_3$	At .050 M $NaNO_3$	At .075 M $NaNO_3$	At .100 M $NaNO_3$
6.0	2.4	6.1	7.6	9.1	10.0
6.5	2.3	6.2	6.4	8.3	10.0
7.0	1.2	2.9	4.4	6.2	21
7.5	2.2	6.5	7.2	16	20
8.0	8.2	15	14	23	26

*All runs made with 50 ppm Pb(II), 100 ppm Al(III) and 30 ppm NLS initially; initial volume = 200 ml, air flow rate = approx. 85 ml/min; duration of run = 20 min.

TABLE 2. FLOC FOAM FLOTATION OF LEAD WITH $Fe(OH)_3$ AND NLS*

pH	Residual lead (ppm)				
	At 0 M $NaNO_3$	At .025 M $NaNO_3$	At .050 M $NaNO_3$	At .075 M $NaNO_3$	At .100 M $NaNO_3$
6.0	1.4	1.4	1.5	1.3	2.1
6.5	.0	.0	.10	1.0	1.1
7.0	.1	.14	.42	.7	5.8
7.5	.0	.20	.56	2.2	2.6
8.0	.1	1.1	2.8	6.3	19

*All runs made with 50 ppm Pb(II), 100 ppm Fe(III) and 30 ppm NLS initially; initial volume = 200 ml, air flow rate = approx. 85 ml/min, duration of run = 15 min.

The tabulated data indicate that: (1) increasing ionic strength does interfere with the separations; (2) pH must be controlled to within roughly one pH unit; and (3) ferric hydroxide is a more effective adsorbing floc for lead than is aluminum hydroxide. The volume of foamate resulting from a typical run was of the order of 1-2 ml. A few runs were made using sodium carbonate as the neutralizing agent; it was found to yield poorer results than sodium hydroxide, probably due to stronger adsorption of this divalent anion on the positively charged floc particles. This would reduce the electric charge of the floc particles, thereby weakening their binding to the negatively charged bubble surfaces. The data also indicate that the $Fe(OH)_3$-NLS system may well be capable of reducing lead levels down to 0.1 ppm in continuous flow systems; this is confirmed by the results presented in Section VII.

A few runs were made with wastes from a secondary lead smelter (battery scrapping wastewater) containing 3.4 and 3.8 ppm lead; foam flotation of these samples resulted in reductions down to about 0.1 ppm when the pH was adjusted to 5.0. Apparently the high concentrations of sulfate present in these wastes shift the optimum pH to a somewhat lower value. Conductivities of these samples were 2.5×10^3 and 3.5×10^3 micromhos (μmhos); they contained 1.53 and 2.03 g of dissolved solids per liter. A few runs were also made with samples containing 2.0 g/ℓ of Na_2SO_4 and 50 ppm Pb; 10-minute runs at pH 6.0 reduced the Pb concentration to 0.2 ppm.

Calcium carbonate was used as the adsorbing colloid with either NLS or HTA in a few runs. HTA did not remove $CaCO_3$ or lead in the pH range 9.0-10.5. NLS reduced the lead concentration from 50 ppm down to about 0.2 ppm (100 ppm Ca(II), 30 ppm NLS) at pH 7.0, but the efficiency of removal decreased very markedly as pH was changed (14 ppm residual lead at pH 6.5, 8.6 ppm at pH 7.5). We felt that the extremely precise pH control required for this separation would be very difficult to maintain in industrial practice, and therefore did not pursue the use of $CaCO_3$ any further.

A few runs were made using $Fe(OH)_3$ and gelatin for lead removal. Occasional good separations were obtained (reductions from 50 ppm lead down to approximately 0.1 ppm), but the results were erratic and seemed to depend fairly critically on the details of the preparation of the gelatin solution. A pH of 7.0, 250 ppm gelatin, and 100 ppm Fe(III) gave the best results. In view of the difficulties in obtaining reasonably reproducible results and the large quantity of gelatin needed, we did not feel that further work on this technique was warranted.

Batch runs with MnO_2 and NLS rapidly removed lead, reducing lead concentration from 25 ppm down to approximately 0.2 ppm in 5 to 10 minutes; 25 ppm NLS and 100 ppm Mn(II) were used, and the optimum pH was approximately 8.0. In this procedure the Mn(II) is rapidly air oxidized to MnO_2 under alkaline

conditions, and then the surfactant is added to effect removal. Increasing ionic strength interferes with the separation. Our results did not indicate that this method was superior to the use of $Fe(OH)_3$ and NLS, and manganous salts are a good deal more expensive than ferric chloride, so further work with manganese was not done.

FOAM SEPARATION OF COPPER(II) BY BATCH TECHNIQUES

The ease with which lead was removed by the system $Fe(OH)_3$-NLS and the low cost of the reagents needed with this system dictated that it be investigated first as a technique for removing copper(II). The effects of varying ionic strength and pH are summarized in Table 3.

TABLE 3. FLOC FOAM FLOTATION OF COPPER WITH $Fe(OH)_3$ AND NLS*

pH	Residual copper (ppm)							
	Added $NaNO_3$ (M)							
	0	.025	.050	.075	.10	.15	.25	.50
5.5	3.0	6.4	7.2	6.2	5.5	>13	>13	>13
6.0	.10	.37	.61	1.4	2.7	1.0	6.5	>13
6.5	.02	.11	.17	.17	.17	.28	1.5	>13
7.0	.02	.11	.07	.06	.22	2.8	1.1	>13
7.5	.01	.07	.13	.55	1.4	13.1	5.2	>13
8.0	.02	.10	.77	.71	>13	>13	>13	>13

*All runs made with 50 ppm Cu(II), 100 ppm Fe(III) and 50 ppm NLS (25 ppm initially, 25 ppm 5 min after the start of the run). Initial volume = 200 ml, air flow rate = approx. 60 ml/min, duration of runs = 25 min.

In these studies the details of the experimental method were changed slightly; the NLS was added in two equal portions, one at the start of the run, and one five minutes later. This resulted in visibly marked improvement in the removal of the floc, and also in lower residual copper levels. The effect is presumably due to the maintenance of the surface concentration of NLS on the bubbles (and therefore the surface electric charge density) at a high level for a longer period of time than is possible when all of the surfactant is supplied at the start of the run.

The residual copper levels obtained with $Fe(OH)_3$-NLS at pH's of approximately 7 and ionic strengths of 0.1 mole/liter or less were sufficiently low that it was felt unnecessary to examine other, more expensive techniques. As will be seen later in this section, it is possible to remove copper as CuS with HTA; we have preliminary data indicating that it can be removed with $Al(OH)_3$-NLS and MnO_2-NLS, but have not determined the optimum pH for these separations.

A number of samples of copper-containing wastewaters were treated by the $Fe(OH)_3$-NLS technique. One sample contained 190 ppm Cu(II), and its electrical conductivity of 3.35×10^3 μmhos and total dissolved solids of 1.3 g/ℓ indicated an ionic strength of about 0.04 m/ℓ as Na_2SO_4. Treatment with 250 ppm of Fe(III) and 100 ppm NLS (50 ppm initially, 25 ppm after 6 min, 25 ppm after 11 min) resulted in final Cu(II) concentrations of about 0.15 ppm after 25 min at a pH of 7.0. Another sample containing 23.5 ppm Cu(II) and having an ionic strength of about 0.04 m/ℓ yielded residual Cu(II) concentrations of about 0.25 ppm with the same treatment at pH 6.0-6.5. A third sample containing 5.8 ppm Cu(II) was reduced to about 0.05 ppm by this treatment at pH 6.0-6.5.

FOAM SEPARATION OF MERCURY(II) AND CADMIUM(II) BY BATCH TECHNIQUES

Precipitate Flotation of HgS, CdS, and $Cd(OH)_2$

Both mercuric sulfide and cadmium sulfide are very insoluble in water, as indicated by the solubility product (89):

$$HgS \rightleftarrows Hg^{++} + S^{=} \qquad pK_S = 53.8$$

$$CdS \rightleftarrows Cd^{++} + S^{=} \qquad pK_S = 28.0$$

The pK_S for HgS suggests that one try to remove mercuric ion by precipitate flotation in the form of mercuric sulfide. The experimental results are given in Table 4.

It was found that mercuric sulfide could not be removed by (anionic) NLS at any pH, although it could be removed by (cationic) HTA. Better results were obtained under highly acidic conditions; the mercury concentration was 0.1 ppm after 30 min flotation at pH 0.8. The sulfide ion added initially was varied from 10^{-4} m/ℓ (the amount required to precipitate 20 ppm Hg(II) or 10 ppm Cd(II) to 2×10^{-3} m/ℓ). It was found that the removal rate and the maximum amount removed were not sensitive to the sulfide ion concentrations in this concentration range. Figure 2 shows the kinetic study of precipitate flotation

TABLE 4. Hg(II) REMOVAL BY PRECIPITATE FLOTATION OF MERCURIC SULFIDE
INITIAL Hg(II) CONCENTRATION = 20 PPM

Sulfide (m/ℓ)	pH	$NaNO_3$ (m/ℓ)	Time (min)	Surfactant	Residual mercury (ppm)
0.0001	10,7,4	0.001	60	NLS	>5
.001	10,7,4	.002	60	NLS	>5
.0001	10,7	.001	30	HTA	>0.5
.0005	10,7	.001	30	HTA	> .5
.001	10,7	.002	30	HTA	> .5
.0003	3.5	.001	60	HTA	.2
.002	1.8	.01	60	HTA	.12
.002	1.8	.01	30	HTA	.30
.002	0.8	.1	30	HTA	.10
.001	0.8	.1	30	HTA	.11

of mercuric sulfide with HTA.

The precipitate flotation of cadmium sulfide had been studied by Ferguson (74). The cadmium concentrations were reported as 0.1 to 0.23 ppm after 30 min flotation at various pH values. No trend with pH could be determined for the cadmium sulfide removals.

Precipitate flotation of cadmium hydroxide was tried. The solubility product of cadmium hydroxide is 2.0×10^{-14} (89). The solution was adjusted to pH 11.5. The precipitate in the form of cadmium hydroxide was foamed with HTA. The cadmium concentration was still 0.8 ppm after 30 min flotation, and this separation technique was not pursued further.

Adsorbing Colloid Flotation with $Al(OH)_3$ or $Fe(OH)_3$

Adsorbing colloid flotation with $Al(OH)_3$ or $Fe(OH)_3$ was tried. The expermental results for the systems containing 20 ppm mercury(II) are illustrated in Tables 5 and 6. It was found that $Al(OH)_3$ could be removed by NLS at pH 7 to 8, but it could not be removed by HTA. $Fe(OH)_3$ could be removed by HTA

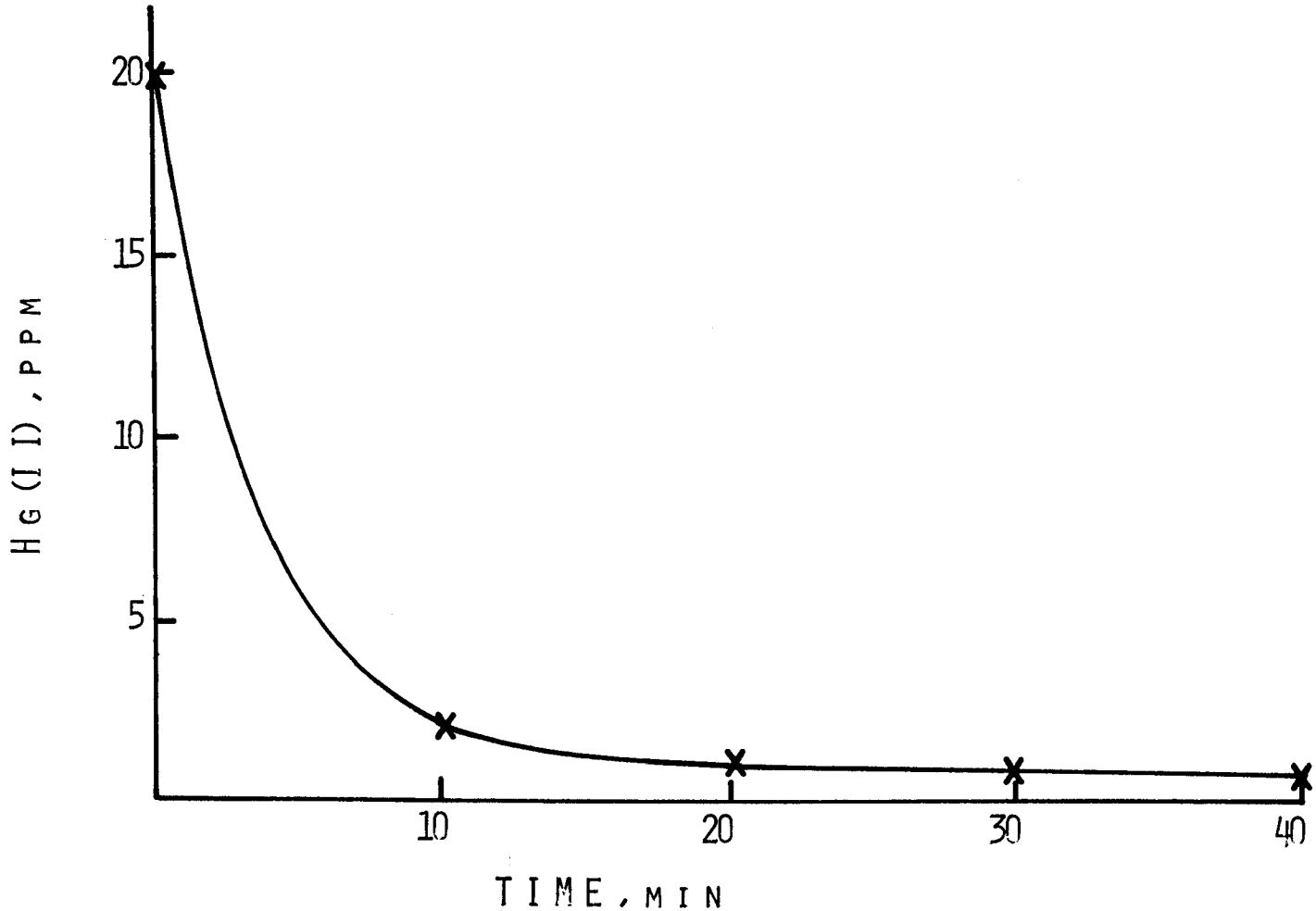


Figure 2. Hg(II) removal by precipitate flotation of HgS with HTA.

TABLE 5. Hg(II) REMOVAL BY FLOC FOAM FLOTATION WITH $Al(OH)_3$

pH	Time (min)	Surfactant	Residual mercury (ppm)
7.2-7.5	60	NLS	>5
7.5-8.0	60	NLS	>5
7.6-7.5	60	HTA	>5
7.5-8.2*	45	HTA	>5

*Removal with Na_2CO_3. In all runs the total salts concentration was .006 M and the initial Al(III) concentration was 50 ppm.

TABLE 6. Hg(II) REMOVAL BY FLOC FOAM FLOTATION WITH $Fe(OH)_3$*

pH	$NaNO_3$ (m/ℓ)	Surfactant	Residual mercury (ppm)
10,12	0.01	HTA	>5
10	0.005	NLS	>5
8	0.005	NLS	>5

*In all runs the run duration was 30 min and the initial Fe(III) concentration was 100 ppm.

at pH 10 to 12; it could also be removed by NLS at pH 8. But even though $Al(OH)_3$ or $Fe(OH)_3$ was removed, the residual mercury concentrations were always higher than 5 ppm after one hour flotation. Adjusting pH with sodium carbonate did not improve the separation.

Adsorbing colloid flotation of cadmium with 100 ppm $Al(OH)_3$ was not successful either. The experimental results are given in Table 7. Cadmium ion concentrations were higher than 4 ppm after each run. If 50 ppm phosphate ion was added, 2 ppm cadmium ion remained in the solution after a run at pH 7.5.

When the ionic strength was lower than 0.01 m/ℓ $Fe(OH)_3$ was very effective in removing cadmium ion from water at highly basic conditions (pH 11 to 12). Sample solutions contained 10 ppm cadmium and 100 ppm ferric ion initially.

TABLE 7. Cd(II) REMOVAL BY FLOC FOAM FLOTATION WITH $Al(OH)_3$*

Phosphate (ppm)	pH	Time (min)	Residual cadmium (ppm)
0	6.5-6.8	30	>5
0	7.5	20	4.5
100	6.5	25	5
50	7.5	25	5
50	7.5	45	2

*In all runs the initial Al(III) concentration was 100 ppm, the surfactant was NLS, and the $NaNO_3$ concentration was 0.01 M.

The solution was adjusted to pH 12 and then 20 ppm HTA was added. The supernatant contained approximately 0.25 to 0.50 ppm after 30 min standing. The supernatant was poured into the flotation column and was treated by foam flotation. HTA was added in pulses to maintain a stable foam. Only 0.01 ppm cadmium ion remained after 30 min flotation. The maximum removal decreased with increasing ionic strength. Table 8 shows the effect of ionic strength and pH on maximum removal.

TABLE 8. EFFECT OF IONIC STRENGTH AND pH ON Cd(II) REMOVAL BY FLOC FOAM FLOTATION WITH $Fe(OH)_3$*

pH	Residual cadmium (ppm)				
	At .006 M $NaNO_3$	At .016 M $NaNO_3$	At .30 M $NaNO_3$	At .056 M $NaNO_3$	At .100 M $NaNO_3$
9.5	0.10	---	---	---	---
10.0	.06	---	---	---	---
10.5	.05	---	---	---	---
11.0	.01	0.10	0.20	0.22	0.22
11.5	.01	.07	.10	.12	.22
12.0	.01	.07	.08	.10	.22

*The supernatant solution containing .25 to .50 ppm of cadmium was treated.

If this method is applied to industrial waste water treatment, filtration before flotation is necessary. Pouring all the precipitate into the flotation column yields no separation at all. The experimental results are shown in Table 9. Adjusting the pH with sodium carbonate was tried; some precipitate remained in the solution after 40 min flotation with HTA, and the final cadmium ion concentration was approximately 1 ppm.

TABLE 9. Cd(II) REMOVAL BY FLOC FOAM FLOTATION WITH $Fe(OH)_3$ AND Na_2CO_3

pH	Added $NaNO_3$ (m/ℓ)	Time (min)	Surfactant	Residual cadmium (ppm)
8.5,10	0.005	30	HTA	>5
8.5,10 (with Na_2CO_3)	.005	30	HTA	>5
11.6 (with Na_2CO_3)	.01	40	HTA	1
5.5 (with Na_2CO_3)	.005	30	NLS	>5
7.7	.005	30	NLS	3.5

*Removal with Na_2CO_3. In all runs the initial Fe(III) concentration was 100 ppm.

Ferric hydroxide could be removed effectively by NLS at pH 5, but the cadmium ion concentration remaining in solution was greater than 3 ppm. Adjusting the pH with sodium carbonate did not improve the separation.

Adsorbing Colloid Flotation of Mercuric Sulfide and Cadmium Sulfide with Ferrous Sulfide

Adsorbing colloid flotation of lead sulfide and cadmium sulfide with ferrous sulfide was tried by Ferguson et al. (74) and was proved to be very effective. The CdS was adsorbed on FeS, then removed by foam with HTA as collector at pH 9. The addition of HTA to the solution of colloidal FeS causes the FeS to coagulate and the CdS apparently adsorbs onto the colloid. The solution may be filtered to remove the bulk of the precipitate, then foamed to remove the remaining traces, or it may just be foamed initially, with all the FeS being removed in the foam. When the initial cadmium ion

concentration was 1 ppm, 20 ppm ferrous ion was added, the sulfide ion concentration was 1×10^{-3} m/ℓ. Approximately 0.012 ppm cadmium remained in the solution after 45 min flotation.

Filtering the solutions left different amounts of Cd in the solution depending on the amount of HTA added to coagulate the precipitate, the length of time the precipitate was allowed to coagulate, and the grade of filter paper used to filter it. Typically 0.3-0.4 ppm CdS was not filtered out from an initial 10 ppm solution by Whatman No. 42 filter paper if 50 ppm FeS had been coagulated with 40 ppm HTA and then allowed to coagulate for 5 minutes. If these filtered solutions were foamed for 30 minutes to remove the final traces of precipitate, typical cadmium ion concentrations in the bulk solution were about 0.003 ppm (74).

We applied the same method to remove mercuric ion from solution. Filtering was not tried, since it would increase costs if applied to industrial wastewater treatment. The sulfide ion concentration was 4×10^{-3} m/ℓ initially. The ionic strengths were adjusted by addition of sodium nitrate. The pH of the solution was adjusted, and then 100 ppm HTA was added to coagulate the colloid. The solution was poured into the flotation column and foaming was initiated. The experiments are summarized in Table 10. After 30 min flotation, the mercuric ion concentration was 0.05 ppm when the ionic strength was 0.01 m/ℓ and 0.07 ppm when the ionic strength was 0.1 m/ℓ. Best results were obtained at pH 9. Under acidic conditions FeS could not be removed effectively.

TABLE 10. Hg(II) REMOVAL BY FLOC FOAM FLOTATION OF HgS WITH FeS*

Fe(II) (ppm)	Sulfide (m/ℓ)	pH	Added $NaNO_3$ (m/ℓ)	Residual mercury (ppm)
20	0.0008	9	0.002	>0.20
20	.0008	5	.002	> .30
50	.004	9	.01	.05
50	.004	9	.1	.07

*The duration of all runs was 30 min, and the surfactant used was HTA.

Adsorbing Colloid Flotation of Mercuric Sulfide and Cadmium Sulfide with Cupric Sulfide

The most effective method for removing mercuric ion and cadmium ion was the adsorbing colloid flotation of mercuric sulfide with cupric sulfide. This method was very effective even when the ionic strength was as high as 2 m/ℓ. It took only 20 minutes to decrease mercury concentrations from 20 ppm to 0.005 ppm. The cadmium concentration was decreased from 10 ppm to 0.02 ppm with 30 minutes flotation. This method was insensitive to variation in pH, such that we could safely run it near neutral pH without adjusting the pH before or after the flotation.

10 ml of 0.2 m/ℓ sodium sulfide solution was added to the solution containing 100 ppm Cu(II) and 20 ppm Hg(II) or 10 ppm Cd(II). The ionic strength was adjusted with sodium nitrate. The total volume of the solution was 500 ml. 40 ppm HTA was added to coagulate the colloid. The solution was permitted to stand for 10 minutes, and then the solution along with the precipitate was poured into the flotation column. The gas flow rate was kept at 80 ml/min. Additional surfactant (HTA) was added in pulses during the run to maintain a stable foam (approximately 10 ppm surfactant was added every 6 min). The foam was quite dry; less than 10 ml solution was carried out by the foam during a 30-minute run. The experimental results for mercury removal are given in Table 11.

TABLE 11. Hg(II) REMOVAL BY FLOC FOAM FLOTATION OF HgS WITH CuS

Cu(II) (ppm)	Sulfide (m/ℓ)	pH	Added $NaNO_3$ (m/ℓ)	Time (min)	Residual mercury (ppm)
12	0.0008	9.5	0.002	30	0.20
12	.0008	6	.002	30	.20
12	.0008	4	.002	30	.20
12	.0008	2	.01	30	.10
12	.0008	1	.1	30	.09
60	.002	1	.1	20	.005
60	.002	0.8	.2	20	.005
60	.002	0.8	.6	60	.50
100	.003	0.8	.6	20	.005
100	.004	6-6.7	.01	20	.005
100	.004	6-7	.1	20	.005
100	.008	6-7	.5	25	.005
100	.008	7-8	2.0	40	.005

Increasing the ionic strength did not affect the maximum ultimate removal of mercury, but it did affect the rate of removal. In order to decrease the mercury concentration to 0.005 ppm, it was necessary to foam for 20 min when the ionic strength was 0.1 m/ℓ, 25 min when the ionic strength was 0.5 m/ℓ, and 40 min when the ionic strength was 2 m/ℓ. Varying the pH within the range 1 to 8 did not affect the maximum removal or the rate of removal. The cupric ion concentrations remaining in the solutions were always less than 0.5 ppm.

Varying the pH and the ionic strength has some effect on the maximum removal of cadmium. Table 12 shows this effect. When the ionic strength was 0.1 m/ℓ or below, the maximum removal was not sensitive to the variation in pH (the residual cadmium ion concentration was 0.02 ppm); but when the ionic strength was 0.5 m/ℓ, better results were obtained at pH 7.0 to 8.5. The experimental results under optimum pH and different ionic strengths are shown in Table 13. About 0.25 ppm cadmium(II) remained in the solution after a 45-minute run when the ionic strength was 2 m/ℓ. The cupric ion concentration remaining in the solution was always less than 0.5 ppm.

TABLE 12. THE EFFECT OF pH VARIATION ON Cd(II) REMOVAL BY FLOC FOAM FLOTATION OF CdS WITH CuS

Ionic strength (m/ℓ)	Residual cadmium (ppm)				
	At pH 3.0-3.1	At pH 4.0-4.1	At pH 5.0-6.5	At pH 6.0-7.8	At pH 7.0-8.5
0.1	0.02	0.02	0.04	0.02	0.02
.5	.07	.07	.12	.07	.05

TABLE 13. THE EFFECT OF INCREASING IONIC STRENGTH ON Cd(II) REMOVAL BY FLOC FOAM FLOTATION OF CdS WITH CuS*

Added $NaNO_3$ (m/ℓ)	Time (min)	Residual cadmium (ppm)	Residaul copper (ppm)
0.1	30	0.02	<0.5
.5	30	.05	< .5
1.0	30	.15	< .5
1.5	45	.25	.5
2.0	45	.25	.5

*The initial Cu(II) concentration was 100 ppm in all runs; the initial sulfide concentration was 0.004 m/ℓ, and the pH was 7-8.

The effect of interference from doubly-charged ions was examined. 0.1 m/ℓ sulfate ion (sodium sulfate) or 0.1 m/ℓ calcium ion (calcium nitrate) had no effect on the maximum removal of mercury, but affected the maximum removal of cadmium. In 0.1 m/ℓ sulfate solution, 0.08 ppm cadmium ion and less than 0.5 ppm cupric ion remained in the solution after a 45-minute run. In 0.1 m/ℓ calcium ion solution, 0.18 ppm cadmium ion and 2 ppm cupric ion remained.

The sulfide ion remaining in the solution after a run was complete was determined by titrating the solution (100 ml) with 0.1 normal $KMnO_4$ standard solution. A typical solution contained 10 ppm Cd(II), 100 ppm Cu(II), 0.1 m/ℓ Na_2SO_4, and 4×10^{-3} m/ℓ sulfide ion initially; the flotation was run at pH 6 to 7 for 30 min; 8×10^{-5} m/ℓ sulfide ion remained in the solution after the end of the run.

A smelter waste containing 30 ppm Cd(II) was treated with 400 ppm Na_2S, 200 ppm Cu(II), and 160 ppm HTA. After 15 minutes of foaming, the Cd(II) level was reduced to 0.08 ppm. A second sample treated with 200 ppm Na_2S, 100 ppm Cu(II) and 80 ppm HTA showed reduction from 30 ppm to 0.1 ppm Cd(II) in 30 minutes.

It was pointed out by Ferguson et al. (74) that cadmium sulfide was not adsorbed to the container walls at any of the pH values studied (pH 6.5 to 9.5). This was checked again for the solutions containing cadmium sulfide or mercuric sulfide. After runs were made at neutral pH (pH 6 to 8), the solution was acidified to pH 2 or below; no increase in the cadmium concentration or the mercury concentration was found.

Adsorbing colloid flotation of mercuric sulfide with cupric sulfide turned out to be the most effective way to remove mercuric ion from waste water. The mercuric ion concentrations remaining in solution after treatment were about 0.005 ppm, which was considered to be safe for drinking water (55). The cupric ion concentration remaining in solution after treatment was less than 0.5 ppm, which was less than the standard for drinking water (1 ppm).

The same method was applied to remove cadmium ion from water. Approximately 0.02 ppm cadmium remained after treatment; which was also comparable to the standard for drinking water (0.01 ppm).

Adsorbing colloid flotation of cadmium sulfide with ferrous sulfide was more effective than the above method. Typical cadmium ion concentrations in the bulk solution after treatment were 0.01 ppm or less.

FOAM SEPARATION OF ARSENIC BY BATCH TECHNIQUES

It was found that arsenic (as arsenate) could be reduced from initial concentrations of 10-20 ppm down to 0.1-0.2 ppm by floc foam flotation with $Fe(OH)_3$-NLS in the pH range 4 to 5 at ionic strengths up to 0.2 m/ℓ. Two preliminary runs indicated that arsenic could also be reduced from 10-20 ppm down to about 0.1 ppm by floc foam flotation with MnO_2-NLS at pH's of about 8.5.

FOAM SEPARATION OF FLUORIDE BY BATCH TECHNIQUES

Attempts to remove fluoride were made using $Fe(OH)_3$, $CaCO_3$, or $Al(OH)_3$ as adsorbing flocs and NLS or HTA as surfactants. Neither $Fe(OH)_3$ nor $CaCO_3$ proved successful in removing fluoride from water when foamed with either HTA or NLS in the pH range 3 to 10. Aluminum hydroxide-HTA is also not effective in removing fluoride; $Al(OH)_3$-NLS, however, is quite effective.

The Al^{+3} (or $Al(OH)_3$) forms a complex with the F^-, making the anion unavailable for analysis by the SPADNS method. Foaming with HTA does not remove the complex at either acidic or basic pH's. NLS, however, does effect removal, performing best in the approximately neutral pH range of 7.3 to 7.8.

At pH's below 7 a hydro-alumino-fluoride complex is formed as evidenced by the low free F^- analysis before any surfactant is added. At acid pH's however, there is no aluminum removal after 30 minutes, as evidenced by colorimetric aluminum analysis. At pH's above 8 the complex appears to decompose, returning free F^- to the solution. An actual example of this follows: A solution containing 10 ppm F^- and 40 ppm Al^{+3} was adjusted to a pH of 2.0; the free F^- was found to be 1.5 ppm. The pH was then adjusted to 8.1; after 60 seconds of agitation, the free F^- concentration was 1.9 ppm. After 20 min at a pH of 8.6, the F^- concentration in the solution had increased to 8.2 ppm.

The removal of the colloidal complex is effected over approximately a 0.5 range in pH for two reasons: (1) The CO_2-free air is mixing with the CO_2-containing water, removing CO_2 and increasing the pH. This effect was observed by not adding the surfactant and noting the pH increase as the air was bubbled through the Al-F solution in the column. (2) The second and probably dominant effect is the ion flotation of H^+ by LS^-. A larger pH range, 7.1 to 7.9, can be successfully employed as long as the majority of the foaming occurs within the 7.3 to 7.8 range.

Parameters of the experimental runs other than pH were: 10 ppm F^-, 40 ppm Al^{+3}, 40 ppm NLS in a total volume of 250 ml, room temperature, 24-25°C, and an air flow rate of approximately 35 ml/min. These conditions and the above pH range will be implied by the subsequent use of the term "optimum system". Both the fluoride and aluminum concentrations of this system were reduced to undetectable levels (less than 0.1 ppm) within a 30-min period, as indicated by their respective quantitative tests.

The amount of fluoride which could be removed was determined as follows: optimum aluminum and NLS concentrations and pH were maintained, and the fluoride concentration was increased to 19.7 ppm. The fluoride concentration remaining in solution after 30 min was 4.0 ppm, a removal of 15.7 ppm. The aluminum concentration was <0.1 ppm. Under the same conditions and an initial F^- concentration of 27.6 ppm, the residual F^- concentration after 30 min was 11.8 ppm, a removal of 15.8 ppm. These data correspond to an Al/F removal ratio (ppm Al added/ppm F removed) of 2.54. Increased NLS concentration (72 ppm) did not improve the F^- removal. A system containing 120 ppm Al^{+3}, 26 ppm F^- and 43 ppm NLS yielded complete (<0.1 ppm residual) F^- removal within 30 min.

$NaNO_3$ was used to vary the ionic strength of an optimum system. An optimum system with no added $NaNO_3$ has an ionic strength of 0.01.

The system's removal efficiency decreases relatively slowly with increasing ionic strength. At concentrations of $NaNO_3$ above 2.5 m/ℓ the foams were very poor and there was essentially no aluminum removal.

Because of its ubiquitous nature and similarity to F^-, chloride ion was studied as a possible interference to the system. Addition of 0.5 m/ℓ NaCl to an optimum system decreased the fluoride removal by at most 8.3% below a similar system containing 0.5 m/ℓ $NaNO_3$. An optimum system containing 1.0 m/ℓ NaCl exhibited decreased fluoride removal by 8.2% below the 1 m/ℓ $NaNO_3$ system. An optimum system containing 8.9 ppm Cl^- showed <0.1 ppm F^- in solution after 30 min of flotation.

When the Al-F-NLS solution was stored for more than a week in laboratory glassware, leaching of Al occurred. Borosilicate glass (pyrex, kimax, etc.) is 2% by weight Al_2O_3. Concentrations as high as 25 ppm Al were found after an 8-day delay when solutions initially containing 0 ppm Al were stored at a pH of about 8. Analyses within one day of sampling indicated negligible leaching.

Batch runs were made with two samples of wet scrubber wastewater from an aluminum smelter. One sample contained 150 ppm F^-; treatment with 600 ppm Al (III), 50 ppm Fe(III), and 100 ppm NLS at pH 6.0 resulted in a residual F^- concentration of 0.9 ppm. A second sample contained 375 ppm F^-; treatment with 1500 ppm Al(III), 150 ppm Fe(III), and 175 ppm NLS resulted in a residual F^- concentration of 2.5 ppm. Precipitation of F^- from this waste with excess $Ca(NO_3)_2$ yielded a residual F^- concentration of 55 ppm.

SECTION VII

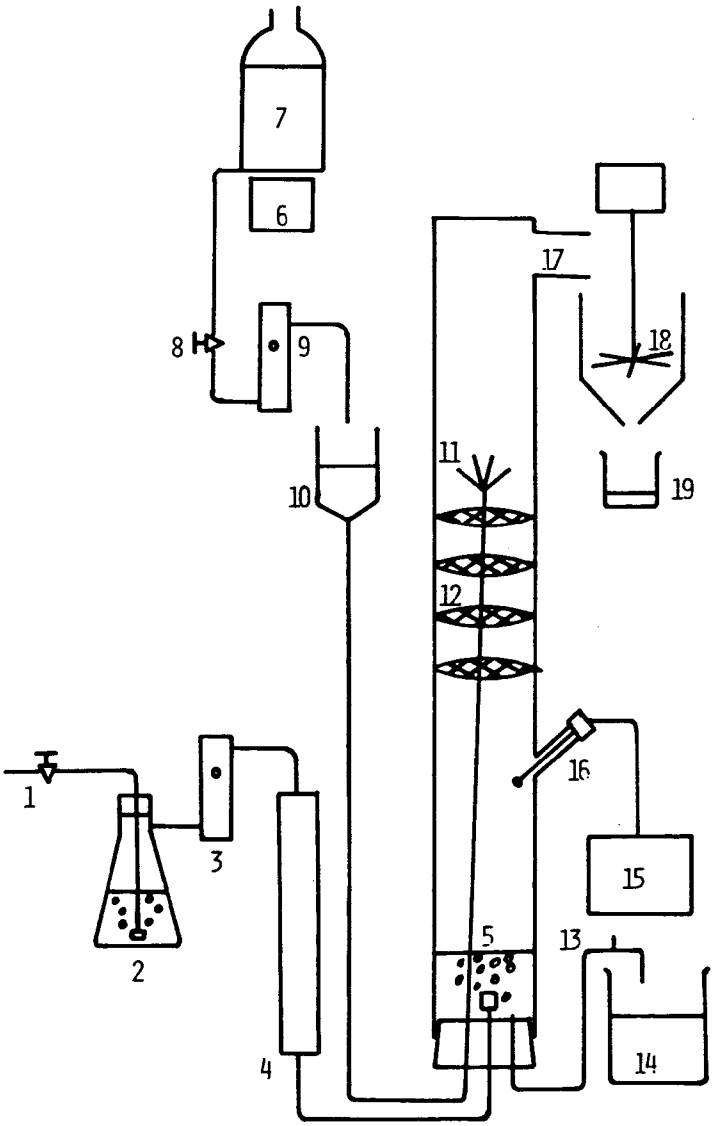
CONTINUOUS FLOW STUDIES

Though batch studies are most conveniently used for preliminary investigation of foam flotation separations, continuous flow methods would be expected to yield closer control of operating conditions, greater reductions in contaminant concentration (by using the foam itself as a stripping column), and reduced labor costs when scaling up for industrial use. As we have seen earlier, fairly accurate control of pH is necessary in a number of these separations; in a flow system such continuous control can readily be achieved with presently available pH control equipment. In the batch technique one is able to obtain only about one equilibrium stage of separation in the column; in continuous flow stripping columns, one uses the foam itself for much the same function as a reflux column in distillation, with corresponding improvement in performance. The batch technique requires frequent preparation of the column batches and draining and charging of the column; also, for optimal results, it is necessary to add surfactant from time to time during the course of a run. All of these would add to the labor costs of the process, and argue for the use of continuous flow methods. Two small continuous flow columns were therefore built, and lead(II) removal with $Fe(OH)_3$-NLS, fluoride removal with $Al(OH)_3$-NLS, and arsenic removal with $Fe(OH)_3$-NLS were carried out.

The smaller column is glass, 4.8 cm-ID by 121 cm in length, with inlet dispersion head 42 cm from the top of the column, foam discharge port 6 cm from the top, and pH electrode port 70 cm from the top (see Figure 3). Bubbles are generated by admitting air through a "fine" fritted glass gas dispersion tube inserted in a stopper closing the bottom of the column. Air flow rates are measured with a small variable area flowmeter and/or with a soap film flowmeter and stopwatch; air flow is controlled with a small needle valve. House air is humidified and passed through glass wool. Influent is prepared by adding the appropriate chemicals to two liters of tap water, adjusting the pH, and transferring the solution to a 3-ℓ polyethylene storage reservoir on a magnetic stirrer. The influent flow is controlled with a screw-type pinchclamp and is measured by a small variable area flowmeter or by simply timing the duration of the run. A small auxiliary reservoir serves to maintain a constant head on the inlet dispersion head, which receives influent via a glass tube passing through the large stopper at the bottom of the column. Effluent is drained from the bottom of the column by means of tygon tubing, the position of which can be adjusted to control the height of the liquid pool at the bottom of the column. The foam is discharged from the foam discharge port near the top of the column into a 3-ℓ funnel, in which the foam is collapsed by a spinning wire spider driven by a laboratory stirring motor. The pH can be monitored continuously by inserting a micro combination glass electrode into the electrode port half-way down the column.

Figure 3. The small continuous flow apparatus.

1- air needle valve
2- humidifier
3- air flowmeter
4- glass wool column
5- fritted glass sparger
6- magnetic stirrer
7- influent reservoir
8- influent valve
9- influent flowmeter
10- constant head reservoir
11- influent dispersion head
12- foam baffles
13- effluent drain
14- effluent
15- pH meter
16- pH electrode port
17- foam discharge port
18- foam breaker
19- collapsed foamate



It is quite important to design and place the distribution head in such a way as to distribute the influent evenly over the cross-sectional area of the column. If this is not done, severe channelling and overturning of the wet foam occur at substantially lower influent flow rates than can be tolerated without column upset in a properly designed system. The tendency to channel and overturn was further decreased by mounting a series of five copper screen baffles in that portion of the column 9 to 22 cm below the influent dispersion head. Even with these precautions, column upset remains the limiting factor in determining the flow rate which can be handled by the column.

The problems mentioned above, together with the fact that the columns must be built so as to handle the maximum flow rate of waste at minimum capital and operating costs, point up the need for good mathematical models of column operation and of the processes determining the adsorption isotherm of the floc on the film surface. Such models are discussed in the next two sections.

The results obtained with this column (described below) were such as to warrant scaling up. We also felt that it would be difficult to estimate the effects of channelling and foam overturn in larger systems from only our work on the 4.8 cm column. A lucite column 10.2 cm-ID by 186 cm length was therefore constructed. Influent is introduced through a tube passing through the top cover plate of the column; on the end of this tube is mounted the dispersion head, normally positioned about 80 cm below the top of the column. The foam discharge port is mounted in the top cover plate. Bubbles are generated by admitting air through a cylindrical 2.5 x 2.5 cm bubbling stone mounted on the bottom cover plate. Air flow rates are measured with a variable area flowmeter; influent rates, by measuring the time required to discharge 1.0 ℓ. House air is humidified and passed through glass wool. Influent is prepared by adding the appropriate chemicals to approximately 40 ℓ of tap water in a large plastic trash container; the solution is stirred continuously while the pH is adjusted and the run is made. The effluent is pumped from the storage reservoir to a smaller constant head reservoir above the column, from which its flow to the dispersion head is controlled by a stopcock. Four screen baffles are mounted 95 to 113 cm below the top of the column; these are made of 0.6 cm stainless steel wire mesh. Effluent is discharged from the column through a tygon tube the position of which can be adjusted to control the level of liquid in the bottom of the column. The foam is discharged to either a spinning screen and wire spider foam breaker or a hot surface foam breaker. At the flow rates possible with this apparatus, the foam breakers tend to become overloaded, and we plan to build a larger one. Reductions of lead levels from 50 ppm to 0.25 ppm at a flow rate of about 1 ℓ/min have been achieved during the preliminary studies with this apparatus.

Twenty-five runs were made using the smaller of the two columns for the removal of lead with $Fe(OH)_3$-NLS. Optimum pH for synthetic samples containing

0 to 6 g/ℓ of Na_2SO_4 was in the range 6.0-6.5. Air flow rates were generally in the range 180-250 ml/min; influent flow rates, in the range 40-80 ml/min. Fe(III) concentration was generally set at 100 ppm; NLS, at 50 ppm; and Pb(II), at 50 ppm. Lead concentrations in the column effluent of 0.1 ppm or less were readily attainable at Na_2SO_4 concentrations of 4.0 g/ℓ, 2.0 g/ℓ, or 0.0 g/ℓ; a run made with 6.0 g/ℓ added Na_2SO_4 yielded effluent containing 0.13 g/ℓ Pb(II). Decreasing the NLS concentration to 25 ppm or the Fe(III) concentration to 50 ppm resulted in higher residual Pb(II) concentrations (11 ppm and 0.3 ppm, respectively, for solutions containing 2 g/ℓ Na_2SO_4). Foamate volumes were measured on ten runs, and ranged from 45 to 90 ml. (The volume of influent was 2000 ml.) Samples of battery waste containing 3.8 and 3.4 ppm lead(II) yielded effluents containing approximately 0.1 ppm residual lead.

Eleven runs were made with the small column separating arsenic(VI) with $Fe(OH)_3$-NLS. Samples containing 20 ppm As(VI), 100 ppm Fe(III), and 80 ppm NLS and 0.1 N $NaNO_3$ consistently yield residual arsenic levels of less than 0.1 ppm at pH's below 4.4. If the inert salt added is Na_2SO_4 (0.1 N), it is necessary to go to a pH of about 3.5 to obtain a residual arsenic level of 0.1 ppm; the procedure fails completely at a pH of 4.4 with 0.1 N Na_2SO_4.

One run with the small column was made with a sample of aluminum smelter wet scrubber wastewater containing 150 ppm fluoride; after treatment with 600 ppm Al(III) and 100 ppm NLS at pH 6.5, the residual F^- concentration was 1.5 ppm.

Twenty-nine runs were made with the small column separating copper(II) with $Fe(OH)_3$-NLS. Four samples containing 200 ppm Cu(II) were treated with 400 ppm Fe(III) and 95 ppm NLS at pH 6.5 to yield 0.39, 0.39, 0.24, and 0.12 ppm residual copper. Air flow rates of about 200 ml/min and influent flow rates of about 50 ml/min were used. At these high copper and iron concentrations difficulty with clogging of the screen baffles occasionally occurred; this results in channelling and breakthrough of iron and copper in the effluent. Actually, 200 ppm Cu(II) is far in excess of what we expected could be handled at all by foam flotation methods. Industrial waste samples containing 82, 23.5, and 5.8 ppm Cu(II) on treatment by the above method yielded effluents containing 0.45, 0.08, and 0.05 ppm residual Cu(II).

SECTION VIII

DISCUSSION

The data summarized in the preceding two sections demonstrate the ability of floc foam flotation techniques to reduce the concentrations of lead, cadmium, mercury, copper, zinc, arsenate, and fluoride to quite low levels. The feasibility of some of these separations when used in the continuous flow mode is demonstrated in Section VII. The results of the batch studies are summarized in Table 14.

TABLE 14. OPTIMAL SEPARATIONS BY BATCH FLOC FOAM FLOTATION TECHNIQUES

Pollutant	Flotation system	pH	Added $NaNO_3$ (m/ℓ)	Residual pollutant (ppm)
Cu(II)	$Fe(OH)_3$-NLS*	∿7.0	<0.05	0.1
Pb(II)	$Fe(OH)_3$-NLS	∿6.5	<.1	.1
Arsenate	$Fe(OH)_3$-NLS	4-5	<.2	.1
Zn(II)	$Al(OH)_3$-NLS	8.0-8.5	<.15	.2
Fluoride	$Al(OH)_3$-NLS	6-7.5	<.2	1.5
Cd(II)	CuS-HTA†	3-8.5	<.1	.02
Hg(II)	CuS-HTA	7-8	<2.0	.005

*NLS - sodium lauryl sulfate. †HTA - hexadecyltrimethylammonium bromide.

To provide practical tests of these separations a number of samples of industrial wastewaters were obtained and treated. The small quantities of wastewater available precluded careful optimization of conditions of separation, but, as is seen in Table 15, levels of separation comparable to those obtainable with synthetic samples are obtained. We note that two wastewater samples were obtained which could not be satisfactorily treated as received. One contained copper, the other lead, and both contained very high concentrations of sulfate (in excess of 15 g/ℓ as sodium sulfate). Dilution of these samples made it possible to treat them, but we wish to point out that floc foam flotation generally is not well-adapted to the treatment of wastes of high ionic strength.

TABLE 15. INDUSTRIAL WASTES TREATED

Wastewater	Pollutant identity and concentration (ppm)		Residual pollutant concentration (ppm)
Copper			
Brass mill waste #1	Cu	82	0.45
Brass mill waste #2	Cu	23.5	.12
Brass mill waste #2	Cu	23.5	.04
Brass mill waste #3	Cu	5.8	.05
Brass mill waste #3	Cu	5.8	.05
Brass mill waste #4	Cu	95	.37
Brass mill waste #4	Cu	95	.28
Brass mill waste #5	Cu	100	.39
Brass mill waste #5	Cu	100	.09
Brass mill waste #5	Cu	100	.13
Brass mill waste #6	Cu	18	.23
Brass mill waste #7	Cu	4.3	.04
Brass mill waste #7	Cu	4.3	.00
Wire plant waste #1	Cu	50	.10
Wire plant waste #8	Cu	190	.15
Secondary lead			
Smelter waste #1	Pb	3.4	.10
Smelter waste #1	Pb	3.4	.10
Smelter waste #1	Pb	3.4	.11
Smelter waste #2	Pb	3.8	.0
Smelter waste #2	Pb	3.8	.12
Smelter waste #3	Pb	3.8	.27
Smelter waste #4	Pb	1.5	.12
Smelter waste #5	Pb	1.9	.0
Smelter waste #1	Cd	30	.1
Smelter waste #1	Cd	30	.08
Aluminum			
Smelter waste #1	F	150	1.3
Smelter waste #1	F	150	1.2
Smelter waste #1	F	150	.9
Smelter waste #2	F	375	1.75
Smelter waste #2	F	375	2.5
Smelter waste #2	F	375	2.5

Two continuous flow runs were made on synthetic samples employing recycled surfactant (actually decanted collapsed foamate). Lead was removed as usual from these samples, indicating the feasibility of cost reduction in these separations by reuse of surfactant. Our data as yet are not sufficient to indicate the fraction of surfactant which is lost at each cycle.

SECTION IX

THEORY OF ADSORPTION ISOTHERMS

Most precipitate flotation and adsorbing colloid flotation processes depend on electrical forces between the charged particles of precipitate being removed and the oppositely charged surfactant layer at the film surface. It is shown in reference 78 that, provided the film is not too thick, the rate of driven diffusion of charged floc particles to the interface is quite rapid, and the time constant for this process is of the order of a few microseconds. We noted in our experimental work on sulfides, MnO_2, $Fe(OH)_3$, and $Al(OH)_3$ with NLS and HTA that the surface films were often quite densely occupied by floc particles, and that any theory assuming sparse occupancy (79) would run into difficulty in calculating isotherms for these very useful systems, and might well grossly over-estimate column efficiencies.

We here present the physical model and results for a theory of floc foam flotation isotherms which is applicable to surface densely occupied by floc particles. The mathematical analysis is given in Appendix C.

The electric potential ψ is given in the vicinity of a charged surface on an electrolyte by formulas developed from the Gouy-Chapman theory. We assume that a floc particle occupies a cubical volume $\underline{a}$ cm on a side, and therefore that the maximum number density c_{max} of floc particles is $1/a^3$. The potential energy of a floc particle having electric charge q and located a distance x from the surface is given by $q\psi(x)$. The configurational free energy per floc particle is

$$\mu_{config} = kT \log_e \frac{c}{c_{max}-c}$$

where c is the concentration of particles in the bulk liquid, k is Boltzmann's constant, and T is the absolute temperature. The number of floc particles per cm^2 of surface within a distance ma of the surface is then given by

$$\bar{S} = \sum_{i=1}^{m} \left[1 + \frac{1-\sigma}{\sigma} \exp \left\{ \frac{q\psi[(i-\frac{1}{2})a]}{kT} \right\} \right]^{-1}$$

where $\sigma = c/c_{max}$, and the surface excess of particles per unit area in this same boundary layer is given by

$$S_{excess} = \sigma(1-\sigma) \sum_{i=1}^{m} \frac{1 - \exp \beta V(i)}{\sigma[1 - \exp \beta V(i)] + \exp \beta V(i)}$$

The results of calculations of $S_{excess}\ a^2$ as a function of σ are shown in Figures 4, 5, 6, and 7. Figure 4 shows the effect of increasing ionic strength (essentially the effective concentration of inert electrolyte) on the isotherms. It is evident that increasing the electrolyte concentration results in very marked decreases in the separation efficiency, consistent with our experience. Figure 5 shows the increase in separation efficiency which results from increasing the magnitude of the surface potential ψ_0; practically, this can be accomplished by using surfactant concentrations which are nearly as large as the critical micelle concentration (at which concentration further increases do not result in any increase in surface concentration or in the magnitude of the surface potential).

Figure 6 illustrates the fact that increasing the charge on the floc particles increases the efficiency of separation by increasing the adsorption isotherm. This parameter can very often be controlled by adjusting the pH, a procedure which is very effective with both $Fe(OH)_3$ and $Al(OH)_3$. The theory predicts that the temperature dependence of the adsorption isotherms should be rather slight, as seen in Figure 7. This is in agreement with the small amount of rather qualitative experimental data we have. We conclude that, within reasonable temperature limits, say 0-60°C, floc foam flotation separations are not likely to be greatly affected by temperature.

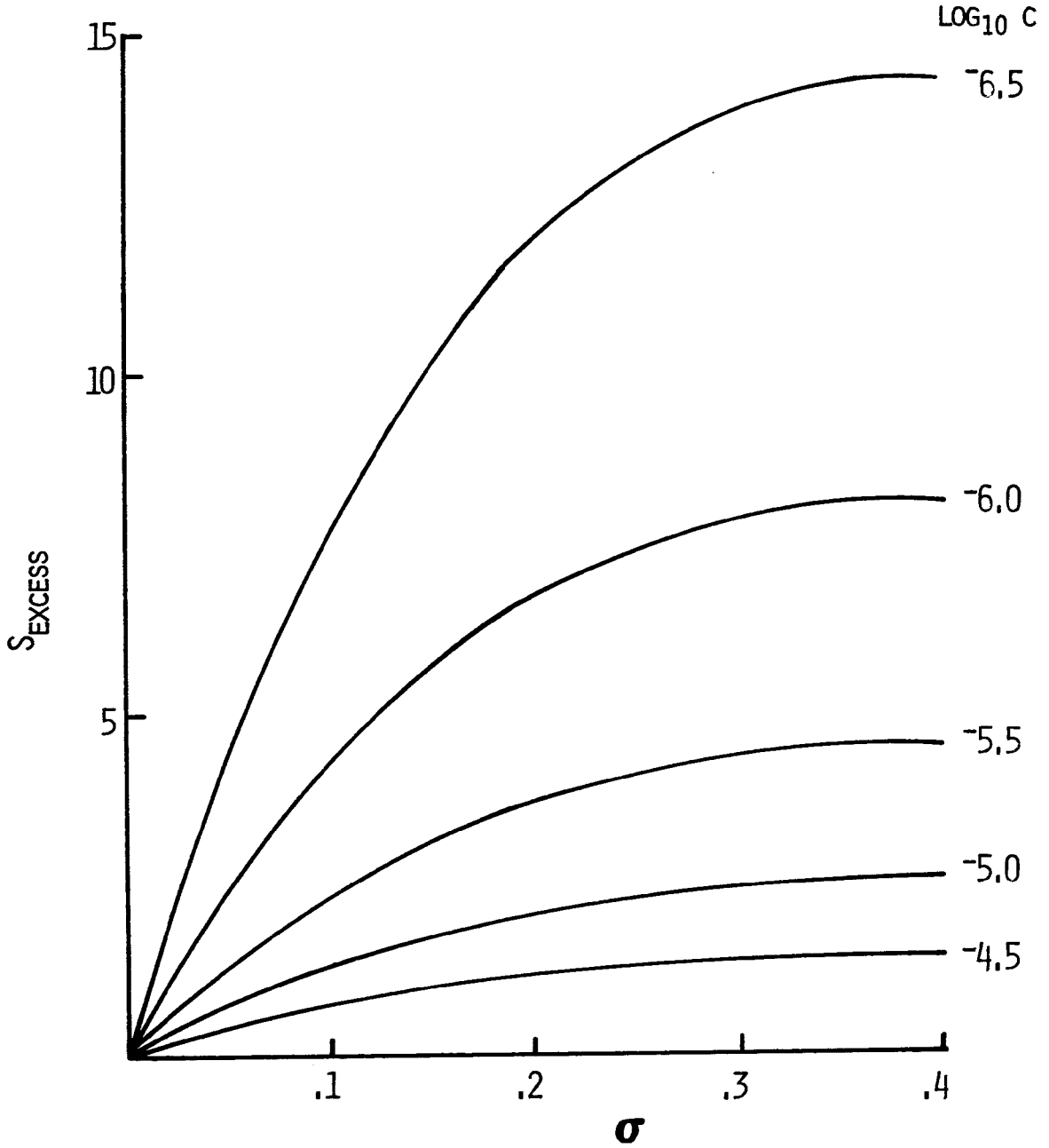


Figure 4. Dependence of isotherms on ionic strength (moles/cm^3). $q = -4.77 \times 10^{-10}$ e.s.u. $\psi_0 = -50$ mn., cell length = 10 Å, T = 298°K.

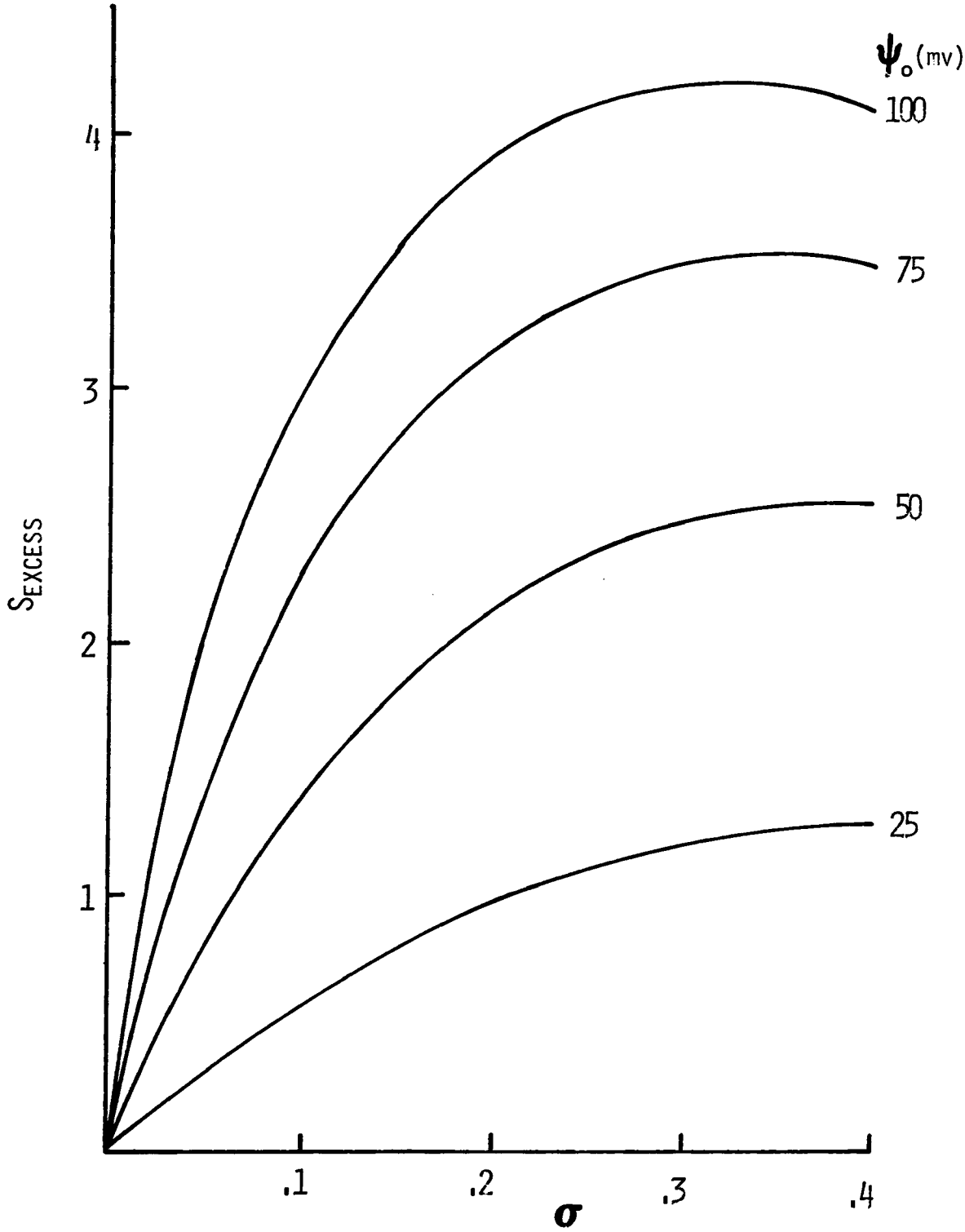


Figure 5. Dependence of isotherms on surface potential ψ_o (mv). Other parameters as in Fig. 4; c = 10^{-5} moles/cm^3.

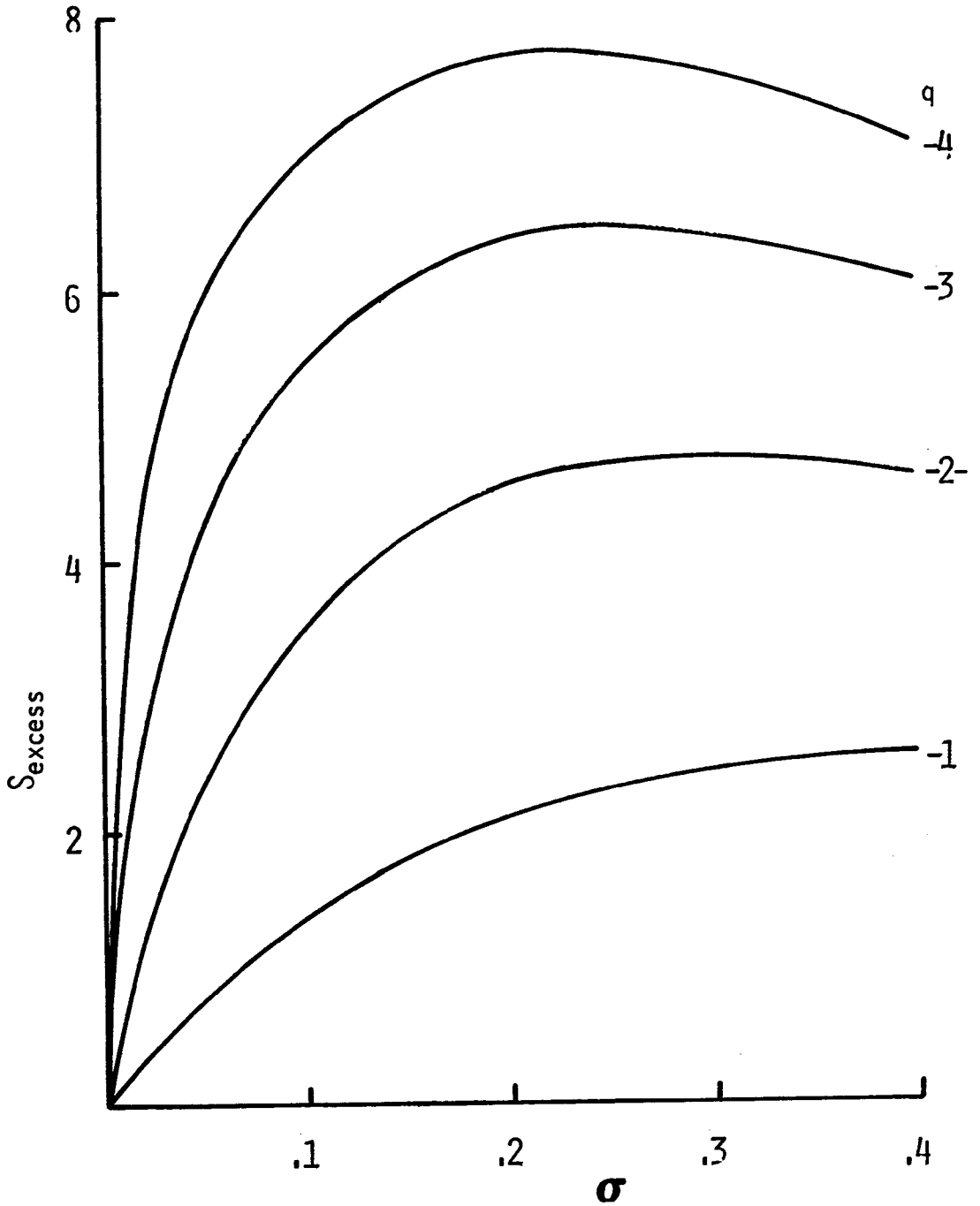


FIGURE 6. Dependence of isotherms on floc particle charge ($q \times 4.77 \times 10^{-10}$ esu). Other parameters as in Figs. 4 and 5.

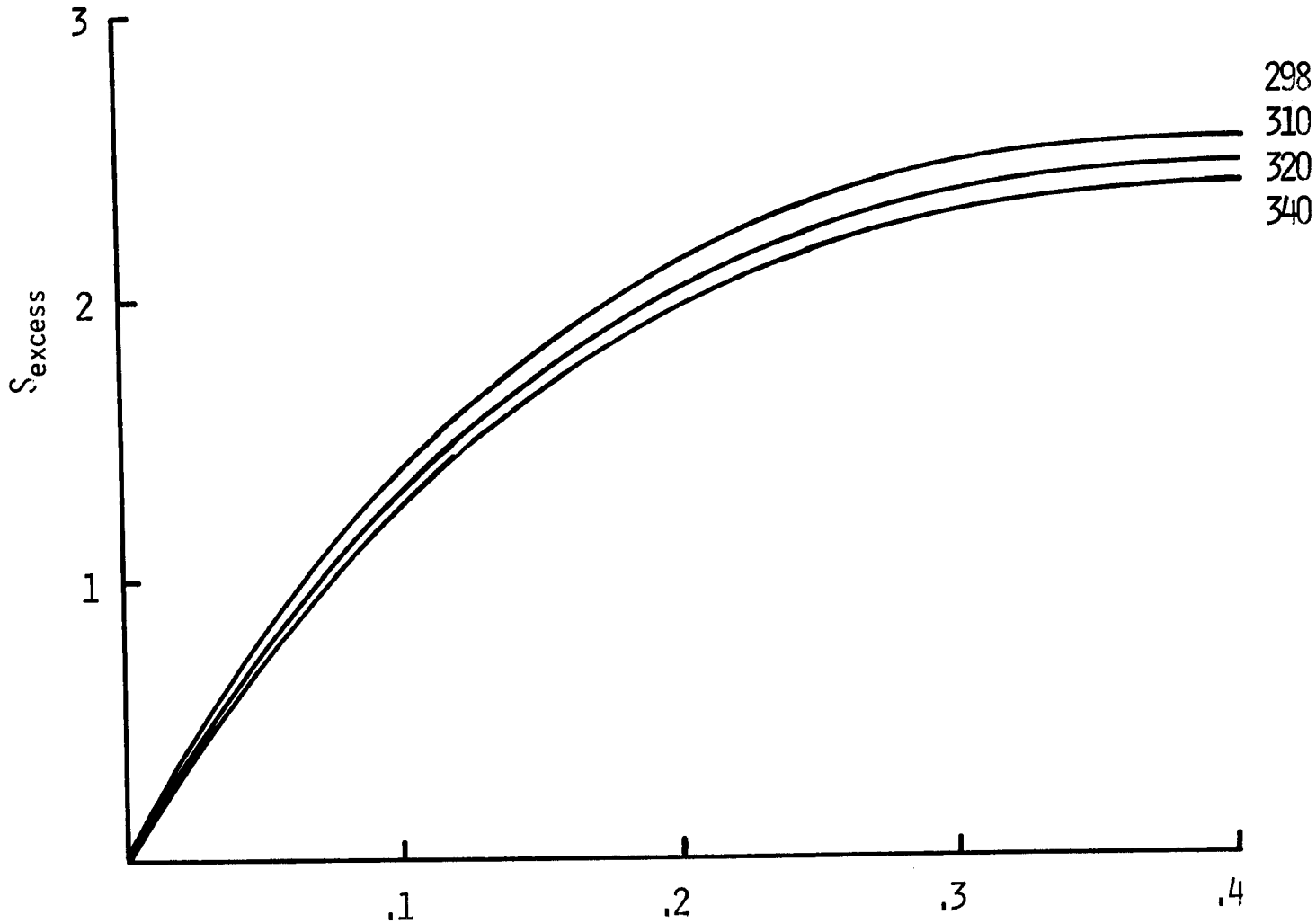


Figure 7. Dependence of isotherms on temperature (°K). Other parameters as in Figs. 4 and 5.

SECTION X

THEORY OF STRIPPING COLUMN OPERATION

If foam flotation techniques are to be used on an industrial scale, highly accurate mathematical models for column design will be needed to facilitate the construction of optimal columns at minimum cost. We present here a mathematical model for a continuous flow stripping column; the model includes the effects of axial dispersion, rate of solute transport between the surface and liquid phases, and non-linear adsorption isotherms. We discuss the model and results here; the mathematical analysis is given in Appendix B.

We take the following steady-state mass balance equations as our starting point:

$$0 = D_\ell V \frac{d^2c}{dx^2} + v_\ell V \frac{dc}{dx} + \frac{k_1 S^2}{V+SK} (\Gamma - kc)$$

$$0 = D_s S \frac{d^2\Gamma}{dx^2} - v_s S \frac{d\Gamma}{dx} - \frac{k_1 S^2}{V+SK} (\Gamma - kc)$$

Terms are defined as follows:

D_ℓ -- effective diffusion constant in the liquid phase.

D_s -- effective diffusion constant in the surface phase.

V -- volume of liquid contained in 1 cm^3 of foam.

S -- surface area contained in 1 cm^3 of foam.

v_ℓ -- velocity of liquid downward.

v_s -- velocity of surface upward.

K -- equilibrium adsorption isotherm; $K = \Gamma/c$ at equilibrium, and is a function of c.

Γ -- surface concentration of solute.

c -- concentration of solute in liquid.

c_{feed} -- concentration of solute in column influent.

k_1 -- rate constant governing solute transport between the surface phase and the liquid phase.

x -- distance from base of column.

ℓ -- column length.

δ -- film thickness of drained film.

$v_\ell V'$ -- flow rate of column influent.

Solvent material balance at the top of the column yields

$$v_\ell V' = v_s S\delta + v_\ell V.$$

Solute material balance at the top of the column yields

$$v_\ell V' c_{feed} - v_s S\Gamma(\ell) = v_\ell V c(\ell) - v_s S\Gamma(\ell) + D_\ell V \frac{dc(\ell)}{dx} + D_s S \frac{d\Gamma(\ell)}{dx} .$$

Solute material balance on the liquid phase at the top of the column yields

$$v_\ell V' c_{feed} = v_\ell V' c(\ell) + D_\ell V \frac{dc(\ell)}{dx} .$$

Solute material balance at the bottom of the column yields

$$v_\ell V c(0) = v_\ell V c(0) - v_s S\Gamma(0) + D_\ell V \frac{dc(0)}{dx} + D_s S \frac{d\Gamma(0)}{dx} .$$

Lastly, the requirement that there be no net flux of solute out of the bottom of the column via the surface phase yields

$$0 = v_s \Gamma(0) - D_s S \frac{d\Gamma(0)}{dx}$$

The two non-linear differential equations with their associated boundary conditions are then solved by iterative use of a quasi-linearization method as presented in Appendix D.

We found that the adsorption isotherms obtained by the method presented in Section VIII and Appendix C could be approximated rather well by a non-linear least squares fit of simple Langmuir isotherms of the form

$$K = \frac{a_1}{1 + c/a_2} .$$

In computations modeling column behavior we have therefore used Langmuir isotherms throughout.

We define the separation parameter F as $Vc(0)/V' c_{feed}$. High column separation efficiencies then correspond to small values of F.

Figure 8 exhibits the anticipated decrease in solute concentration in the column effluent as the specific foam area S increases; this parameter increases with decreasing pore size in the frit of the gas dispersion device generating the bubbles at the bottom of the column. The effect of varying the surface flow belocity v_s is shown in Figure 9; this quantity is increased by increasing the gas flow rate through the gas dispersion device; it is approximated in these calculations that increasing the gas flow rate does not affect the wetness of the foam. The expected increase of F with increasing liquid flow velocity v_ℓ is shown in Fig. 10. Increasing axial mixing (increasing D_s and D_ℓ) results in increasing F, as seen in Figure 11. D_x and D_ℓ are minimized by design of the influent dispersion head to distribute the influent as uniformly across the cross-section of the column as possible and by the use of screen baffles to break up incipient channelling in the foam. Overloading the column with influent has been found experimentally to result in very serious axial mixing and degradation of column performance.

The magnitude of the rate constant for solute transfer between the liquid and the surface phases decreases with increasing bubble wall thickness (proportional to foam wetness, or V, and increasing with increasing feed rate). The effect of increasing k_1 in improving column performance is seen in Figure

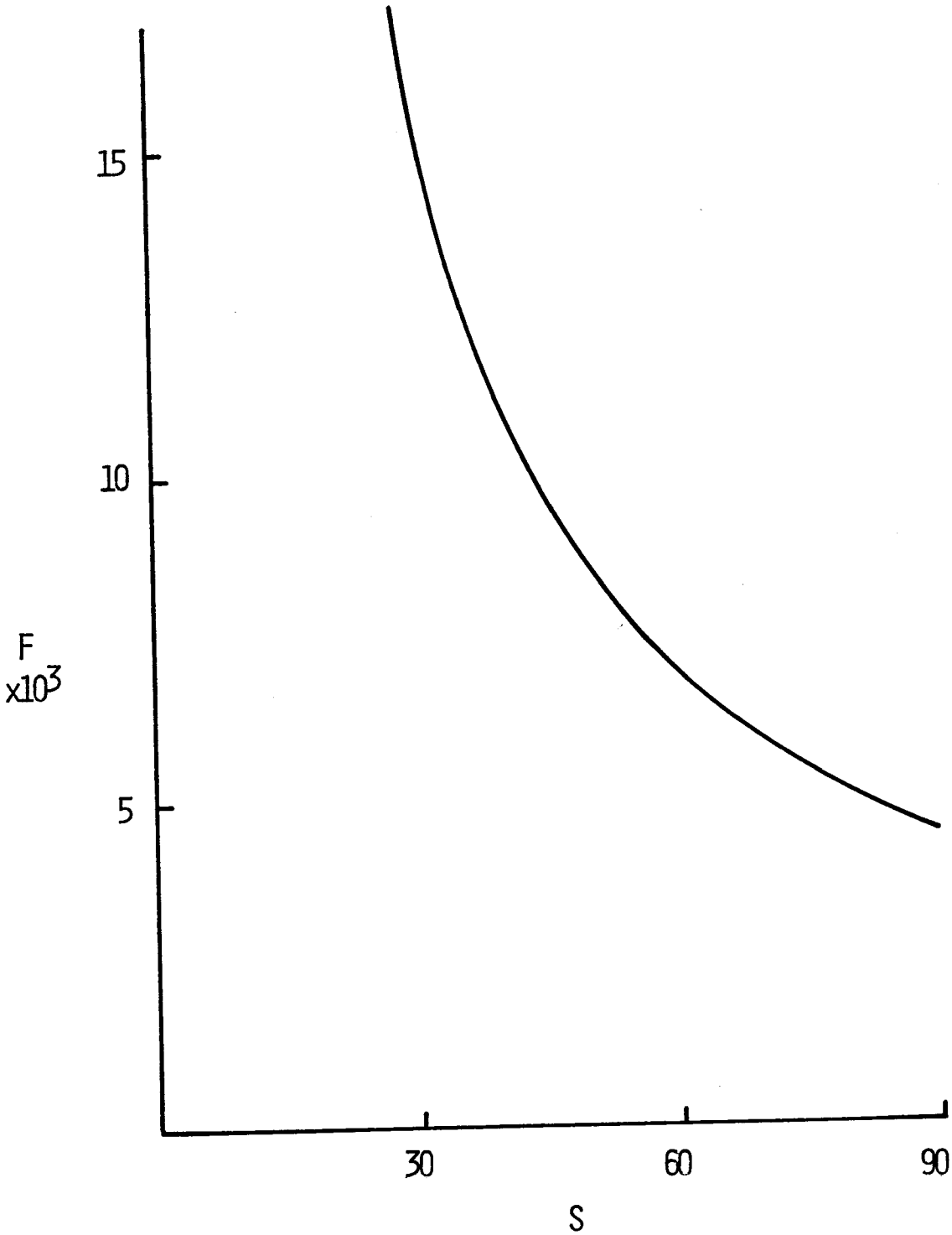


Figure 8. Dependence of separation factor F on specific foam area $S(cm^{-1})$. $D_s = D_\ell = 500$, $v_s = v_\ell = 1$, $V = .0025$, $k_1 = .1$, $L = 50$, $c_{Feed} = 1.4 \times 10^{-7}$ moles/cm^3, $a_1 = 6 \times 10^{-3}$, $a_2 = 10^{-8}$; all constants in c.g.s. units.

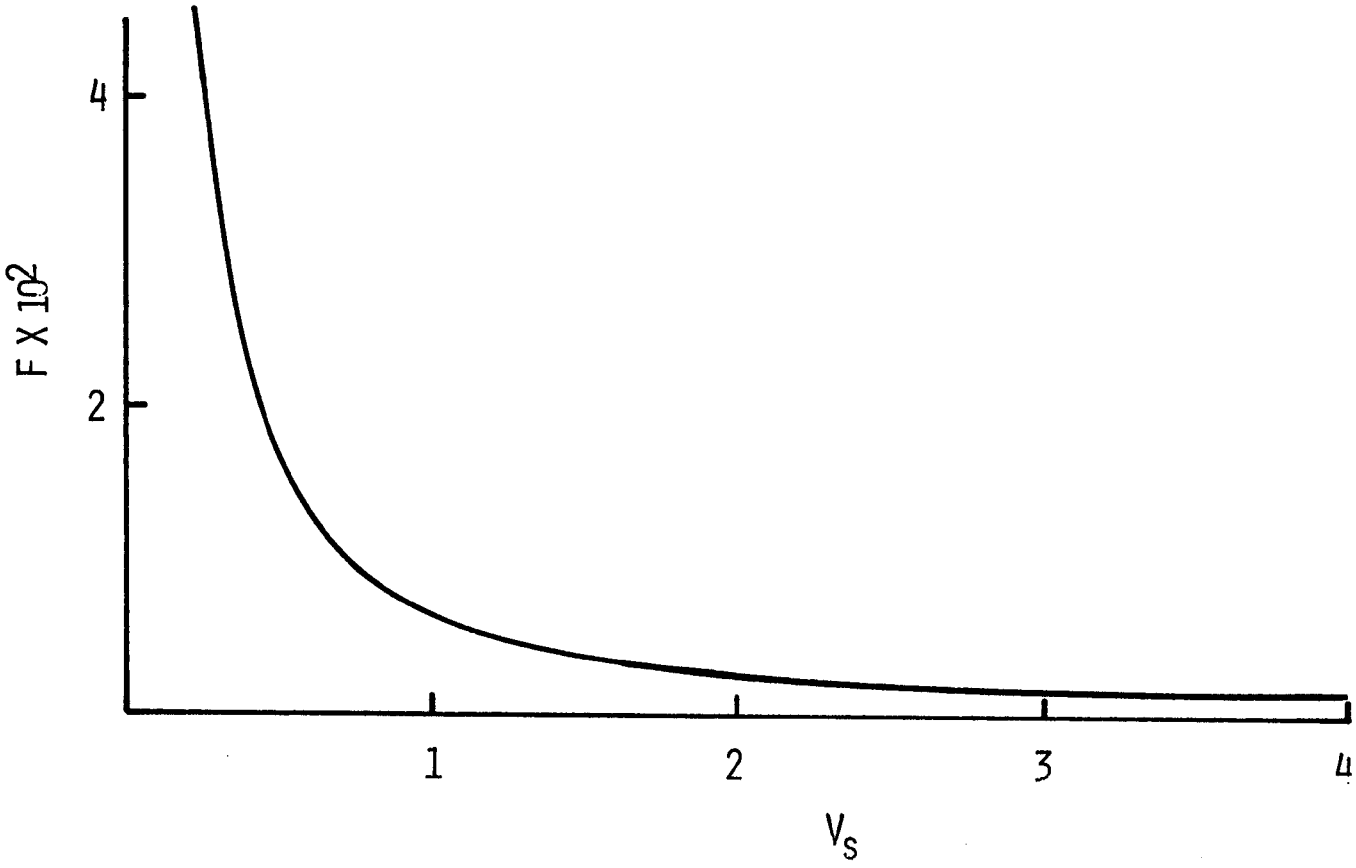


Figure 9. Dependence of separation factor F on surface velocity v_s(cm/sec). S = 60, other parameters as in Fig. 8.

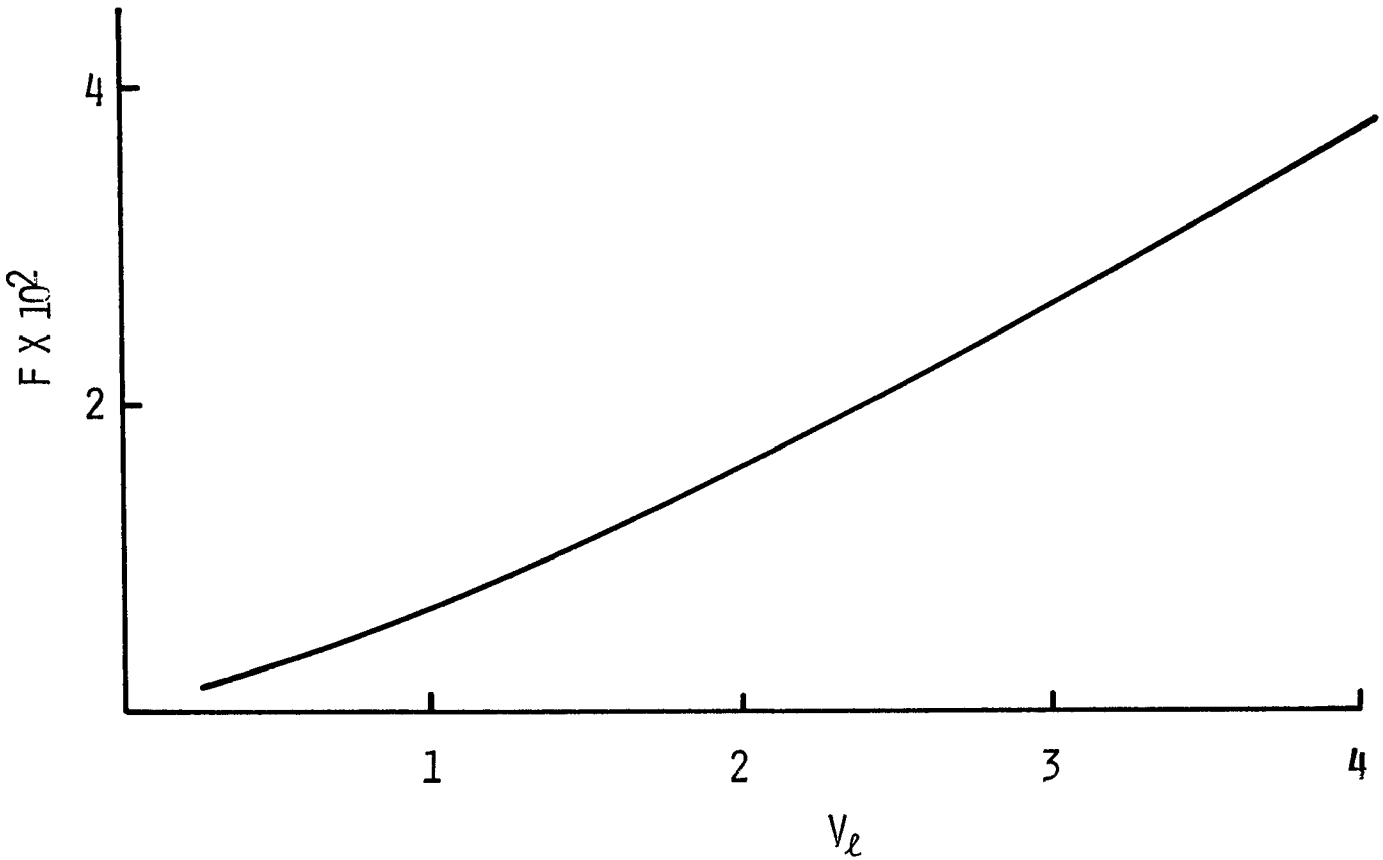


Figure 10. Dependence of F on liquid velocity (cm/sec). Other parameters as in Figures 8 and 9.

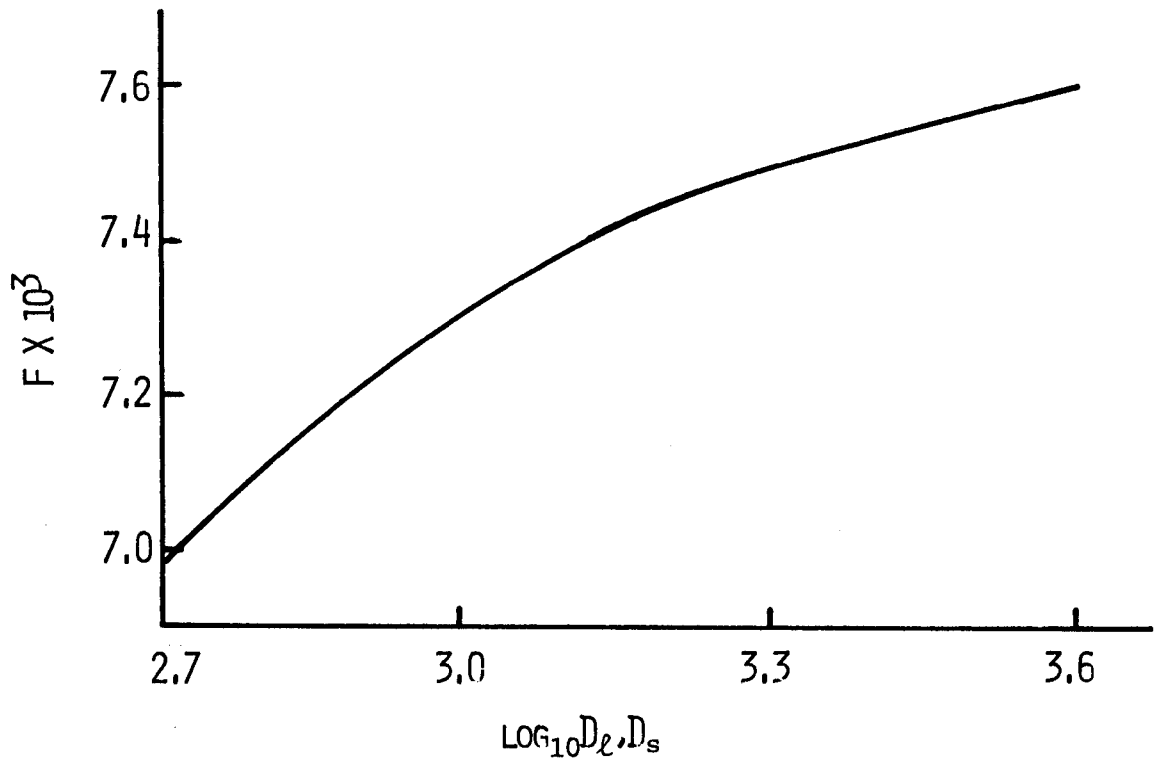


Figure 11. Dependence of F on effective diffusion constants D_s and D_ℓ (cm^2/sec). We have here set $D_s = D_\ell$. Other parameters as in Figures 8 and 9.

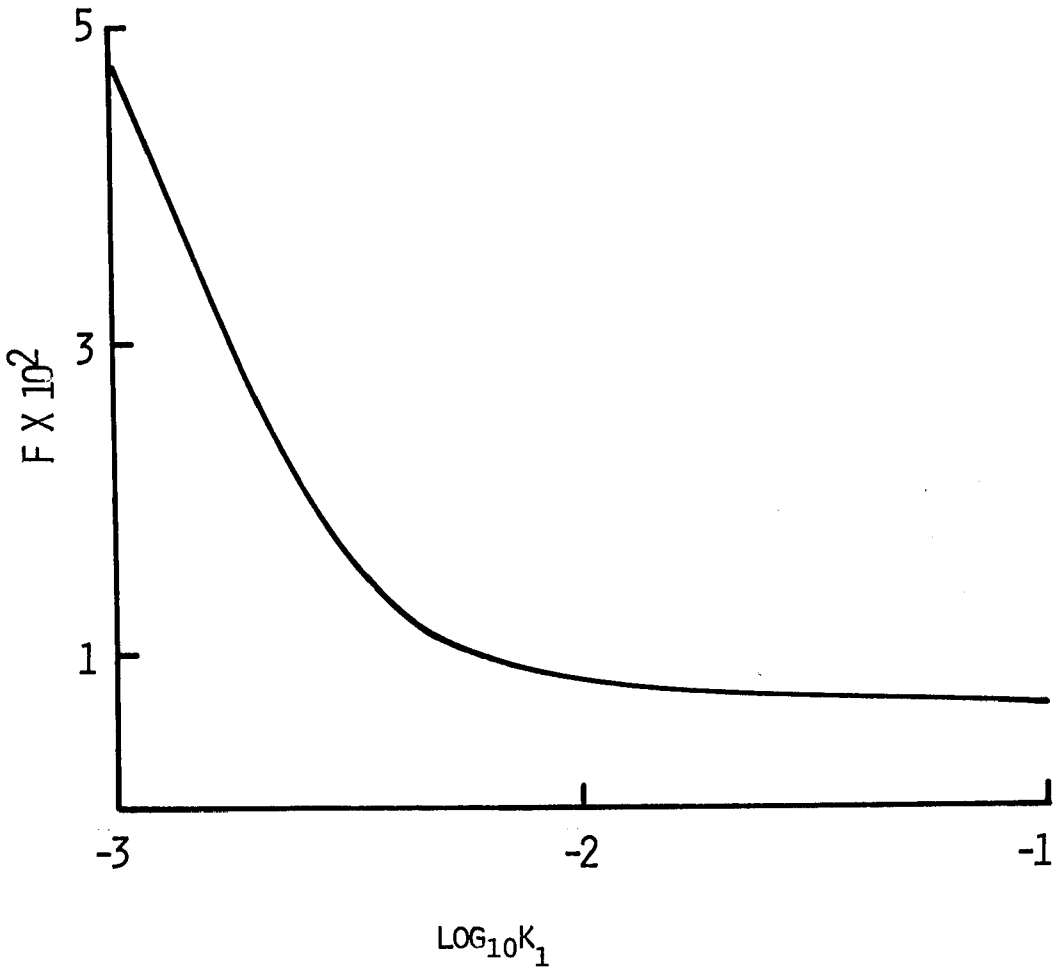


Figure 12. Dependence of F on mass transfer rate constant k_1 (cm/sec). Other parameters as in Figures 8 and 9.

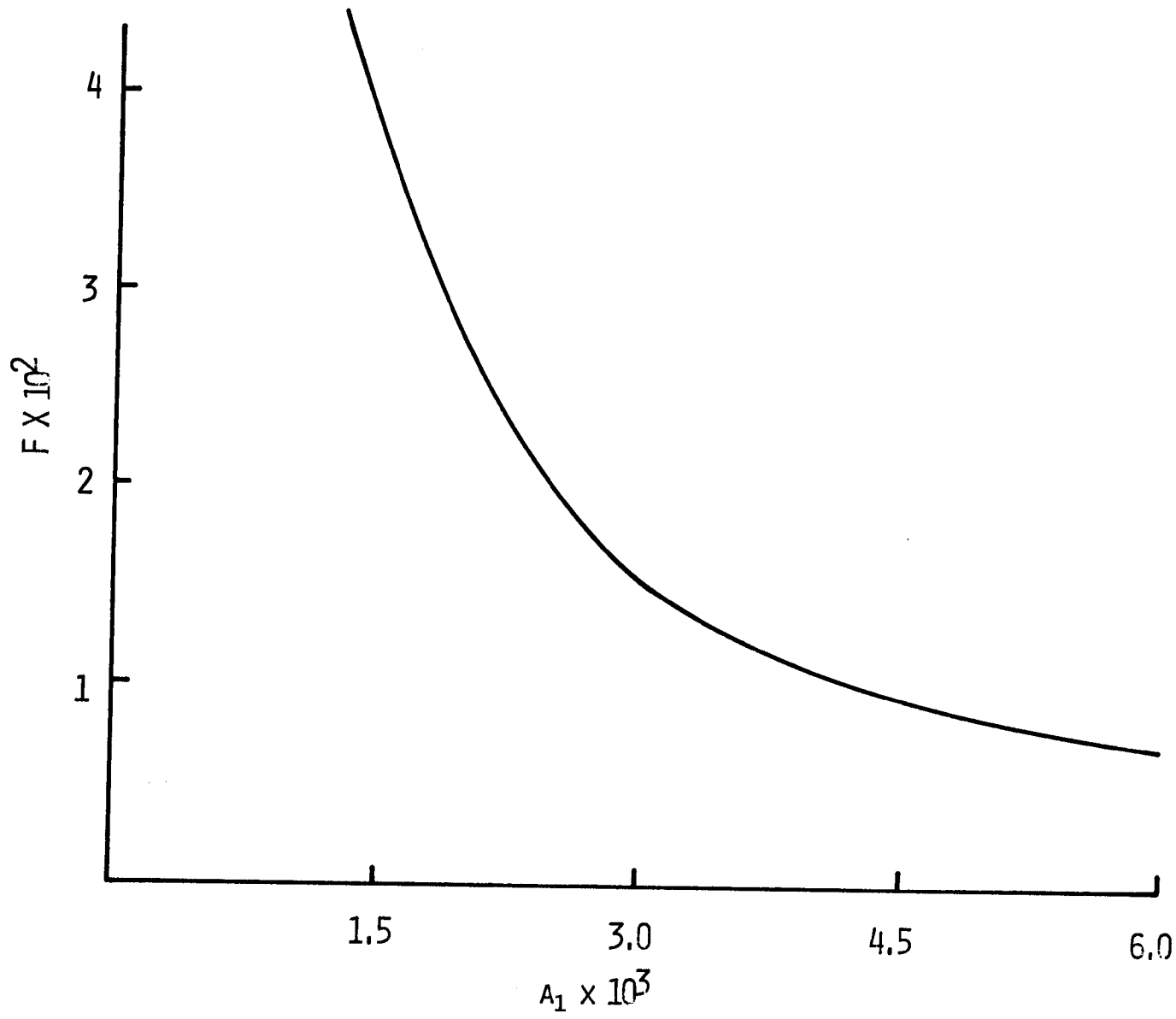


Figure 13. Dependence of F on Langmuir parameter a_1 (cm). Other parameters as in Figures 8 and 9.

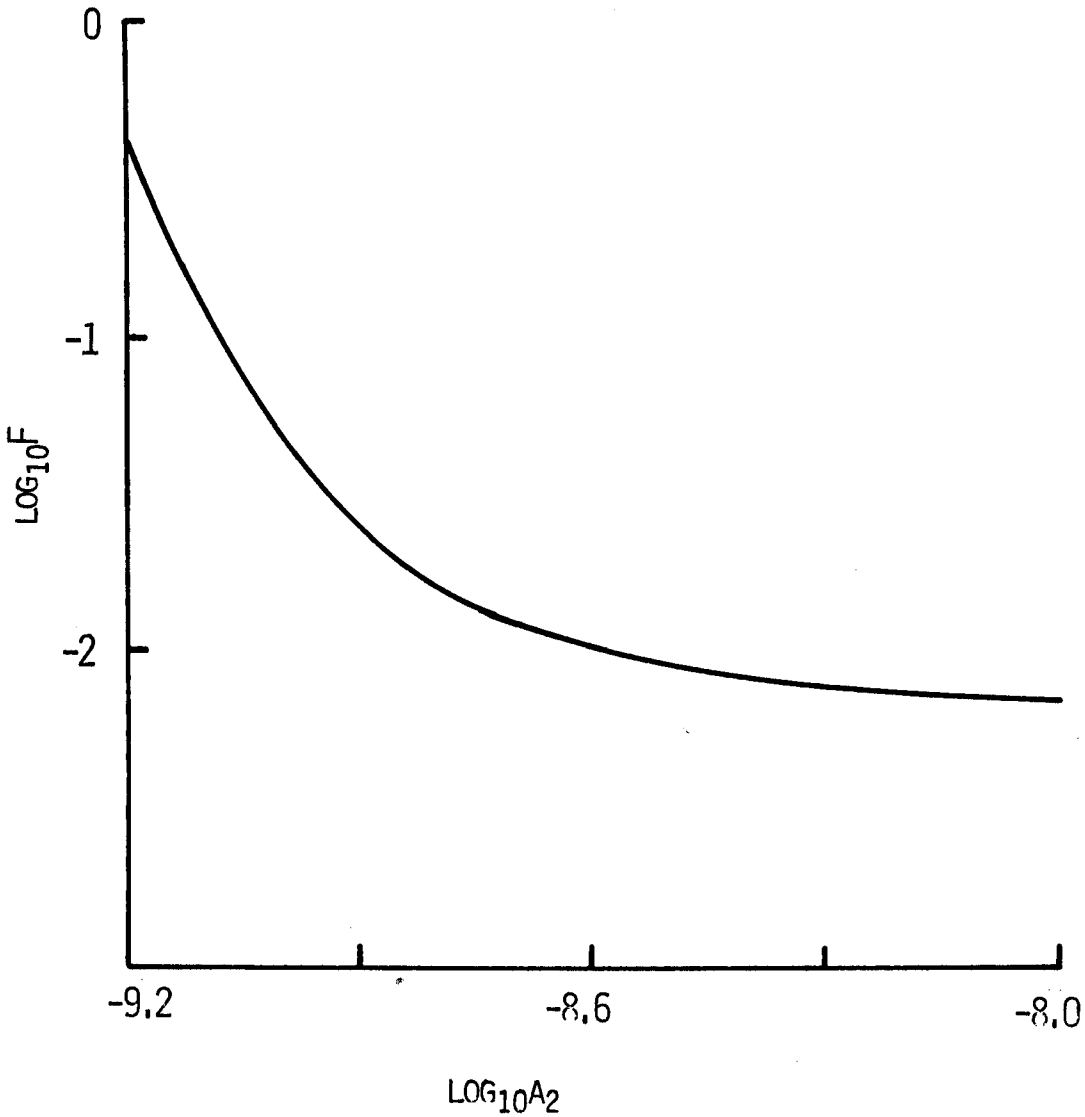


Figure 14. Dependence of F on Langmuir parameter a_2 (moles/cm^3). Other parameters as in Figures 8 and 9.

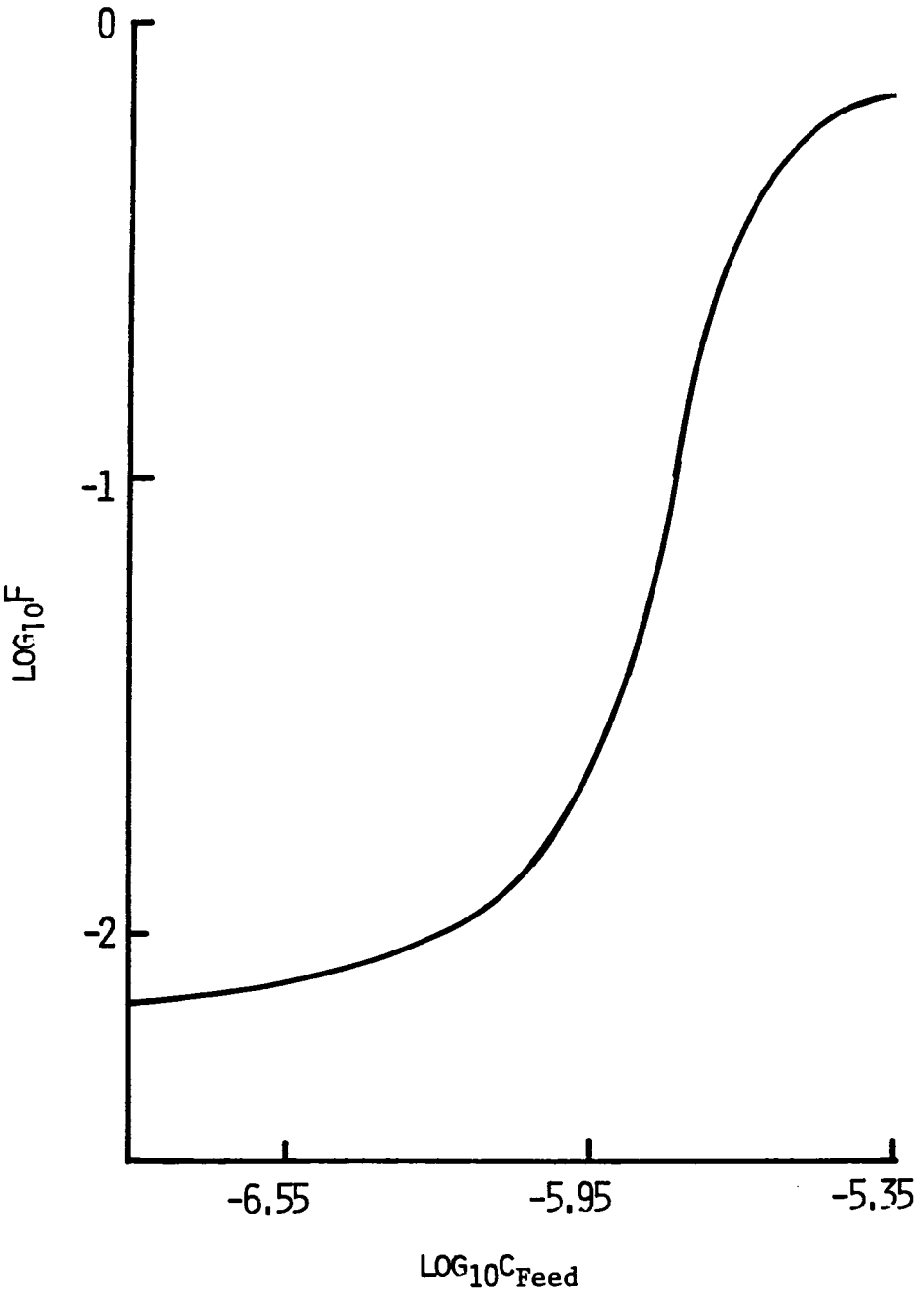


Figure 15. Dependence of F on c_{Feed} (moles/cm^3). Other parameters as in Figures 8 and 9.

12; beyond a certain value additional increase in k_1 does not significantly improve performance because equilibrium characteristics and axial diffusion become the limiting factors, as is seen on the right side of the figure.

The dependence of the separation parameter on the constants a_1 and a_2 in the Langmuir adsorption isotherm is exhibited in Figures 13 and 14, and are qualitatively what one could intuitively expect. The effect of such a non-linear isotherm is also shown in Figure 15, in which the dependence of separation parameter on feed concentration is shown. As the feed concentration increases, the surface film becomes saturated; at this point the separation parameter increases rather rapidly to unity, corresponding to negligible separation.

SECTION XI

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SECTION XII

APPENDICES

APPENDIX A. ADSORPTION ISOTHERMS

Here we examine a Gouy-Chapman type model for the interaction of a floc particle and a surfactant-covered surface (79, 82, 82). The electrical attraction between the charged surface of the film and the oppositely charged floc particles may be reduced by the presence of an ionic atmosphere, the width and density of which are determined by the dissolved salt concentration and the temperature.

For thick films such as are likely to be encountered in stripping column operation, the electric potential $\psi(x)$ and the distance from the film surface are related by Eq. A-1:

$$x = a_1 \log_e \left[\frac{(\cosh \frac{e\psi\beta}{2} + 1)(\cosh \frac{e\psi_o\beta}{2} - 1)}{(\cosh \frac{e\psi\beta}{2} - 1)(\cosh \frac{e\psi_o\beta}{2} + 1)} \right] \qquad \text{A-1}$$

Here β = $(kT)^{-1}$

ψ_o = electric potential at x = 0 in stat volts

k = 1.38×10^{-16} ergs/deg

T = absolute temperature

C = concentration of 1-1 electrolyte

D = dielectric constant of water, approximately 78

e = |electronic charge|, 4.77×10^{-10} esu

N_o = Avogadro's number, 6.023×10^{23}

$a_1^{-2} = \frac{8\pi e^2 N_o C\beta}{D}$

We assume that a floc particle occupies a volume of a^3 cm^3, and we examine the rectangular parallelopiped of liquid extending to the right of a square of film surface of area a^2. This constitutes a binding site on our surface film which is capable of binding 1,2...m particles. We let $q(s) = \sum_j \exp[-\beta\varepsilon_j(s)]$ be the site partition function when the site is occupied by

$$q(s) = \sum_{j_1=1}^{j_2-1} \sum_{j_2=2}^{j_3-1} \cdots \sum_{j_s=s}^{m} \sum_{\varepsilon(js)} \exp(-\beta\varepsilon) \qquad \text{A-2}$$

If a_s sites have s particles bound to them, then the canonical ensemble partition function for the collection of M sites and N particles is given by

$$Q(N,M,T) = \sum_{a_i\text{'s}} M! \prod_{i=o}^{m} \frac{[q(i)]^{a_i}}{a_i!}, \qquad \text{A-3}$$

where the a_i's must satisfy $\sum_{s=o}^{m} a_s = M$ and $\sum_{s=o}^{m} sa_s = N$. The

grand partition function of the system is given by

$$\Xi = \sum_{N=O}^{mM} Q(N,M,T)\lambda^N \qquad \text{A-4}$$

$$= \sum_{a_i\text{'s}} M! \prod_{i=o}^{m} \frac{[q(i)\lambda^i]^{a_i}}{a_i!} \qquad \text{A-5}$$

where $\sum_{s=o}^{m} a_s = M$ is our only constraint. But this is evidently just

$$\Xi = [\xi(\lambda T)]^M, \qquad \text{A-6}$$

where

$$\xi(\lambda,T) = \sum_{s=o}^{m} q(s)\lambda^s. \qquad \text{A-7}$$

The average number of particles per site is then given by

$$\bar{S} = \lambda \left(\frac{\partial \log \xi}{\partial \lambda} \right)_T = \frac{\sum_{s=o}^{m} sq(s)\lambda^s}{\sum_{s} q(s)\lambda^s} \qquad \text{A-8}$$

We assume that

$$\varepsilon(j_1, j_2, \ldots j_s) = \sum_{k=1}^{s} \varepsilon(j_k), \qquad \text{A-9}$$

the energy of any configuration of s particles at the site is simply the sum of the independent one-particle energies. This permits us to write

$$q(s) = \sum_{j_1=1}^{j_2-1} \sum_{j_1=2}^{j_1-1} \cdots \sum_{j_s}^{m} {}_S \left[\sum_{\varepsilon(j_1)} \sum_{\varepsilon(j_1)} \cdots \sum_{\varepsilon(j_s)} \exp\left\{ -\beta \sum_{i=1}^{s} \varepsilon(j_1) \right\} \right]$$

$$= \sum_{j_1} \sum_{j_2} \cdots \sum_{j_s} \prod_{j_s=1}^{s} [Pf(j_i)], \qquad \text{A-10}$$

where $[Pf(j_1)]$ is a one-particle partition function for a particle in compartment j_1. We write $[Pf(j_i)]$ as $\exp[-\beta V(j_i)]q(j_i)$, where $V(j_i)$ is the binding energy of a particle in compartment j_i to the surface, $Q\psi[(j_i-\frac{1}{2}a]$, where Q is the particle charge.

On substituting eq. (11) into eq. (8) we obtain

$$\xi = \sum_{s=o}^{m} \lambda^s \sum_{j_1=1}^{j_2-1} \sum_{j_2-2}^{j_3-1} \cdots \sum_{j_s=S}^{m} \prod_{j_1=1}^{s} q(j_1) \exp[-\beta V(j_i)] \qquad \text{A-11}$$

$$= \prod_{j_i=1}^{m} \left\{1 + q(j_i)\lambda \exp[-\beta V(j_i)]\right\} \qquad \text{A-11}$$

From this result and eq. (8) we readily obtain

$$\bar{s} = \sum_{k=1}^{m} \frac{\lambda\, q(k) \exp[-\beta V(k)]}{1 + \lambda\, q(k) \exp[-V(k)]} \qquad \text{A-12}$$

Now q(k) involves partition function factors associated with a particle in a box, essentially, and with rotational motions. This is true for all k, and we therefore make the reasonable approximation that q(k) = q, independent of k, which yields

$$\bar{s} = \sum_{k=1}^{m} \left[1 + \frac{\exp[\beta V(k)]}{\lambda q} \right]^{-1} \qquad \text{A=13}$$

Now $\log \lambda q = \beta\mu_{total} - \beta\mu_{internal}$

$= \beta\mu_{configurational}$,

where the μ's represent chemical potentials. It is shown in ref. 82, that

$$\beta\mu_{configurational} = \log \frac{\sigma}{1 - \sigma} \qquad \text{A-14}$$

where σ is the "density of particles in the bulk liquid," the average number of particles in L compartments a large distance away from the surface, divided by L. This then yields

$$\bar{s} = \sum_{k=1}^{m} \left[1 + \frac{1 - \sigma}{\sigma} \exp[\beta V(k)] \right]^{-1} \qquad \text{A-15}$$

We define S_{excess} as

$$S_{excess} = \bar{s} - M\sigma, \qquad \text{A-16}$$

the net excess of particles bound per site in the surface layer. Substitution of eq. (15) in (16) then yields Eq. (17) as the expression for the adsorption isotherm.

$$S_{excess} = \sigma(1 - \sigma) \sum_{k=1}^{m} \frac{1 - \exp\beta V(k)}{\sigma[1-\exp\beta V(k)] + \exp\beta B(k)} \qquad \text{A-17}$$

APPENDIX B. MODEL OF STRIPPING COLUMN OPERATION

Introduction

Several mathematical models for foam flotation columns have been described in the literature; these generally consist of equations derived from steady state material balance considerations at the ends of the column, (9, 13, 20). An integral part of these models is the assumption of instantaneous equilibrium between the surface and the bulk phases. Also, they are confined to the plug flow regime. Goldberg and Rubin (87) review a number of these models, and also present a model applicable to a stripping column without solute transfer in the countercurrent region. Wang et al (84, 85, 86) treat continuous bubble fractionation, and present a model which includes axial dispersion and the use of equilibrium absorption isotherms. Cannon and Lemlich (88) present a detailed analysis based upon the assumption of linear isotherms, and Lee has given a somewhat similar treatment (89).

We here present an approach derived from Wilburn's analysis of two phase countercurrent extraction (90); he includes effects of diffusion, convection, and mass transfer, and assumes a linear isotherm. We analyze a continuous flow foam flotation column operating at steady state in the stripping mode, and we include effects of diffusion and turbulence, rate of mass transfer, and non-linearity of the isotherm.

Analysis

We take equations (1) and (2) as our starting point:

$$0 = D_\ell V \frac{d^2c}{dx^2} + v_\ell V \frac{dc}{dx} + \frac{k_1 S^2}{V + SK} (\Gamma - Kc) \qquad \text{B-1}$$

$$0 = D_s S \frac{d^2\Gamma}{dx^2} - v_s S \frac{d\Gamma}{dx} - \frac{k_1 S^2}{V + SK} (\Gamma - Kc) \qquad \text{B-2}$$

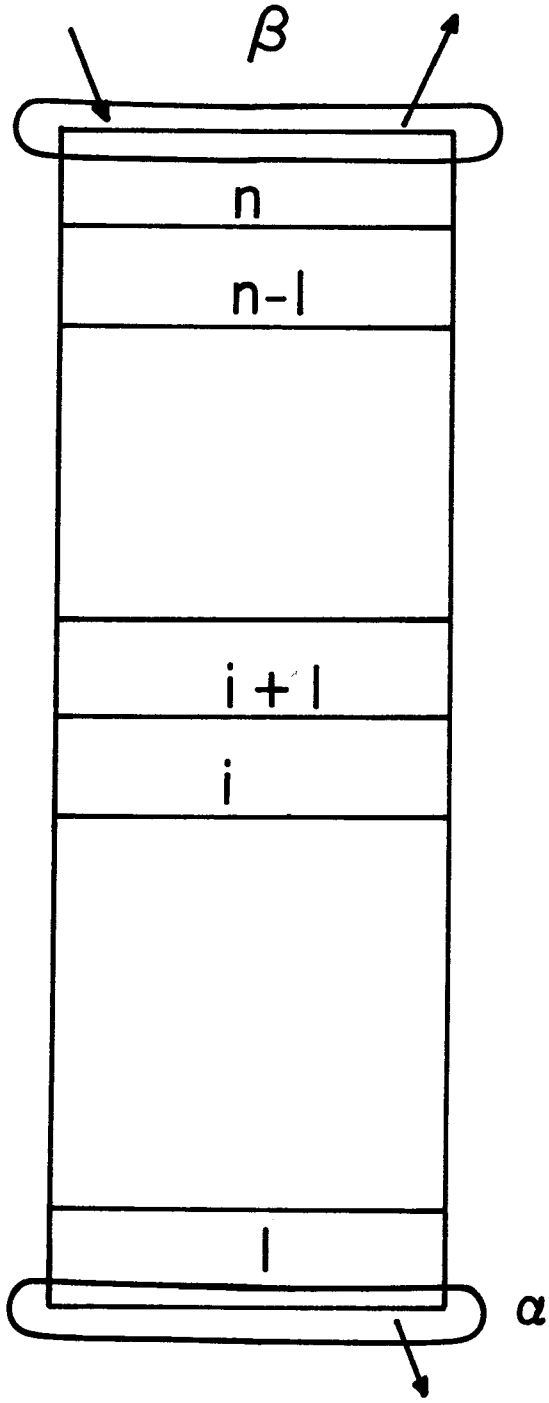

Figure B-1. Material Balance Diagram of the Column.

Terms are defined as follows:

D_ℓ	-	effective diffusion constant in the liquid phase
D_s	-	effective diffusion constant in the surface phase
V	-	volume of liquid contained in one cm^3 of foam
S	-	surface area contained in one cm^3 of foam
V_ℓ	-	velocity of liquid downward
V_s	-	velocity of surface upward
K	-	equilibrium isotherm; $K = \Gamma/c$ at equilibrium
Γ	-	surface concentration of solute
c	-	concentration of solute in liquid
c_{feed}	-	concentration of solute in column influent
k_1	-	rate constant governing mass transport between the surface phase and the liquid phase
x	-	distance from base of column
ℓ	-	column length

The boundary conditions of the problem are determined in the following way. First, solvent material balance at β (see Fig. B-1) yields

$$v_\ell V' = v_s S\delta + v_\ell V, \qquad \text{B-3}$$

where δ is the film thickness of drained film and $v_\ell V'$ is the flow rate of column influent. Solute material balance at β yields

$$v_\ell V' c_{feed} - v_s S\Gamma(\ell) = v_\ell V c(\ell) - v_s S\Gamma(\ell) + D_\ell V \frac{dc}{dx}(\ell) + D_s S \frac{d\Gamma}{dx}(\ell) \qquad \text{B-4}$$

Solute material balance at α yields

$$v_\ell Vc(0) = v_\ell Vc(0) - v_s S\Gamma(0) + D_\ell V \frac{dc}{dx}(0) + D_s S \frac{d\Gamma}{dx}(0) \qquad \text{B-5}$$

The requirement that there be no net flux out of the bottom of the column via the surface phase yields

$$0 = v_s \Gamma(0) - D_s S \frac{d\Gamma}{dx}(0) \qquad \text{B-6}$$

Solute material balance on the liquid phase at the top of the column yields

$$v_\ell V' c_{feed} = v_\ell Vc(\ell) + D_\ell V \frac{dc}{dx}(\ell) \qquad \text{B-7}$$

Equations (4) through (7) can be simplified and combined to yield boundary conditions identical to those used by Misĕk and Rod for counter-current extraction (91):

$$\frac{V}{V'} c(\ell) + \frac{V D_\ell}{v_\ell V'} \frac{dc}{dx}(\ell) = c_{feed} \qquad \text{B-8}$$

$$\frac{d\Gamma}{dx}(\ell) = 0 \qquad \text{B-9}$$

$$v_s \Gamma(0) - D_s \frac{d\Gamma}{dx}(0) = 0 \qquad \text{B-10}$$

$$\frac{dc}{dx}(0) = 0 \qquad \text{B-11}$$

We regard K as a function of c (non-linear isotherm), and solve the differential equations (1) and (2) as follows. We subdivide the column into n compartments as indicated in Fig. 1, and define

$$\xi_i = (x_{i-1} + x_i)/2 \qquad \text{B-12}$$

$$K_i = K[c(\xi_i)] \qquad \text{B-13}$$

We shall be constructing an iteractive quasi-linearization method (16) whereby we make an initial choice of the K_i (based on the calculation of c(x) when K(c) is set equal to K(0). In the ith compartment our differential equations are now

$$0 = -v_s S \frac{d\Gamma^i}{dx} + SD_s \frac{d^2\Gamma^i}{dx^2} - \frac{k_1 S^2}{V + SK_i} (\Gamma^i - K_i c^i) \qquad \text{B-14}$$

$$0 = v_\ell V \frac{dc^i}{dx} + VD_\ell \frac{d^2c^i}{dx^2} + \frac{k_1 S^2}{V + SK_i} (\Gamma^i - K_i c^i) \qquad \text{B-15}$$

We solve these in the ith region by setting $c^i(x) = c^i \exp \lambda^i x$, $\Gamma^i(x) = \Gamma^i \exp \lambda^i x$ to obtain

$$0 = \Gamma^i (SD_s \lambda^{i_2} - v_s S\lambda^i - \frac{k_1 S^2}{V + SK_i} + c^i \frac{k_1 S^2 K_i}{V + SK_i} \qquad \text{B-16}$$

$$0 = \frac{\Gamma^i k_1 S^2}{V + SK_i} + c^i (VD_\ell \lambda^{i_2} + v_\ell V\lambda^i - \frac{k_1 S^2 K_i}{V + SK_i}) \qquad \text{B-17}$$

The requirement that Γ^i and $c^i \neq 0$ yields

$$0 = \begin{vmatrix} \left(SD_s \lambda^{i_2} - v_s S\lambda^i - \frac{k_1 S^2}{V + SK_i}\right) & \frac{k_1 S^2 K_i}{V + SK_i} \\ \frac{k_1 S^2}{V + SK_i} & \left(VD_\ell \lambda^{i_2} + v_\ell V^{\lambda i} - \frac{k_1 S^2 K_i}{V + SK_i}\right) \end{vmatrix} \qquad \text{B-18}$$

We solve this secular equation (which has one zero root) to get the λ_j^i, (c_j^i, Γ_j^i), j = 1, 2, 3, 4. We choose the $c_j^i = 1$ for all i and j, which then permits calculation of the Γ_j^i from equations (16) or (17). Then

$$c^i(x) = \sum_{j=1}^{4} \alpha_j^i \exp \lambda_j^i x \qquad \text{B-19}$$

$$\Gamma^i(x) = \sum_{j=1}^{4} \alpha_j^i \Gamma_j^i \exp \lambda_j^i x, \qquad \text{B-20}$$

where the α_j^i are to be determined from (1) the four boundary conditions [equations (8) - (11)], and (2) the requirements that

$$c^i(x_i) = c^{i+1}(x_i) \qquad \text{B-21}$$

$$\Gamma^i(x_i) = \Gamma^{i+1}(x_i) \qquad \text{B-22}$$

$$\frac{dc^i}{dx}(x_i) = \frac{d}{dx} c^{i+1}(x_i) \qquad \text{B-23}$$

$$\frac{d}{dx} \Gamma^i(x_i) = \frac{d}{dx} \Gamma^{i+1}(x_i) \qquad \text{B-24}$$

$$i = 1, 2, \ldots n - 1$$

This yields a total of 4n equations to be solved for the 4n α_j^i. We substitute Eqs. (19) and (20) into (21) - (24) to obtain

$$\begin{pmatrix} 1 & 1 & 1 & 1 \\ \Gamma_1^i & \Gamma_2^i & \Gamma_3^i & \Gamma_4^i \\ \lambda_1^i & \lambda_2^i & \lambda_3^i & \lambda_4^i \\ \lambda_1^i\Gamma_1^i & \lambda_2^i\Gamma_2^i & \lambda_3^i\Gamma_3^i & \lambda_4^i\Gamma_4^i \end{pmatrix} \begin{pmatrix} \exp \lambda_1^i x_i & 0 & 0 & 0 \\ 0 & \exp \lambda_2^i x_i & 0 & 0 \\ 0 & 0 & \exp \lambda_3^i x_i & 0 \\ 0 & 0 & 0 & \exp \lambda_4^i x_i \end{pmatrix}$$

$$X \begin{pmatrix} \alpha_1^i \\ \alpha_2^i \\ \alpha_3^i \\ \alpha_4^i \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ \Gamma_2^{i+1} & \Gamma_2^{i+1} & \Gamma_3^{i+1} & \Gamma_4^{i+1} \\ \lambda_2^{i+1} & \lambda_2^{i+1} & \lambda_3^{i+1} & \lambda_4^{i+1} \\ \lambda_1^{i+1}\Gamma_1^{i+1} & \lambda_2^{i+1}\Gamma_2^{i+1} & \lambda_3^{i+1}\Gamma_3^{i+1} & \lambda_4^{i+1}\Gamma_4^{i+1} \end{pmatrix}$$

$$X \begin{pmatrix} \exp \lambda_1^{i+1} x_i & 0 & 0 & 0 \\ 0 & \exp \lambda_2^{i+1} x_i & 0 & 0 \\ 0 & 0 & \exp \lambda_3^{i+1} x_i & 0 \\ 0 & 0 & 0 & \exp \lambda_4^{i+1} x_i \end{pmatrix} \begin{pmatrix} \alpha_1^{i+1} \\ \alpha_2^{i+1} \\ \alpha_3^{i+1} \\ \alpha_4^{i+1} \end{pmatrix}$$

or, in more compact notation,

$$F(i)D(i,i)\underset{\sim}{\alpha}(i) = F(i+1)D(i,i+1)\underset{\sim}{\alpha}(i+1) \qquad \text{B-25}$$

Then

$$\underset{\sim}{\alpha}(i) = D^{-1}(i,i)F^{-1}(i)F(i+1)D(i,i+1)\underset{\sim}{\alpha}(i+1) \qquad \text{B-26}$$

or

$$\underset{\sim}{\alpha}(i) = T(i)\underset{\sim}{\alpha}(i+1).$$

So

$$\underset{\sim}{\alpha}(1) = T(1)T(2)\ldots T(n-1)\underset{\sim}{\alpha}(n) \equiv \tau\underset{\sim}{\alpha}(n) \qquad \text{B-27}$$

Our equations (8) - (11) become

$$c_{feed} = \sum_{j=1}^{4} \alpha_j^n \exp(\lambda_j^n \ell) \left[\frac{V}{V'} + \frac{VD_\ell \lambda_j^n}{V' v_\ell} \right] \qquad \text{B-28}$$

$$0 = \sum_{j=1}^{4} \alpha_j^n \exp(\lambda_j^n \ell) \Gamma_j^n \lambda_j^n \qquad \text{B-29}$$

$$0 = \sum_{j=1}^{4} \alpha_j^1 \Gamma_j^1 (v_s - D_s \lambda_j^1) \qquad \text{B-30}$$

$$0 = \sum_{j=1}^{4} \alpha_j^1 \lambda_j^1, \qquad \text{B-31}$$

or, more compactly,

$$\begin{pmatrix} c_{feed} \\ 0 \end{pmatrix} = B\underset{\sim}{\alpha}(n)$$

$$\begin{pmatrix} 0 \\ \\ 0 \end{pmatrix} = A\underset{\sim}{\alpha}(1)$$

where A and B are matrices defined by eqns. (28) - (31). On using eq. (27) with these we obtain

$$\begin{pmatrix} c_{feed} \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} B \\ \\ A\tau \end{pmatrix} \underset{\sim}{\alpha}(n) \qquad C\underset{\sim}{\alpha}(n) \qquad \text{B-32}$$

Then

$$\underset{\sim}{\alpha}(n) = C^{-1} \begin{pmatrix} c_{feed} \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \text{B-33}$$

and

$$\underset{\sim}{\alpha}(i) = T(i)\underset{\sim}{\alpha}(i+1), \qquad \text{B-34}$$

as before. Solute concentrations in the middle of the various compartments are obtained from

$$c^i(\xi_i) = \sum_{j=1}^{4} \alpha_j^i \exp(\lambda_j^i \xi_i), \qquad \text{B-35}$$

where ξ_i is given by eq. (12). These $c^i(\xi^i)$ are then used to calculate a new set of K_i's, at which point we go back to eq. (18) and repeat the calculation up through eq. (34). We continue these iterations until results from successive iterations are in sufficiently close agreement.

The amount of solute which is discharged per second in the column effluent is given by

$$v_\ell V c(0) = v_\ell V \sum_{j=1}^{4} \alpha_j^1;$$

the total amount of solute flowing into the column per second is given by $v_\ell V' c_{feed}$; we define a separation parameter, F, as

$$F = Vc(0)/V'c_{feed} \qquad \text{B-36}$$

the smallness of which gives us a criterion of column performance.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

Laboratory studies demonstrated that the floc foam flotation techniques are effective in removing lead, cadmium, mercury, copper, zinc, arsenic, and fluoride from dilute wastewaters to very low levels. Simulated as well as real industrial wastewaters were studied. Industrial wastewaters studied originated from primary aluminum smelters, secondary lead smelters, and brass mills. Copper, lead and arsenic are readily removed with $Fe(OH)_3$ and sodium lauryl sulfate; fluoride and zinc, with $Al(OH)_3$ and sodium lauryl sulfate; cadmium and mercury, with CuS and hexadecyltrimethylammonium bromide. Batch techniques as well as continuous flow systems were used; the latter proved to be more efficient. Possibility of surfactant recovery was investigated. Flotation column simulator computer program was also constructed. Floc foam flotation techniques are not suitable for treatment of wastes containing high concentrations of dissolved salts and adequate pH control is essential in most separations.

Foam separation processes combine the attractive features of simplicity, economy, potential for recovery, and effective removal of pollutants at low concentrations in wastewaters.

17. KEY WORDS AND DOCUMENT ANALYSIS

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