

COLOR REMOVAL FROM KRAFT MILL EFFLUENTS BY A
COAGULATION-FLOTATION PROCESS

by

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A B S T R A C T

The technique of coagulation-flotation has been evaluated for the removal of color bodies from kraft mill effluents. The process was based upon coagulation of the colloidal chromophores using a cationic surfactant (didodecyldimethylammonium bromide) as a coagulant and flotation agent. Several sets of batch experiments were designed and carried out in a flotation cell. The effects of pH over the range 3.6-5.6 and of surfactant concentrations from 100-200 ppm were investigated. An interaction was shown to exist between these two factors. The best results were obtained at pH 3.6 and 100 ppm of surfactant. Since the percentage of color removed was proven not to be reliable in expressing the process result, another approach had to be developed.

Other studies embraced: a) the floatability of the surfactant in aqueous solution at different pHs and initial concentrations; b) the behaviour of the kraft mill waste during several acidification-alkalization sequences; c) the effect of storage on the color and solids content of the effluent. Variables such as premixing time, stirrer speed,

air flow rate, sparger size, introduction of the surfactant and temperature were briefly inspected.

Laboratory scale continuous equipment was assembled and run at the optimum batch conditions. The presence of a premixing stage turned out to be essential for the process. The results were comparable to those previously obtained in batch and hence the possibility of developing a continuous coagulation-flotation process was established.

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I N T R O D U C T I O N

In recent years the color of effluents discharged into receiving waters has emerged as an important environmental problem. In addition to the aesthetic aspects, it has been suggested that the color introduced into these waters may be partly responsible for the deterioration of the structure of marine biological communities (1) because the development of phytoplanktonic organisms is inhibited by the reduced penetration of sunlight.

Kraft pulp mill effluents are complex mixtures of the by-products of the pulping and bleaching processes. The pollutants in kraft mill waste water are primarily wood extractives, and lignin and cellulose degradation products. It is believed that the colored materials originate from lignin and lignin fragments which have a quinone type structure (2). These compounds impart a brown color to the effluent causing the receiving waters to turn the color of dark tea.

Present treatment processes for kraft mill wastes are primarily devoted to the removal of BOD. These processes

such as the activated sludge process or aerated lagoons do not have much effect on color, probably because color is associated with lignin like materials which are resistant to microbiological degradation. A variety of processes have been proposed for color removal from kraft mill waste waters. These include treatment with lime, adsorption on calcium carbonate or activated carbon, reverse osmosis, filtration, liquid-liquid extraction, and flotation. The lime treatment process at present seems to be the one favored by industry.

The flotation process has been used in water treatment processes and in the treatment of paper mill wastes in South Africa and Sweden but has been little used in North America (3). An ion flotation process specific for color removal from kraft mill waste water was developed by Herschmiller (4). This process is based on the coagulation of the negatively charged soluble or colloidal chromophores (the *colligend*) using a cationic surface active agent (the *collector*). The product of the coagulation reaction, a surface active complex called *sublate* is floated to the surface by the introduction of air bubbles. At the surface a froth containing most of the color is formed and can be easily removed. The results obtained showed the feasibility of the process at least on a batch, laboratory scale.

The purpose of the present investigation was to expand upon the results of Herschmiller in terms of the effects of certain variables on color removal, to see if there were any interaction effects between variables in a statistical sense, to develop a better criterion for evaluating the effectiveness of the process, and to attempt to try out the process on a continuous basis. The information thus made available should be useful in optimizing the process and in determining its economic suitability.

Chapter 1

BACKGROUND INFORMATION

1.1 The Color Bodies in Kraft Mill Effluents:

A Potential Pollutant

The color of the kraft mill wastes results from the presence of soluble or colloidal components of wood as modified by the pulping and bleaching operations. During the chlorination stage of a conventional kraft pulp bleaching sequence, the color-producing compounds are rendered soluble and are mostly removed in the subsequent caustic extraction stage. The waste water from the pulp washers of the caustic extraction stage constitutes the greatest source of color in the effluent (5).

Lignin and/or its degradation products are responsible for most of the color of the effluent (2). Despite the considerable amount of work which has been performed with the intention of identifying the specific chromophoric groups responsible for color, the matter has not yet been completely resolved. According to Hayes and Munroe (3),

. . . the dark color in kraft mill effluent originates in double bonds conjugated with aromatic rings, chalcones, quinoid structures, free radicals, metallic complexes (6), alkaline degradation products of sugar and chlorinated lignin derivatives (7). Much of the color is in the form of colloidal particles (8).

Known toxic impurities are also present in the effluent: resin acids, fatty acids, inorganic and organic sulfides, tetrachloro-o-benzoquinone and 4-p-tolyl-1-pentanol (9). Certain of these compounds, e.g. resin acids, fatty acids and lignin are surface active, hence partly responsible for the generation of foam.

All the published material on the subject agrees that "a large portion of the pollutants behave as strongly hydrophilic, negatively charged colloids" (3,4,10,11,12,13). The majority of the techniques suggested for removal of the color fraction from the effluents are based on that feature (Appendix E).

The lignin-related components of the waste, which as mentioned provide most of the color, are largely unaffected by bio-oxidation. These compounds have not been found toxic to any aquatic species yet observed - at least, at normal effluent concentrations. But, although no conclusive reasons have been given against dumping highly colored effluents into receiving waters, the color of effluent is meeting increased criticism on the following grounds:

1. By reducing sunlight penetration, the color might: a) inhibit the photosynthetic activities of aquatic plants and microorganisms thereby causing an

upset in the ecology of that particular body of water (14,15); b) affect the grazing habits of zooplankton and other marine organisms which depend upon sight for discriminatory feeding (16).

2. The colored components might be toxic to some of the lower scale of organisms in the aquatic eco-system.
3. At some downstream point, the colored water may become part of a municipal water supply, where color removal might be troublesome.
4. Esthetically, strong color is inconsistent with present public attitudes.

Several attempts have been made to estimate light absorption values of kraft mill effluents, these have not yet been fully successful specifically because of the lack of a standard method more directly applicable to the effluents. Herschmiller (4) studied the changes in absorbance of first caustic extraction stage effluent at different concentrations and wavelengths (Figure 1).

B.C. Research (15) has published highly interesting results concerning theoretical estimates of light depletion due to different color concentrations in kraft mill effluents (Table 1). From their results it is obvious that differences in color values as small as 10 units can dramatically reduce the penetration of light. Since photosynthetic activities depend entirely on visible radiation, the extinction of light would correspond to elimination of primary production and consequently, of all the dependent aquatic life.

figure 1.

**ABSORBANCE VERSUS WAVELENGTH
FOR VARIOUS CONCENTRATIONS OF
FIRST CAUSTIC EXTRACTION STAGE
EFFLUENT**

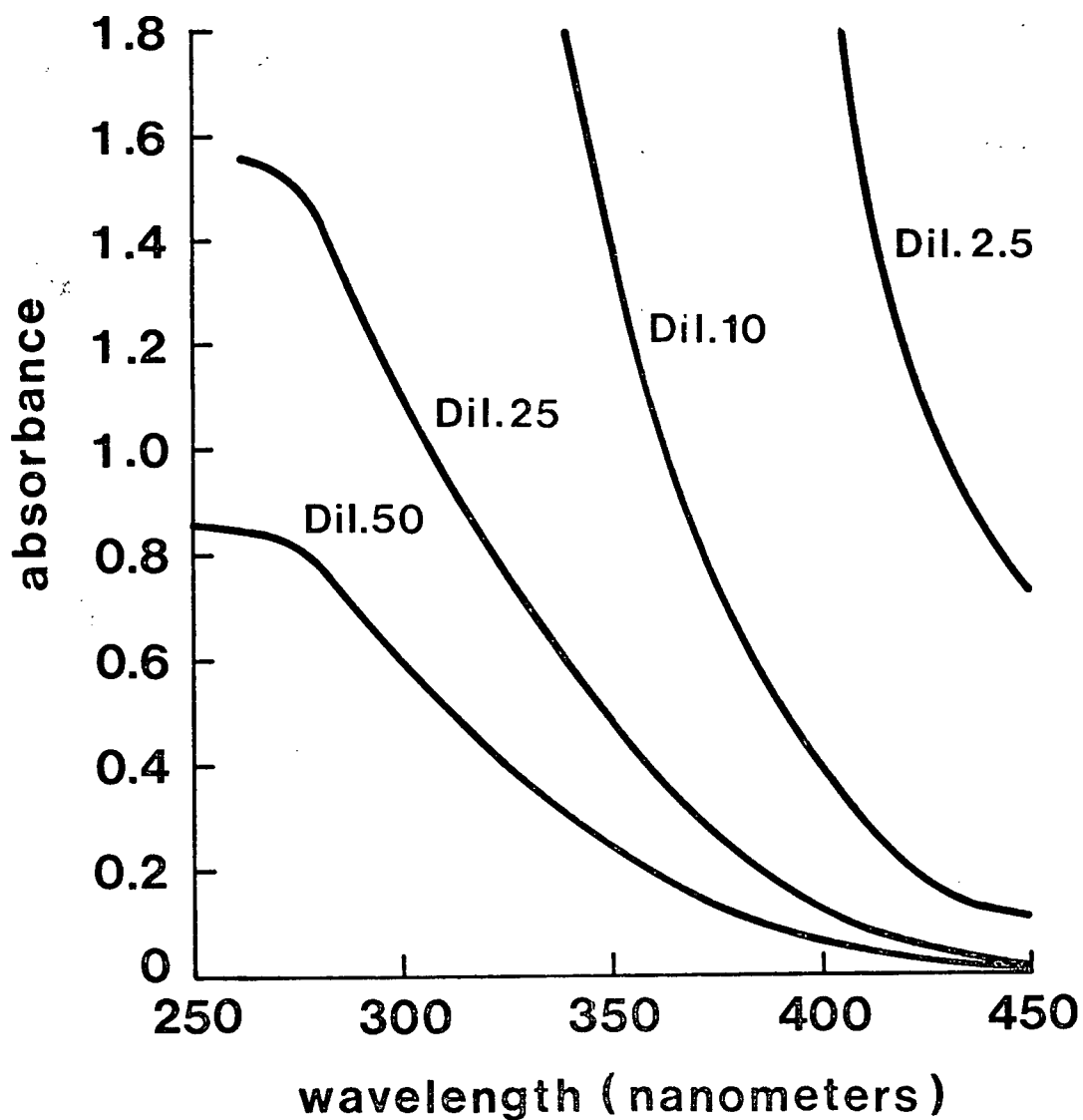


Table 1
Theoretical Estimations of Percentage of Light Transmission at Various Depths
of Water with Various Concentrations of Color, 580 mu

Depths (m)	PERCENT TRANSMISSION AT VARIOUS COLOR UNITS																		
	1	2	3	4	5	6	7	8	9	10	15	20	25	30	35	40	45	50	
1	97.1	94.2	91.4	88.7	86.1	83.6	81.1	78.7	76.4	74.2	63.8	55.0	47.3	40.8	35.1	30.2	26.0	22.4	
2	94.2	88.7	83.6	78.7	74.2	69.9	65.8	61.9	58.4	55.0	40.8	30.2	22.4	16.6	12.4	9.1	6.8	5.0	
3	91.4	83.5	76.4	69.9	63.8	58.4	53.3	48.7	44.6	40.8	26.0	16.6	10.6	6.8	4.3	2.8	1.8	1.1	
4	88.7	78.7	69.9	61.9	55.0	48.7	43.2	38.4	34.1	30.2	16.6	9.1	5.0	2.8	1.5				
5	86.1	74.2	63.9	55.0	47.3	40.8	35.1	30.2	26.0	22.4	10.6	5.0	2.4	1.1					
6	83.5	69.9	58.4	48.7	40.8	34.1	28.5	23.8	19.9	16.6	6.8	2.8	1.1						
7	81.1	65.8	53.3	43.2	35.1	28.5	23.1	18.7	15.2	12.4	4.3	1.5							
8	78.7	61.9	48.7	38.4	30.2	23.8	18.7	14.7	11.5	9.1	2.8								
9	76.4	58.4	44.6	34.1	26.0	19.9	15.2	11.5	8.9	6.8	1.8								
10	74.2	55.0	40.8	30.2	22.4	16.6	12.4	9.1	6.8	5.0	1.1								
11	71.9	58.8	37.3	26.8	19.3	13.9	10.0	7.2	5.2	3.7									
12	69.8	48.7	34.1	23.8	16.6	11.5	8.1	5.7	3.9	2.8									
13	67.8	45.9	31.1	21.1	14.3	9.7	6.6	4.5	3.0	2.1									
14	65.8	43.2	28.5	18.7	12.4	8.1	5.3	3.5	2.3	1.5									
15	63.3	40.8	26.0	16.6	10.6	6.8	4.3	2.8	1.8	1.1									
16	62.0	39.4	23.8	14.7	9.1	5.7	3.5	2.2	1.3										
17	60.1	36.2	21.7	13.1	7.9	4.7	2.8	1.7	1.0										
18	58.4	34.1	19.9	11.5	6.8	3.9	2.3	1.3											
19	56.6	32.1	18.1	10.3	5.8	3.3	1.9	1.0											
20	55.0	30.2	16.6	9.1	5.0	2.8	1.5												
21	53.4	28.5	15.1	8.1	4.3	2.3													
22	51.8	26.8	12.0	7.2	3.7	1.9													
23	50.2	25.2	12.6	6.4	3.2	1.6													

CONTINUED

CONTINUED

Table 1 (Continued)

Depth (m)	PERCENT TRANSMISSION AT VARIOUS COLOR UNITS																	
	1	2	3	4	5	6	7	8	9	10	15	20	25	30	35	40	45	50
24	48.8	23.8	11.5	5.7	2.8	1.3												
25	47.3	22.4	10.6	5.0	2.4	1.1												
30	40.8	16.6	6.8	2.8	1.1													
35	35.1	12.4	4.3	1.5														
40	30.2	9.1	2.8															
45	26.0	6.8	1.8															
50	22.4	5.0	1.1															
60	16.6	2.8																
70	12.4	1.5																
80	9.1																	
90	6.8																	
100	5.0																	
110	3.7																	
120	2.8																	
130	2.1																	

1.2 Removal of Color from Kraft Mill Effluents

There have been numerous techniques proposed for color removal from pulp and paper mill effluents. Of these methods the best prospects for a commercially viable process are: a) lime coagulation, b) adsorption on activated carbon, c) flotation techniques, and more recently ultrafiltration. The bulk of all the published material related to color removal from kraft mill waste waters is summarized in Appendix E. The present discussion is concerned only with previous work directed toward removal of the color of the wastes by applying flotation techniques. The main features of these flotation techniques will be outlined in the next section.

First Hutchinson (17) in 1958, followed by Waldichuk (18) and several other authors (19,20), pointed out very interesting developments in which advantage was being taken of the natural foaming tendency of kraft mill effluents to remove certain undesirable constituents from the wastes.

The experimental work performed by Warner and Miller (21) indicated that it is possible to remove 18 to 37% of the lignin dispersed in water by means of foam thus removing a considerable amount of the color present in the kraft effluent.

Of special interest is a paper published by Wilson and Wang (12) in 1970. Their work compared the percentage of color removed, in terms of lignin concentration, achieved

by two different flotation techniques: foam fractionation and ion flotation. The effects of different factors, such as pH, surfactant dosage, dissolved and suspended solids concentration were also studied. Their most striking result was to prove the ineffectiveness of foam fractionation as a method for color removal as opposed to ion flotation.

Recently Das (11) explored the possibilities of a precipitation-flotation process. First, multivalent cations, i.e. Ca^{++} , Mg^{++} , Al^{+++} were added to the kraft effluent at a pH below the level of their hydroxide precipitation. The cations reacted with the strongly negatively charged chromophoric colloids forming an insoluble, hydrophilic, gelatinous precipitate. Next, sufficient cationic amine was added to render the precipitate hydrophobic and hence to remove it as a dry scum by flotation. Nevertheless, the objective - to float the precipitate (dispersed air flotation) by treating with amine, even up to 500 ppm dosage, was not successful. Instead, it was noted that the cationic amine alone, at substantially lower dosage, was capable of reacting with the color bodies at pHs between 3 and 4 forming a hydrophobic precipitate which floated without any aeration. The results indicated that at an optimum amine dosage of 300 ppm, pollution reduction to the extent of 88% color, 67% COD (chemical oxygen demand), 70% TOC (total organic carbon), 42% BOD (biochemical oxygen demand) and 100% turbidity could be obtained.

The work reported by Hayes and Munroe (3) represented a new approach to the general trend followed in ion flotation experiments. They evaluated the removal of color bodies from kraft mill effluents by adding, to a fixed amount of alum, various concentrations of selected cationic, synthetic, high molecular weight polyelectrolytes at different pHs. The dosage of each flocculant-aid ranged from 0.5 to 3 ppm and the pH values from 5.5 to 10.0. The presence of interaction between pH and flocculant concentration became evident from the resulting plots, although the authors made no attempt to explain it. It was also established that the flotation time decreased as the dosage of flocculant-aid was increased. The highest value obtained was 5-6 minutes with calgon WT-2600. All the experiments were performed with a dispersed air flotation system because of the faster formation and separation of the floc. In their miniplant studies it was claimed that a decrease of 90% in color, 50% in BOD and 66% in COD occurred.

The most extensive work done on the subject was carried out by Herschmiller in his M.A. Sc. thesis (4). He performed a series of batch runs in a rather simple flotation cell. The waste water used was Canadian Forest Products Limited, Port Mellon Division, combined effluent. The temperature of the effluent was adjusted to 22°C, and the amount of waste used was 2.5 liter in each run. The collector used was didodecyldimethylammonium bromide. The per cent of color

removed and of solids floated were evaluated under different values of the following parameters: i) surfactant or collector dosage, ii) pH, iii) sparger porosity and hence, indirectly, bubble size, iv) surfactant premix time, v) air sparge rate, vi) colligend-collector ratio. However, the possibility of any interaction between such factors, was not investigated. In his batch results, flotation recovery and color removal were found in excess of 95% at optimum conditions; also precipitate flotation of the third type was pointed out as the principal mechanism of the process.

Further research based on Herschmiller's thesis was carried out by Chan *et al.* (10) in another set of batch experiments. They screened a wide variety of surfactants and found that quaternary ammonium salts worked best. The most effective commercial one found was Aliquat 221 (dimethyl dicoco ammonium chloride manufactured by General Mills Chemicals Inc., Kanakee, Illinois). They also noticed that there was an optimum dosage of surfactant (500 ppm). If this optimum was exceeded the treated effluent became cloudy or turbid. The best pH range was found to be 3.0 to 5.0. A total decrease of 95% in color and 80% in floatable solids was claimed.

Up to the present the ion flotation process has not been applied commercially to the removal of color from kraft mill wastes.

1.3 Essentials of Adsorptive Bubble Separation Techniques (22)

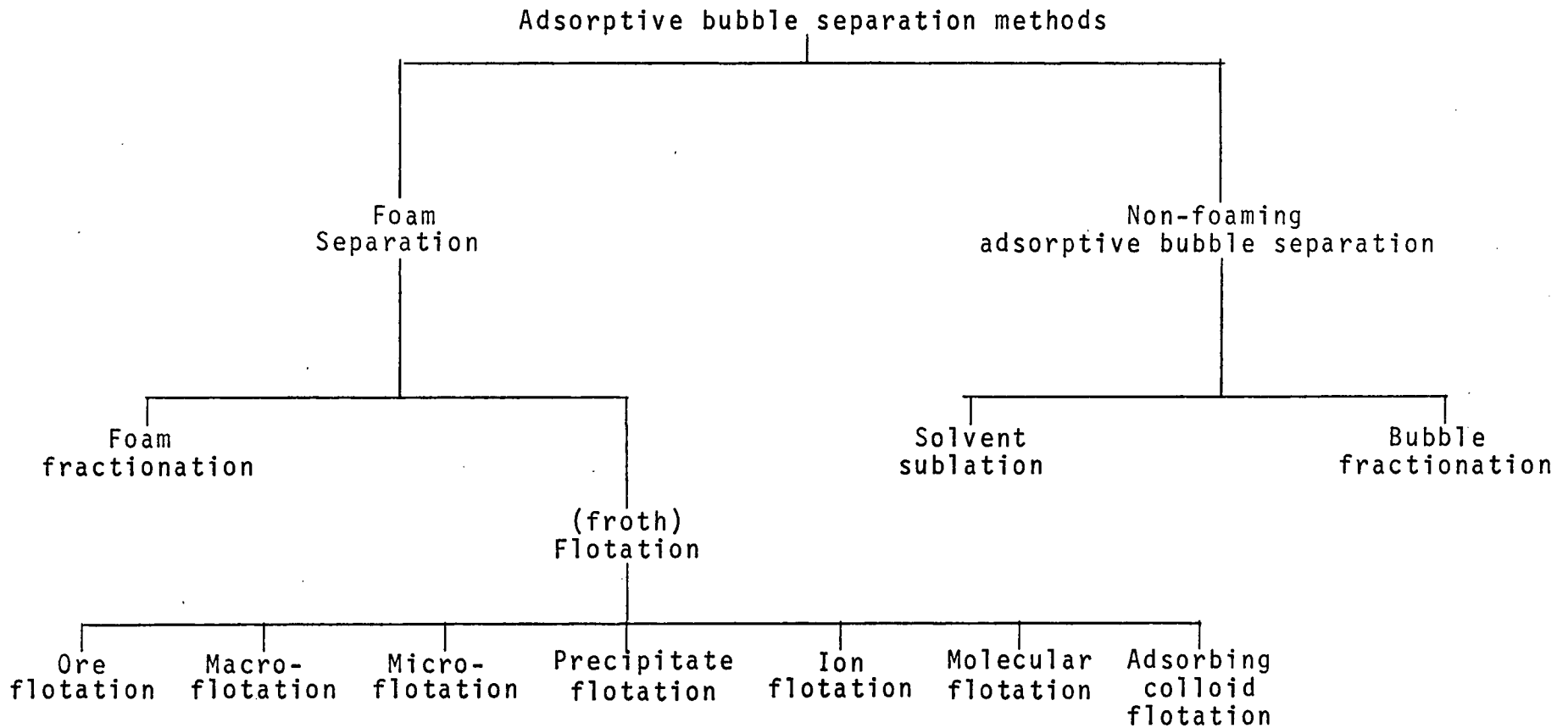
Adsorptive bubble separation techniques are based on differences in surface activity. Material, which may be molecular, colloidal, or macroparticulate in size, is selectively adsorbed or attached at the surfaces of bubbles rising through a liquid, and is thereby concentrated or separated. A substance which is not surface active itself can often be made effectively surface active through union with or adherence to a surface active *collector*. The substance so removed is termed a *colligend* (23).

There are a number of individual adsorptive bubble separation techniques. Table 2 shows the scheme of classification proposed by Karger *et al.* (24). These techniques (or methods) are divided unequally into two main groups: the larger, called foam separation, requires the generation of a foam or froth to carry off material. The smaller, which is termed nonfoaming adsorptive bubble separation, does not.

This smaller division is further divided. Bubble fractionation (25) is the transfer of material within a liquid by bubble adsorption or attachment, followed by deposition at the top of the liquid as the bubbles exit. Solvent sublation (23) is the similar transfer to, or to either interface of, an immiscible liquid placed on top of the main liquid. The larger division is also subdivided. Foam fractionation is the foaming off of dissolved material from a solution via

Table 2

Schematic Classification of the Adsorptive Bubble Separation Techniques



adsorption at the bubble surfaces. Froth flotation, or simply flotation (26), is the removal of particulate material by frothing (foaming).

Froth flotation, in turn, has many subdivisions. Ore flotation (26) is the separation of minerals. Macroflotation is the separation of macroscopic particles. Microflotation (27) is the separation of microscopic particles, especially colloids or microorganisms (under certain conditions, the separation of colloids may sometimes be termed colloid flotation). Molecular flotation is the separation of surface inactive molecules by foaming with a collector which gives an insoluble product. Adsorbing colloid flotation is the separation of a solute through adsorption on colloidal particles which are then removed by flotation.

Theoretically ion and precipitate flotation differ from one another in that with the latter process the component to be removed is precipitated before the addition of collector. Still, Lemlich (22) defines three types of precipitate flotation:

- a) Precipitate flotation of the first kind involves the flotation of precipitated particles by a surface-active species; the latter is not a chemical constituent of the precipitate substance and occurs only on the surface of the particles.
- b) Precipitate flotation of the second kind uses no surfactant to float the particles but two hydrophilic ions precipitate to form a solid with hydrophobic surface.

- c) Precipitate flotation of the third type is a form of ion flotation, in which ions are precipitated by surfactants, and the resulting particles are floated.

According to Rubin and Johnson (28), while ion flotation requires stoichiometric or greater concentrations of collector, precipitate flotation is effective in some systems in which the colligend ion concentration is 100 times that of the collector. In addition, ion flotation is very sensitive to gas flow rate which affects the rate of removal; to collector concentration which determines the amount removed but not the rate; and to ionic strength which affects both the rate and total removal. Precipitate flotation on the other hand is relatively insensitive to gas flow rate and collector concentration and completely independent of ionic strength. Since the difference between any two of these processes is very subtle and most of the time there is an overlap in the definition, the reader is referred to the excellent treatise of Lemlich (22) for more details on each specific method.

1.4 Micelle Formation and Critical Micelle Concentration in Aqueous Solutions of Surfactants

A distinctive feature of surface active ions and molecules is their tendency to form, in the interior of their solutions, aggregates known as *micelles*, with resultant anomalies in the physical and electrical properties of their solutions. Micelle formation takes place above a certain

temperature (*Krafft point*) and a certain concentration (*Critical Micelle Concentration*). The aggregates arrange themselves in such a way that the hydrocarbon chains are close together and directed away from the water, and the charged hydrophilic ends are in contact with the water (23). This structure gives the micelles a thermodynamically more stable state. The presence of a hydrophobic part in the amphipathic monomer confers on the molecule its surface active properties but its micelle forming capability as well. Therefore, in striking contrast to monomers, the micelles which have a hydrophilic exterior, are not surface active (29).

The *Krafft point* (20) is characterized by a sudden increase in the surfactant solubility, reached at a certain temperature, below which the solubility of the surfactant is negligible. Above the *Krafft point* the micelle is the thermodynamically preferred form (31). For that reason only the micelle and not the solid agent exists (32). At this point the saturation concentration stays almost constant and is called *Critical Micelle Concentration* (33,34,35,36,37).

In the interests of strict accuracy (38) it is important to emphasize that the formation of micelles from the constituent monomers involves a rapid, dynamic, association-dissociation equilibrium. Experimentally it is found that micelles become detectable over a narrow range of concentrations as the total concentration of solute is increased.

As such, the concentration dependence of the degree of micellization changes gradually. A truly abrupt, discontinuous transition is excluded (32,39,40). Besides there is not a unique number of monomers which can form a micelle but a range with relatively wide limits. Hence micelles are polydisperse (41). This is in agreement with the fact that the average micellar size varies continuously with conditions such as temperature, concentration of surfactant, concentration of counterions or other additives, nature of counterion, chain length and structure. It follows that in the Critical Micelle Concentration region not one kind of micelle, but many kinds appear, each with a slightly different ionic dependence and most likely different charges or even none at all (35).

The concentration at which micelles become first detectable depends on the sensitivity of the experimental probe used. Because the Critical Micelle Concentration is not a sharply defined point above which some properties are qualitatively different from those below it, all properties of a solution in this region are expected to vary in a continuous manner. There is, nevertheless, a relatively narrow region of concentrations in which those changes are most marked. Operationally, the Critical Micelle Concentration, is usually obtained by plotting some solution property against surfactant concentration and taking it to be the first evident deviation from monomeric behavior (37).

Well above the Critical Micelle Concentration, in aqueous media, there occur extensive interactions between micelles, which are often difficult to unravel, particularly if the micelles are ionic. In such concentrated solutions, many physical properties of solutions exhibit breaks or kinks somewhat similar to the ones that take place at the Critical Micelle Concentration where micelles first form. The concentrations where such breaks or kinks happen are frequently described as "the second Critical Micelle Concentration" (42,43). This phenomena is not well understood but it clearly involves changes in inter-micellar interactions as also monomer-micelle interactions.

The preceding information has been exclusively concerned with those facts that will be proven important in discussing the results of the present work. For a complete discussion of micelles, in general, any one of a number of excellent texts on surfactants or surface activity could be consulted (35, 36,37,44,45).

1.5 A Word of Caution Concerning the Design and Analysis of Flotation Experiments (46)

A properly designed experimental investigation of the effects of changes in flotation variables will provide for measurement of the effects of interactions among the variables. Yet many flotation experimenters

are victims of erroneous ideas as to how experimentation should proceed. They attack investigation of several process variables by holding all constant except one, varying it over a range until an apparently optimum level for best results is obtained. They then hold this variable constant at its optimum level, varying a second variable until its optimum level is found. Holding the first two constant at their supposed optimums, they proceed in similar fashion for the third variable. Finally, they end up with what they consider to be an optimum combination of levels of the variables. Implicit in such a procedure is the assumption that the effects of each variable are independent of the levels of all others; there are no interactions. In flotation this is seldom the case, nor is the combination so arrived at necessarily the optimum.

No one has any real understanding of any flotation operation unless he understands the nature of the significant interactions among the important process variables. Such understanding can seldom be deduced from theoretical knowledge, and, in fact, most apparent discrepancies between expected behaviour based on theory and actual behaviour of flotation systems are probably simply manifestations of such interactions. Only by including studies of the effects of several variables in the same group of experiments can such interactions be properly delineated, and this is but one more reason for proceeding by groups of tests in any experimental program.

Chapter 2

OBJECTIVES OF THIS WORK

The efficiency of the flotation process in removing the color fraction from kraft mill effluent is generally defined in terms of the percentage of color removed. A standard color technique is applied to this purpose. In his thesis work Herschmiller (4) introduced the concept of floatable solids under certain assumptions and suggested an analytical technique to determine them (see Appendix C). After preliminary experiments it was found that neither procedure was accurate in expressing the flotation efficiency. The results of both techniques are affected by the required filtration stage and can even be highly misleading, as it will be proven later in this essay. For that reason, the first objective in mind was to develop a method of expressing the process result. The amount of floatable solids was determined with a completely different approach (see Appendix C). Through this, it was feasible to express the response of the process in three complementary ways: a) % surfactant floated, b) ratio of solids floated/surfactant floated, c) % solids floated.

Once the primary difficulty was solved, it was possible to lay out the experimental objectives as follows:

1. Studies on the floatability of the pure surfactant.

The main objective of these experiments was to investigate the behavior of an aqueous solution of the surfactant:

- i) at different pHs
- ii) at different surfactant dosages

2. Studies on the flotation process applied to kraft mill waste water. The effects of pH and surfactant dosage on each of the responses was investigated in order to disclose any significant interaction among them. Depending on the results, a general regression model for the effects of the studied factors or the optimum set of conditions was to be established and applied to a continuous process. The outline of the experiments was:

2.1 Batch Experiments

- i) interrelation between % surfactant floated, pH and amount of surfactant added,
- ii) interrelation between ratio of solids floated/surfactant floated, pH and amount of surfactant added,
- iii) interrelation between % solids floated, pH and amount of surfactant added.

2.2 Continuous Experiments

Since most previous work had been done on a batch basis, and since the process, if it were ever to be used industrially, would have to operate continuously, experiments, using the best conditions observed in batch runs, were done on a continuous operation basis.

3. Studies of the influence of the pH adjustment and elapsed time on kraft mill waste water. A careful record was kept of the observed changes in color values and total solids content of the ageing effluent after its pH adjustment, in comparison to the original sample. The relative filterability of the effluent was also noticed but in a rather qualitative manner.

4. Studies on the behavior of the kraft mill waste in the following sequences: i) acidification-alkalization-acidification; ii) alkalization-acidification-alkalization-acidification.

Chapter 3

EXPERIMENTAL

3.1 Batch Studies

3.1.1 Design of Experiments

As mentioned, the main objectives of the set of batch experiments were: a) to determine if the two factors, pH and amount of surfactant added, had an influence on the responses; b) to disclose whether there was a significant interaction between the factors and if so, to establish the optimum conditions for the process. For these purposes a set of 3^2 factorial experiments was designed. The set was chosen with one replication per cell, with evenly spaced values of the fixed variables (*Model I*) and executed in a completely randomized order. The selected design had the following advantages:

- i) Any interaction between the factors was detectable;
- ii) A general regression model for the effect of the main factors on the response could have been easily computed in the event that no interaction had been present.
- iii) Any effect due to ageing of the effluent within one set of

experiments or any variation in the quality of the effluent from set to set would have been counteracted by the randomization of the experimental order.

To collect the required data for the eighteen intended experiments it was necessary to carry out a total of 27 batch experiments, grouped in three different sets; see Appendix D. The eighteen selected experiments are summarized in Table 3.

3.1.2 Apparatus

Figure 2 shows a schematic of the apparatus used in this work. Laboratory air was passed to the flotation cell through a pressure regulator and its flow was measured and adjusted with a rotameter. The rotameter was calibrated at the working pressure of 10 psig with a bubble meter. All gas flows are reported in ml/sec at 10 psig and room temperature.

The flotation cell consisted of a large pyrex glass bottle from which the bottom had been removed. The cell was about 16 cms in diameter at the top and held a volume of 2.5 liters, with room for a two and one-half centimeter froth bed.

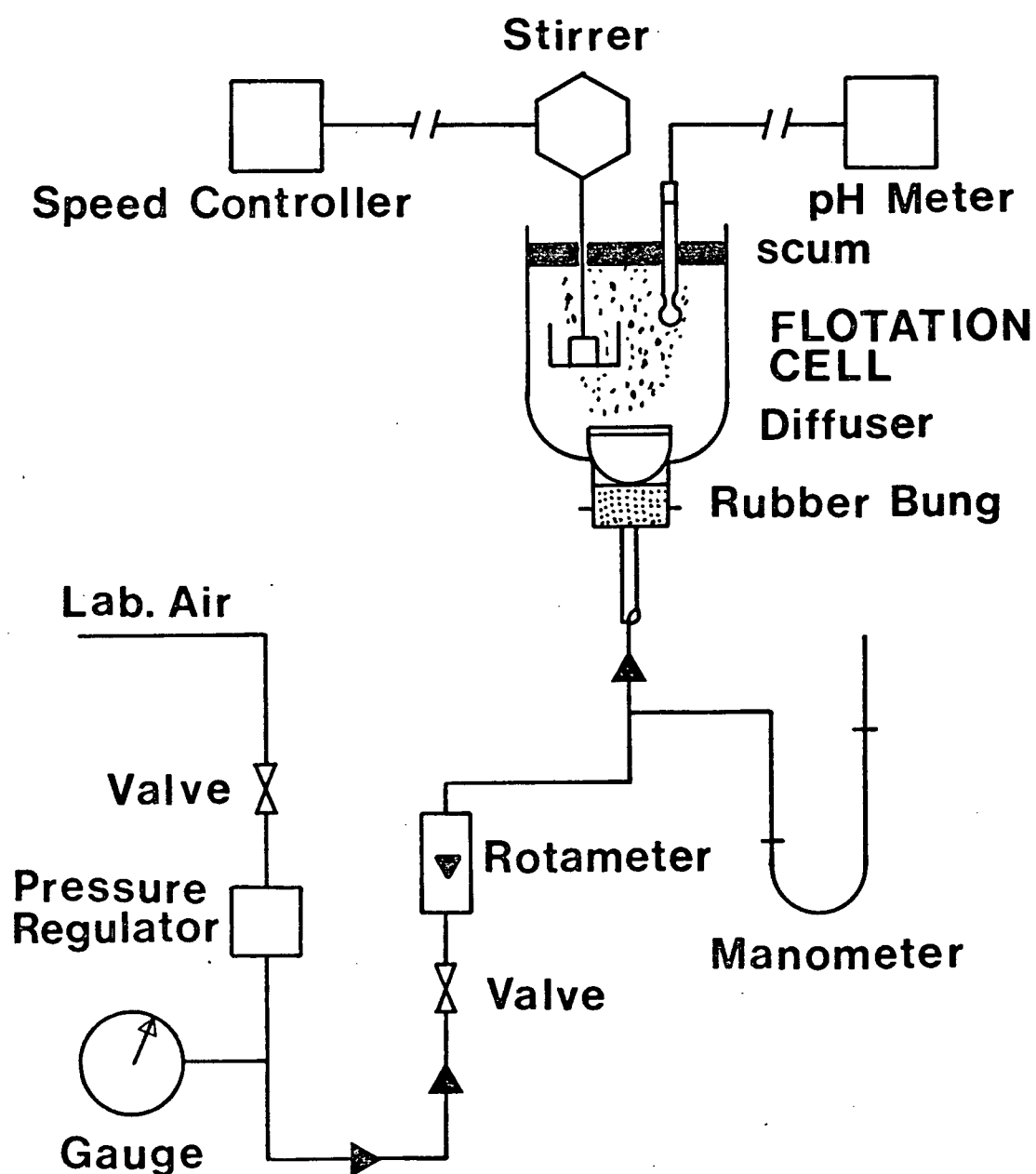
The diffuser consisted of a 5.4 cm diameter fritted glass sparger (Corning Glass Works). The nominal-maximum pore size was of 4-5.5 microns. The diffuser was positioned

Table 3
Experimental Results from the Factorial Experiments

pH	ppm of Surfactant Added	Set	Days After Sampling	% Surfactant Floated	<u>Solids Floated</u> <u>Surfactant Floated</u>	% Solids Floated
3.6	100	2	5	90.38	1.67	20.49
3.6	100	3	7	90.0	1.47	24.26
3.6	150	2	4	87.33	1.34	20.80
3.6	150	3	3	80.33	0.875	21.65
3.6	200	2	12	81.25	0.97	20.08
3.6	200	2	19	81.	0.802	19.11
4.6	100	2	17	30.0	0.80	3.41
4.6	100	3	5	17.0	1.24	4.0
4.6	150	2	7	67.66	1.36	15.66
4.6	150	2	13	70.66	1.25	17.25
4.6	200.	2	16	75.0	0.94	18.23
4.6	200	3	6	51.0	0.64	13.23
5.6	100	1	14	24.5	0.53	1.78
5.6	100	2	8	27.0	0.185	0.581
5.6	150	2	6	24.66	0.16	0.71
5.6	150	3	1	6.66	.53	0.819
5.6	200	3	2	25.0	1.78	17.52
5.6	200	3	20	32.0	0.88	11.27

figure 2.

SCHEMATIC DIAGRAM OF THE APPARATUS USED IN THE BATCH EXPERIMENTS



11.5 cms from the top of the vessel by means of a rubber bung, which also sealed the bottom of the cell. The froth was removed manually with a small scoop.

A digital pH meter was used for measuring the pH. The color test readings were taken in a Unicam SP.800B scanning spectrophotometer and the surfactant concentrations were determined colorimetrically using a Bausch and Lomb Spectronic 20. Provisions for initial stirring of the surfactant were available in the form of a lab stirrer with speed control.

3.1.3 Materials

The waste waters used were different samples from Crown Zellerbach (Elk Falls Division) effluent. The waste was shipped from the mill in five-gallon containers; upon arrival some was stored at a temperature of 4°C and the rest frozen. As the time and temperature of storage of the waste water could have a marked influence on the experimental results, it was necessary to keep a careful record of the sample's history. The collector solution was prepared by dissolving a weighed quantity of didodecyldimethylammonium bromide (obtained from Eastman Kodak) in 10 ml of low water content (0.10%) methanol. The required amount of methanol and the stirrer speed were determined in earlier experimental runs.

3.1.4 Procedure

One and a half liters of the stored waste water were poured into a one gallon battery jar and mixed with an equal volume of distilled water. Dilute sodium hydroxide, or hydrochloric acid was added to adjust the pH of the effluent to a value required for the particular test. The temperature of the solution was recorded, then two liters were transferred to the flotation cell and the rest saved for color and total solids analysis. In the third set of experiments the same analyses were also performed on samples of the diluted solution taken previously to its pH adjustment. The stirrer was placed in the effluent and started at 950 RPM. At this point the collector solution was added by means of a hypodermic syringe at an approximate rate of 0.2 cc/sec. The stirring was continued for five additional minutes at the same speed. Next the stirrer was removed from the flotation cell and the air flow started and adjusted to 1.66 cc/sec. The air was allowed to bubble for fifteen minutes, regarding zero time as the moment when the bubbles first emerged through the diffuser. Once the set time had elapsed the air flow was stopped and sample of the remaining solution were taken to analyse for color, total solids and residual surfactant.

The experiments performed with distilled water to study the surfactant behavior were carried out with the

same general procedure. Herschmiller's modified color test (4) was used unaltered to determine the color of the samples. The method of van Steveninck and Maas for quaternary ammonium detergents was adapted for determining the concentration of residual surfactant (see Appendix C). At first the determination of floatable solids was done after Herschmiller's suggestion but later on this was found to be not satisfactory for the experimental work intended and thereafter a different approach was developed (see Appendix C).

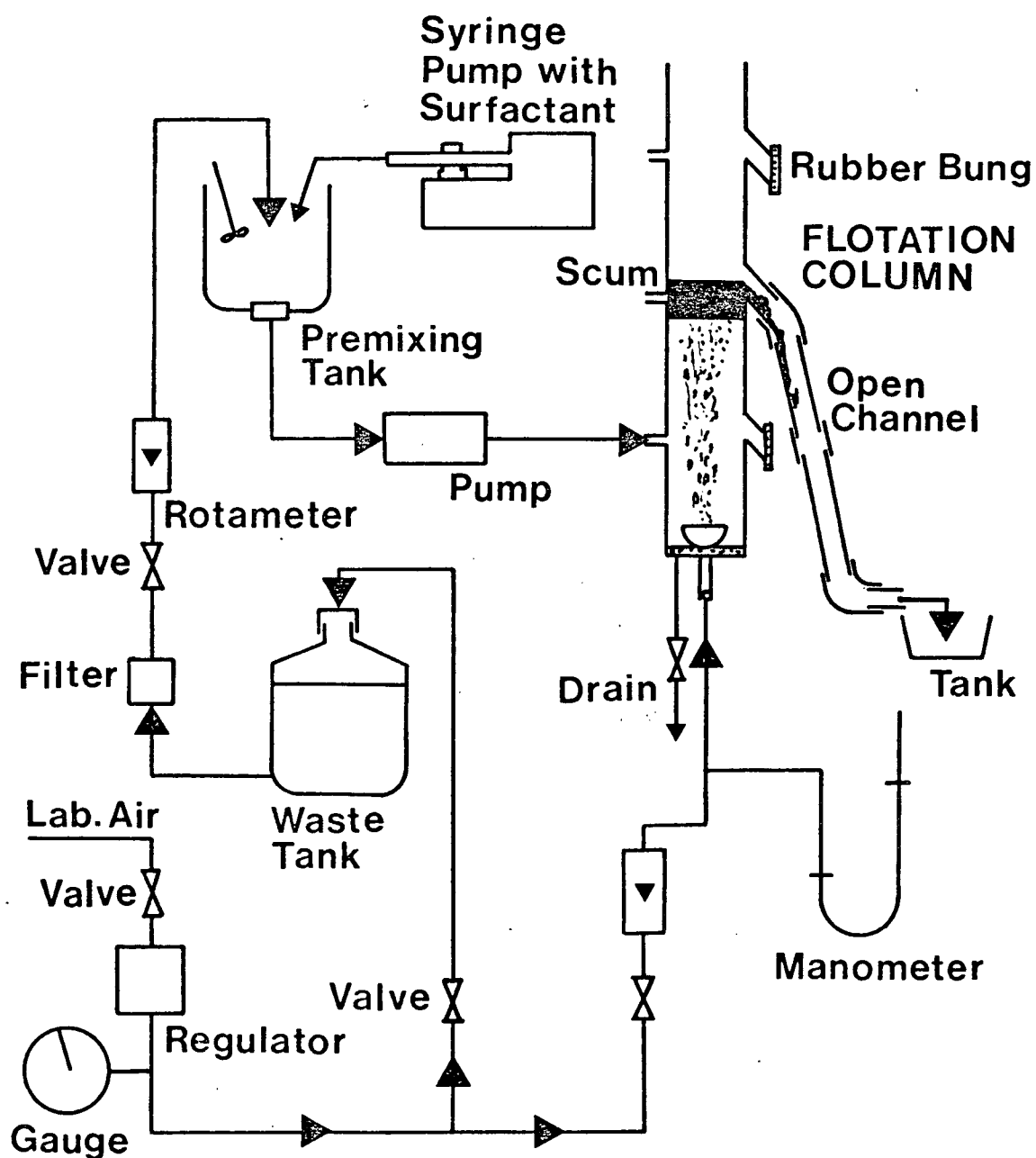
3.2 Continuous Studies

3.2.1 Apparatus

The continuous apparatus assembled is shown schematically in Figure 3. It can be divided into three functional component groups: the effluent and surfactant feeding system, the premixing tank and the flotation column. The effluent feeding system consisted of a 13 gallon, polyethylene tank with an inlet for regulated laboratory air on top and with its bottom connected via a rotameter to the mixing tank. A cartridge filter was placed in-line before the rotameter to prevent it from clogging. Calibration of the rotameter was undertaken but no sensible departure was found from the manufacturers calibration curve. The surfactant solution

figure 3.

SCHEMATIC DIAGRAM OF THE FLOTATION APPARATUS USED IN THE CONTINUOUS EXPERIMENTS



was prepared in a separate container and then added through a syringe pump. Both streams discharged into the top of the premixing tank.

A glass bottle, with its bottom removed, served as the premixing tank. It was conveniently sized to give the required retention time. A rubber bung was used to seal the container and a short outlet placed in it. The stirrer used in the batch experiments provided the necessary mixing. A peristaltic pump coupled to a variable speed drive transferred the mixture to the flotation column. Tygon tubing 1/4 O.D. was employed for all the different liquid carrying conduits. The required settings for the different delivery rates used had to be previously determined for both pumps.

The plastic flotation column was three inches in inside diameter and four feet high. Three one-inch diameter froth removal ports were provided 15, 27 and 39 inches from the bottom flange of the column. Two liquid feed positions were located opposite to the first two ports and one was placed four inches from the column bottom. The system was quite versatile allowing a wide variation in liquid height and feed position in the column, enhanced by the variable speed pump. The diffuser from the batch experiments was fitted to the bottom of the column. The same instruments previously described were used for analysis and pH adjustment.

3.2.2 Materials

These were the same as those used in the batch studies.

3.2.3 Procedure

The raw effluent was diluted with an equal amount of distilled water and its pH adjusted to 3.6. These two steps took place in an open glass container which facilitated both operations. The solution was poured into the effluent tank and its temperature recorded. Samples were saved for color and total solids analysis. The weighed surfactant was dissolved in methanol up to a concentration of 10 mg/cc and transferred to the syringe pump. Regulated laboratory air was allowed into the waste tank and the pressurized effluent delivered to the mixing tank. The flow was adjusted to the desired rate. After two or three minutes the stirrer and the syringe pump were started. The stirrer speed was set at 950 RPM. The surfactant was added so as to keep the ratio 100 mg of surfactant/liter of effluent. The retention time in the premixing tank was five minutes. During the first eight minutes the effluent from the tank was discarded. Next, the aeration of the column was commenced; the air flow rate was adjusted to 1.66 cc/sec (at 10 psig) and the surfactant-waste mixture was connected to the lowest liquid inlet of the column. The liquid level was allowed to rise to

the required height, and kept constant thereafter. Once the process was running under these conditions for two hold-up times and fifteen extra minutes, the first sample was drawn. The second sample was taken fifteen minutes later. All the samples withdrawn were analysed for residual surfactant and total solids.

It must be emphasized, that any attempt made to run the process continuously omitting the stirring during the premixing stage or the entire stage completely did not succeed. On the other hand, one qualitative continuous run in which the air entrained during the stirring stage was the only source of aeration; was highly satisfactory.

Chapter 4

RESULTS AND DISCUSSION

4.1 Studies on the Floatability of Pure Surfactant

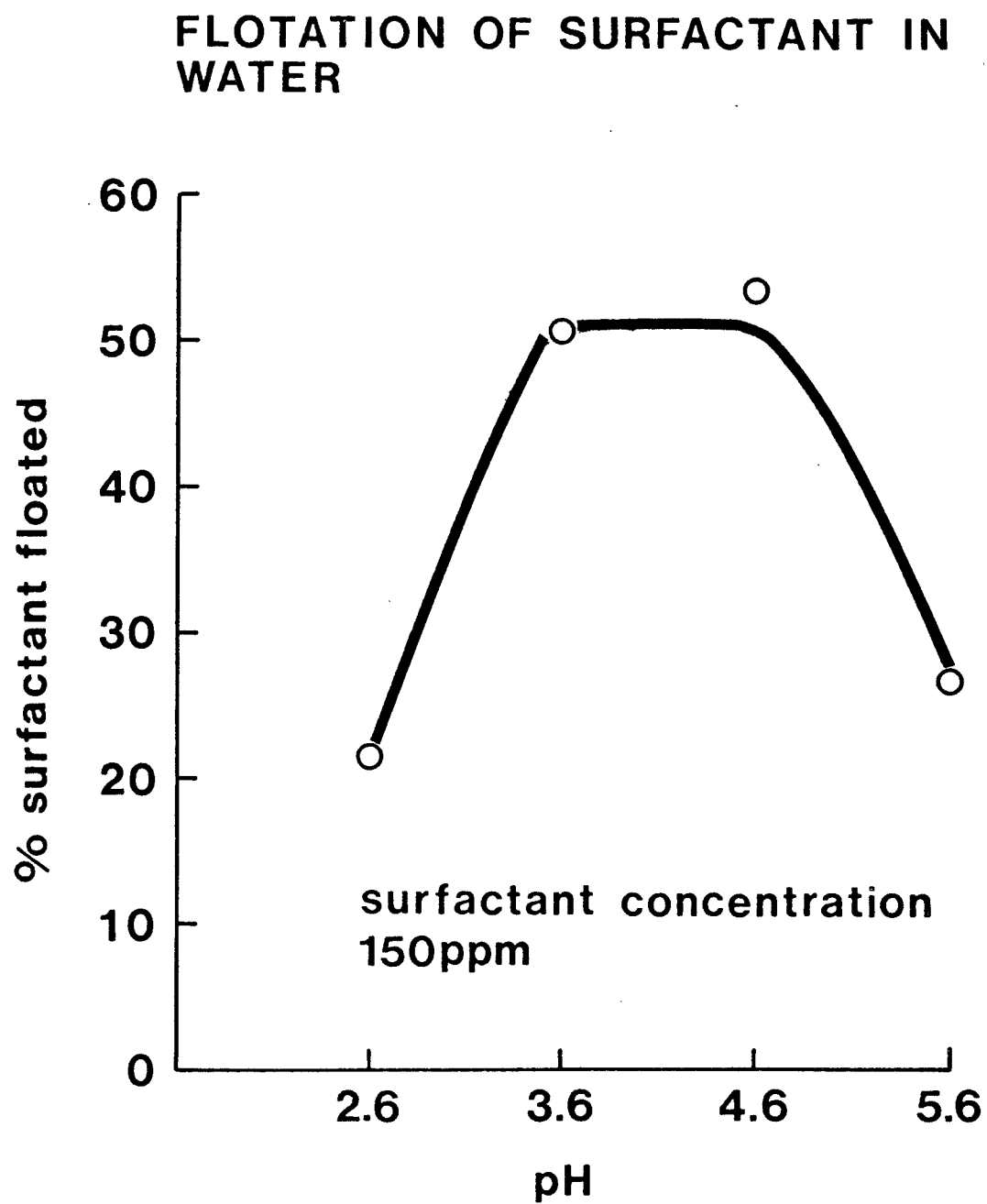
Two series of batch experiments were carried out to establish the effects of hydrogen-ion concentration and of surfactant dosage on the amount of surfactant recovered by flotation. As mentioned before, the same general experimental procedure was applied in all runs. The temperature was kept constant at 25°C.

4.1.1 Effect of pH

All experiments involved initial solutions of concentration 150 ppm in surfactant. The chosen amount was the midpoint of the exploratory range intended to be used later, with the kraft mill effluent. The effects of the hydrogen-ion concentration were determined at pH values of 2.6, 3.6, 4.6 and 5.6 as indicated in Figure 4.

It is evident from Figure 4 that the maximum recovery of surfactant is constant over the range pH 3.6-4.6. At lower

figure 4.



or higher pH values the percentage of surfactant floated drops to almost half its maximum. Quaternary ammonium salts are generally considered to be almost completely ionized in solution (47) and therefore to function as ordinary strong electrolytes (48). Nevertheless McBain (49) has held that associated ions are present even in very dilute solutions. Moreover Ralston *et al.* (50,51) have established the presence of ionic aggregates for higher dialkylquaternary ammonium chlorides (didodecyldimethylammonium chloride among them) in the vicinity of their CMC. Since the property of foaming depends on single ions (23) rather than on ionic aggregates, it seems plausible to conclude that the overall electrostatic equilibrium between ions and ionic aggregates is greatly affected by pH. For that reason, the percentage of surfactant floated could be indicative of the relative amount of un-associated species in solution.

From the data obtained in Figure 4, the following conclusion can be inferred for the pH values studied:

At 150 ppm of surfactant and 25°C, the range of pH 3.6-4.6 forms a plateau outside of which the concentration of ions in solution is greatly diminished.

4.1.2 Effect of Surfactant Dosage

The second series of experiments was performed with the pH adjusted to 4.6, its most promising value for an

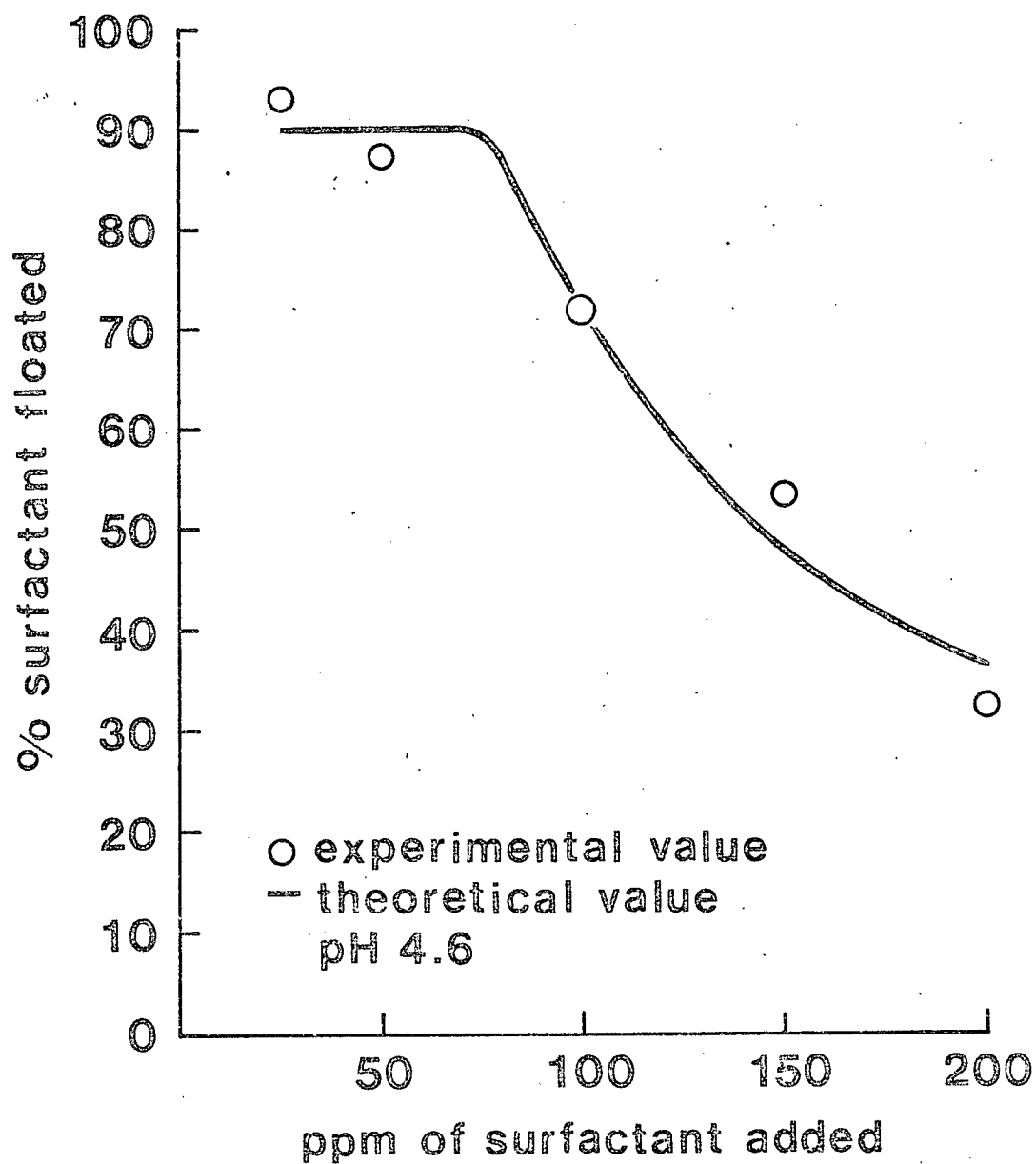
ion flotation process. The effect of the surfactant concentration was determined over the range 5.41×10^{-5} , to 4.2×10^{-4} (25-200 ppm) as indicated in Figure 5.

Very scarce information has been published dealing with the expected Krafft point for the higher dialkylquaternary ammonium compounds. All the work done in this field has been limited to establishing the Critical Micelle Concentration of a certain surfactant at a certain temperature, regardless of how far above the Krafft point the temperature is. The main reason for this particular attitude seems to lie in the fact that

. . . although the solubility of amphipathic electrolytes changes very rapidly in a small temperature interval when the Critical Micelle Concentration has been reached, the Critical Micelle Concentration is not itself markedly influenced by temperature. (35)

Ralston *et al.* (50,51) pointed out the dependence of Critical Micelle Concentration on temperature. From their experiments it can be seen that as the temperature is increased, the slope of the precritical range becomes steeper but the critical point itself occurs at almost the same concentration for temperatures ranging from 20° to 60°C. Hutchinson and Winston (33) found no significant difference in the Critical Micelle Concentration of dodecylammonium chloride in a temperature increase of 10°C. Adam and Pankhurst (52) established 20°C as the Krafft point for hexadecyl (cetyl)

figure 5.

FLOTATION OF SURFACTANT IN
WATER

trimethylammonium bromide. The Critical Micelle Concentration for didodecyldimethylammonium chloride is given as 1.8×10^{-4} moles/liter (75 ppm) by Shinoda (36). The original paper (34) mentioned 30°C as the temperature at which the experiment was carried out, but no reference is made concerning the expected Krafft point.

Another important piece of information is that the Critical Micelle Concentration for an alkylquaternary bromide is equal or slightly less than its corresponding chloride (36). Thus, bearing in mind all these facts, it will be assumed:

- a) The Critical Micelle Concentration of didodecyldimethylammonium bromide is in the vicinity of 75 ppm. (36)
- b) The temperature at which the experimental work was done (25°C) is above the Krafft point of the referred surfactant.

A quick inspection of the experimental results (Table 4) indicates that any increase of surfactant concentration above a certain critical point causes a marked depression in the percentage recovered by flotation. Additionally, below this critical concentration, the percentage of surfactant floated levels out at a definite constant value.

This critical point is regarded by most authors (32,33,39,53,54,55,56,57,58,59,60) as,

Table 4
Experimental Results Obtained for Didodecyldimethylammonium
Bromide at pH 4.6 and 25°C

Concentration in ppm	% Floated ± 3%	Amount not Floated, in ppm	Amount Floated, in ppm	Theoretical Amount to be floated, in ppm
25	93.12	1.72	23.28	22.5
50	87.50	6.25	43.75	45.0
100	72.5	27.50	72.5	72.5
150	53.33	70.0	80.0	72.5
200	32.50	135.0	65.0	72.5

. . . a saturation point for single surfactant ions; above this concentration micelles form, and any surfactant in excess of this concentration which is added to the solution is entirely in the form of micelles.

It was already mentioned that higher dialkylquaternary ammonium compounds associate first, at low concentrations, into ionic aggregates; followed by the formation of micelles once the Critical Micelle Concentration is reached. The micelles are attributed to the incorporation of undissociated molecules into the ionic aggregates (34). Taking into account all these facts it is possible to conclude from the obtained data:

- a) The Critical Micelle Concentration for didodecyldimethylammonium bromide at pH 4.6 and 25°C is $72.5 \pm 3\%$. Note the close agreement of this value with the figure reported by Shinoda (36) for the chloride.
- b) Below the Critical Micelle Concentration only 90% of the surfactant was found to be in the ionic form and hence recoverable by flotation. Presumably, ageing of the stored surfactant is partially responsible for such behavior.
- c) Above the Critical Micelle Concentration only 72.5 ppm of the surfactant is recovered by flotation. The remaining amount is associated either in the form of large ionic aggregates, ionic micelles or neutral micelles. In any case the association rendered the colloidal particulates unfloatable.

Figure 5 compares the theoretical behavior against the actual values. The agreement is quite good and in most cases within the percentage of error attributed to the analytical techniques used for determining the surfactant concentration. The theoretical points were calculated on the following basis: a) Below the Critical Micelle Concentration 90% of the surfactant is recoverable by flotation, b) Once the CMC region is passed only 72.5 ppm of the surfactant are recoverable by flotation.

Because no other type of interaction is present, it is most probable that the tendency displayed in Figure 5 will be followed at other pH values. The main predictable difference would be a shift in the Critical Micelle Concentration from 72.5 ppm at a pH 3.6-4.6 to a much lower value at ranges 2.6-3.6, 4.6-5.6. Since the pH values outside the 3.6-4.6 range lacked any practical interest for the work intended, this assumption was not confirmed.

4.2 Studies of the Flotation Process Applied to Kraft Mill Waste

4.2.1 Batch Experiments

The design of the set of batch experiments has already been described. Preliminary experiments indicated that the most instructive results about the flotation process would be obtained, at initial surfactant concentrations ranging

from 100-200 ppm and pH values varying from 3.6 to 5.6. The temperature of the effluent was kept mostly between 25° and 35°C, although no attempt was made to fix it to a certain particular value. It is important to stress that the composition of kraft mill effluent is not always the same. The amount of each component present varies within certain limits depending on the type of wood and process conditions. Each set of batch experiments was performed with different samples from the same mill.

Figures 6, 7, and 8 show the typical average behaviors of each response at the chosen levels of each factor. In each case, the presence of interactions can be inferred by just inspecting the plots. This was confirmed beyond any doubt in the Analysis of Variance performed on the set of data (Appendix A). At this point, it becomes quite obvious that the trends in the data should be analyzed observing the influence of each factor at fixed levels of the other. Any effort to draw general inferences on the main effects caused by the studied factors would be meaningless. Still, it is possible to select pH 3.6 and 100 ppm of surfactant as the best parameters for the process, within the studied ranges.

Since each response has a definite meaning in the process, i.e.

- i) % surfactant floated determines the amount of surfactant consumed during the flotation process, irrespective of whether any color body is being attached to it,
- ii) ratio of solids floated/surfactant floated measures a sort of efficiency of the flotation process,
- iii) % solids floated gives an idea of the possible amount of floatable solids that could be removed from the effluent at certain fixed conditions,

it is mandatory to discuss their tendencies together. Figure 9 will also be helpful in the following discussion.

4.2.1.1 pH 3.6

It has been repeatedly pointed out that the removal of color from kraft mill wastes by addition of cationic surfactants is more successful at low pHs (10,11,12,61). This is in agreement with the behavior displayed by the process in graphs 6, 7, 8. The changes that the flotation process undergoes as the initial dosage of surfactant is increased are remarkably interesting. At 100 ppm, a dark thick scum is formed on top of the solution, during the first two or three minutes that bubbling air is passed through the flotation cell. Thereafter neither scum nor foam is formed and the clear solution remains unaltered. If the surfactant dosage is raised to 150 and 200 ppm, still the scum would be

figure 6.

FLOTATION OF SURFACTANT IN KRAFT MILL EFFLUENT

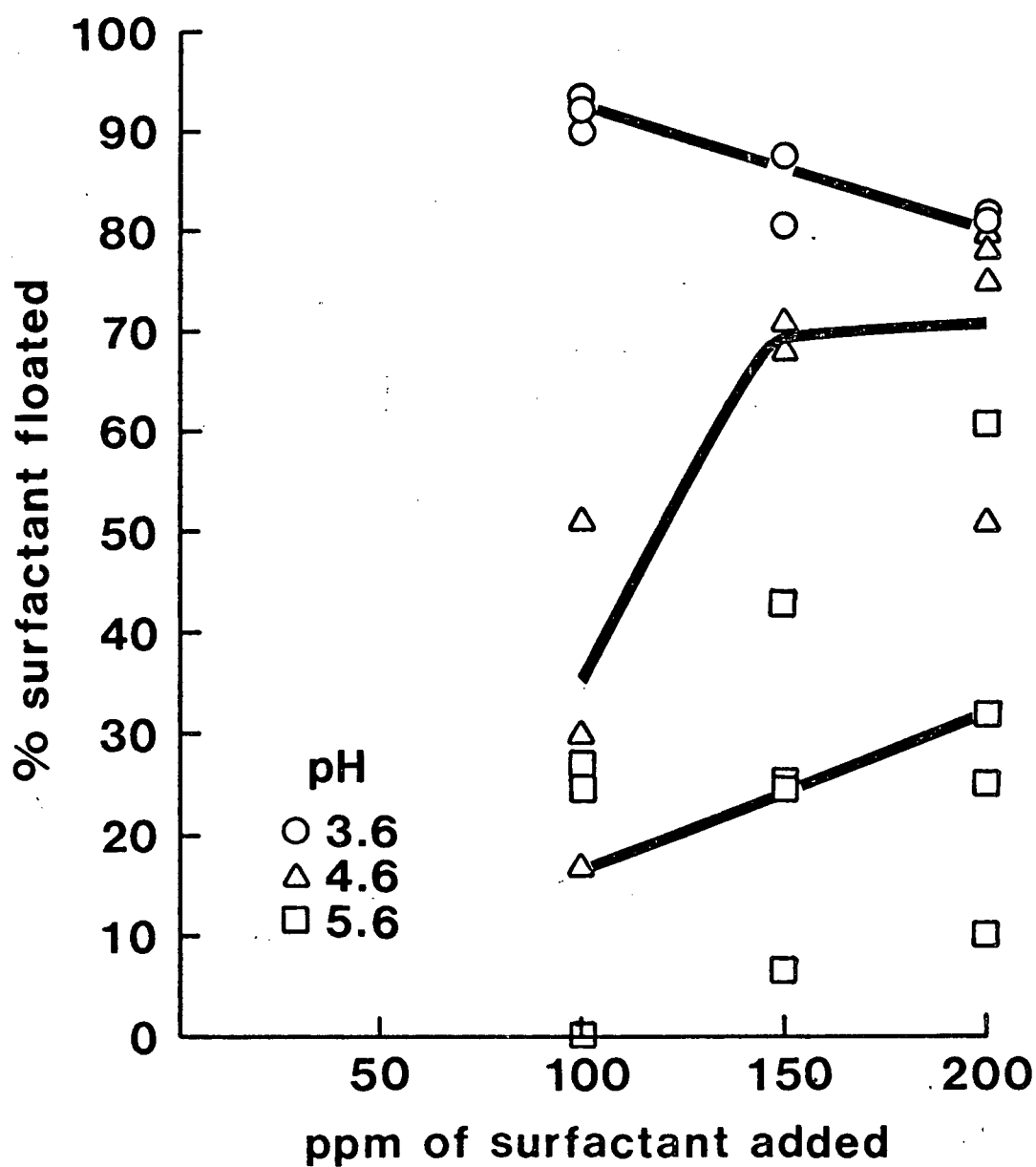


figure 7.

RATIO OF SOLIDS FLOATED TO SURFACTANT FLOATED IN KRAFT MILL EFFLUENT

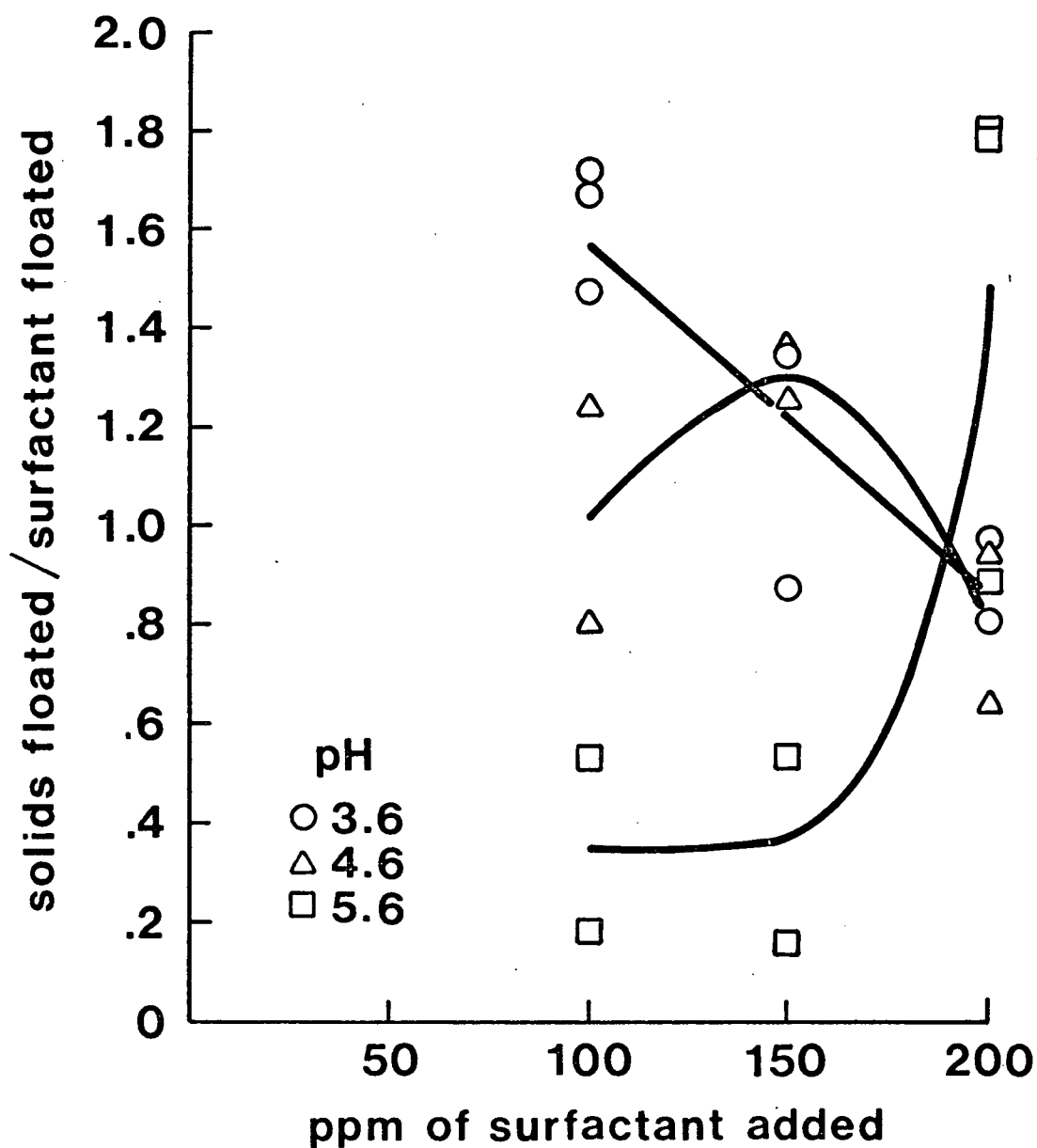


figure 8.

FLOTATION OF SOLIDS FROM KRAFT MILL EFFLUENT

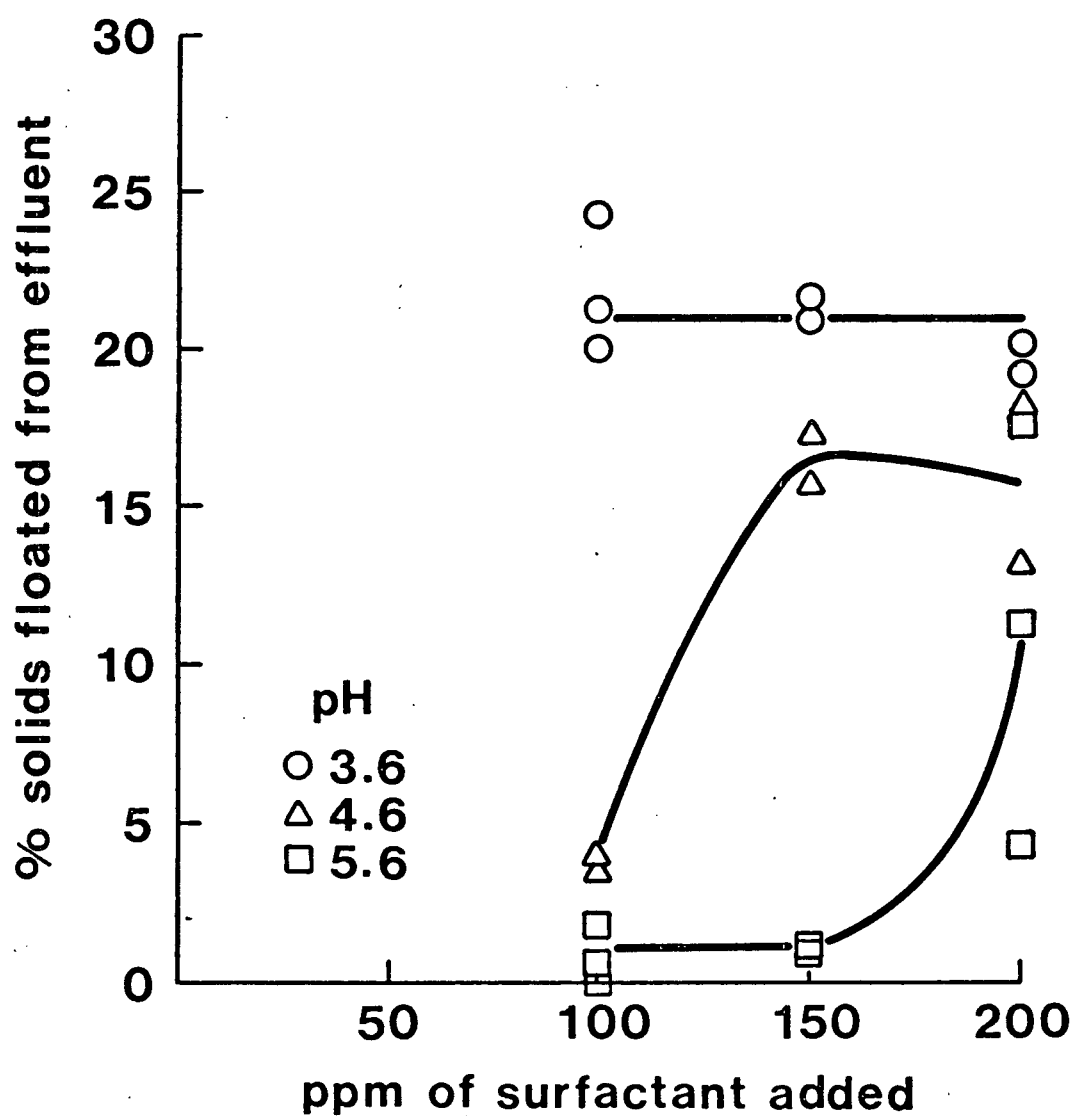
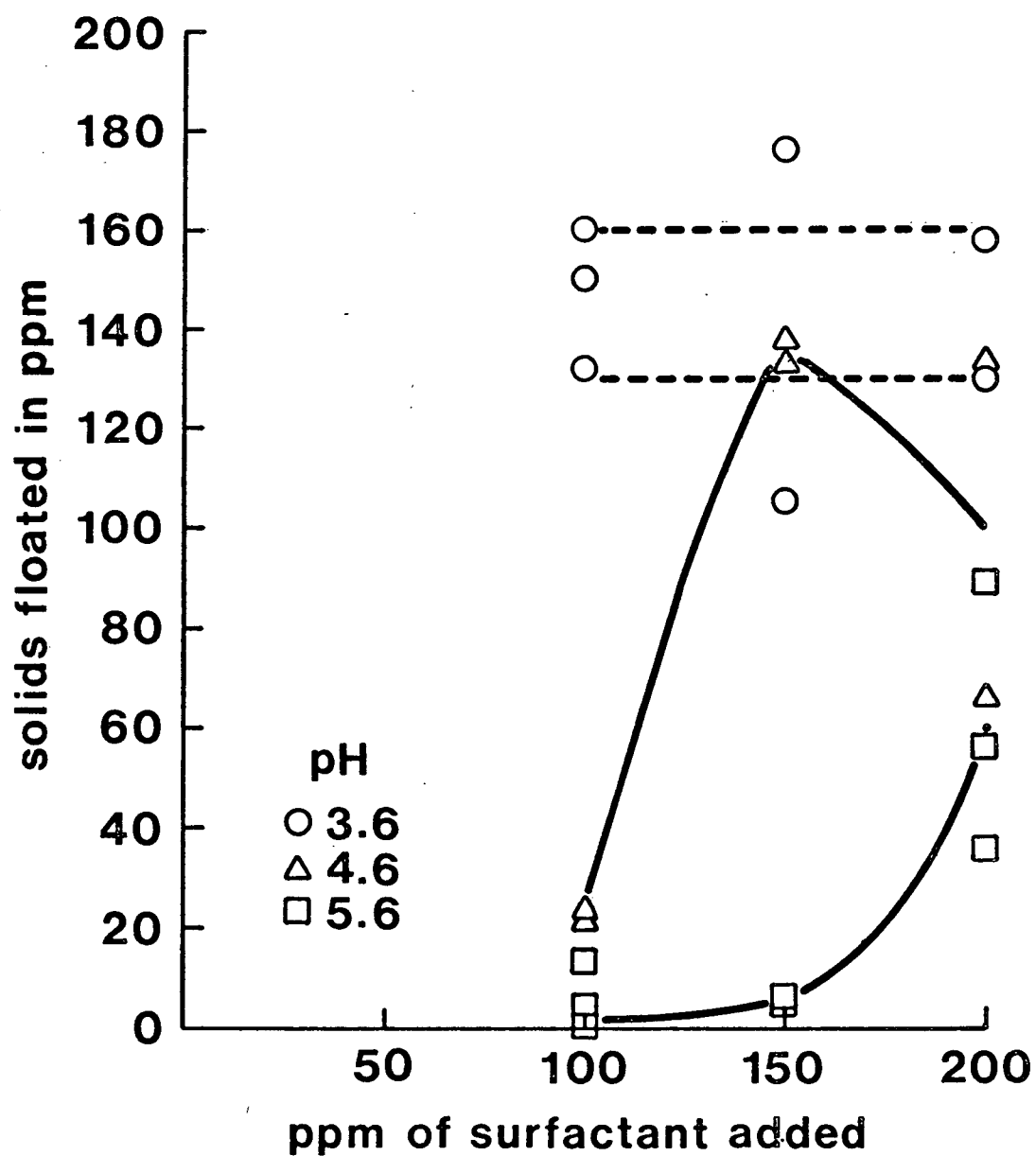


figure 9

FLOTATION OF SOLIDS FROM KRAFT MILL EFFLUENT



formed within the first few minutes, but followed by an increasing amount of a heavy compact, white foam. The following conclusions can be made based on the behavior followed by the process in the studied ranges:

1. The majority of the negatively charged colloids present in the effluent are chromophores. Most of these chromophores are not associated with any other chemical species in the solution.
2. An instantaneous coagulation reaction takes place between the negatively charged chromophores and the hydrophobic cation of the surfactant. The complex (sublate) is insoluble, hydrophobic and easily separable by flotation.
3. The foaming process developed at higher surfactant concentrations must be caused by the excess of surfactant ions in solution. This conclusion is based on the similarity of the type of foam formed with the one produced in aqueous solution of the surfactant at the same pH.
4. There might also be other chromophoric species present in the solution but, most likely, in the form of neutral, insoluble, colloidal aggregates which therefore would not interfere with the electrostatic process described in (2). Nevertheless, they are removed from the solution during the coagulation-flotation process.

According to Figure 8 the percentage of solids floated from the effluent is the same for the three surfactant dosages used. This trend is supported by the linear regression analysis of the data (Appendix B). In terms of Figure 9 this means that the amount of solids that could be possibly

floated is constant and ranges from 130 to 160 ppm. Therefore, any surfactant used in excess of 100 ppm would be wasted. Figure 7 confirms this conclusion since the "efficiency" of the process is highly decreased at surfactant dosages over 100 ppm. These results verify the earlier conclusions made. At the beginning of the process, the primary mechanism is a coagulation reaction between chromophores and cationic surfactant which is not interfered with by any other chemical species present in the solution. Since the reaction is instantaneous and the substrate is immediately floated, there is no interaction with the surfactant in excess, at least in the range under study. Figure 6 implies that, at 100 ppm, 90% of the surfactant is in its ionic form and therefore free to react with the chromophores. This value suggests that the ionic aggregates do not form so readily in the kraft effluent as they do in aqueous solutions. Most likely because of the presence of other competitive species in the waste. At concentrations higher than 100 ppm, the % of surfactant floated does not stay constant at 90%; instead it begins to decrease in a linear relationship (Appendix B). The reason is presumably the development of Van der Waal bonds by the long chain hydrocarbons weaving around colloidal particles still in solution rather than any interaction between the surfactant ions among themselves. In any event

the aggregates are not surface active and consequently not removable by flotation.

4.2.1.2 pH 4.6

The flotation process under study displays its most dramatic changes at pH 4.6. Therefore, it is especially important to understand the nature of those changes since they represent the best source of information regarding the mechanisms involved in the process. At 100 ppm, the process fails completely to produce any scum; only an incipient, light brown froth is formed. Increasing the surfactant dosage to 150 ppm produces spectacular modifications in the process. Immediately, a dark thick scum is formed supported by a heavy, stable, color laden froth. No further development of either froth or scum is observed in the solution. In general, this behavior resembles very much the one exhibited by the process at pH 3.6, 100 ppm. Nevertheless, the turbidity of the remaining solution is considerably higher at pH 4.6. A surfactant dosage of 200 ppm produces, during the first few seconds of the process, a chocolate-colored froth with a cream-colored ring underneath it. Next the ring becomes bigger and paler, finally acquiring the characteristics of the heavy white foam produced by an excess of free surfactant ions in solution. The increase in the turbidity of the

remaining solution becomes quite noticeable. At this point, it seems logical to conclude for the pH under study that:

1. Although the larger percentage of the negatively charged chromophores are not associated, still a certain fraction of them is attached to other chemical species in the solution.
2. The attached moiety of the chromophores competes preferentially for the hydrophobic cation, probably because of the presence of several nucleophilic groups in the aggregate, i.e. a higher intensity of negative charges. The complex formed either is not surface active or it is too strongly bound to the bulk of the solution to be separable by flotation. For that reason, an almost entire lack of froth is observed, as is an increase in the turbidity of the solution.
3. Once the concentration of surfactant is increased to an optimum value where the interfering species are electrostatically satisfied, the coagulation reaction between the unattached chromophores and the hydrophobic cation takes place. The substrate is surface active and is removed by flotation in the form of a froth with a coagulated scum on top.
4. If the concentration of surfactant exceeds the optimum value, the hydrocarbon chains of the substrate begin to associate, a phenomenon akin to the formation of micelles in aqueous solutions and called hemimicelles by Gaudin and Fuerstenau (62). The hemimicelles are not surface active. As the amount of collector is increased, the percentage of free ions also increases and consequently the foaming process.

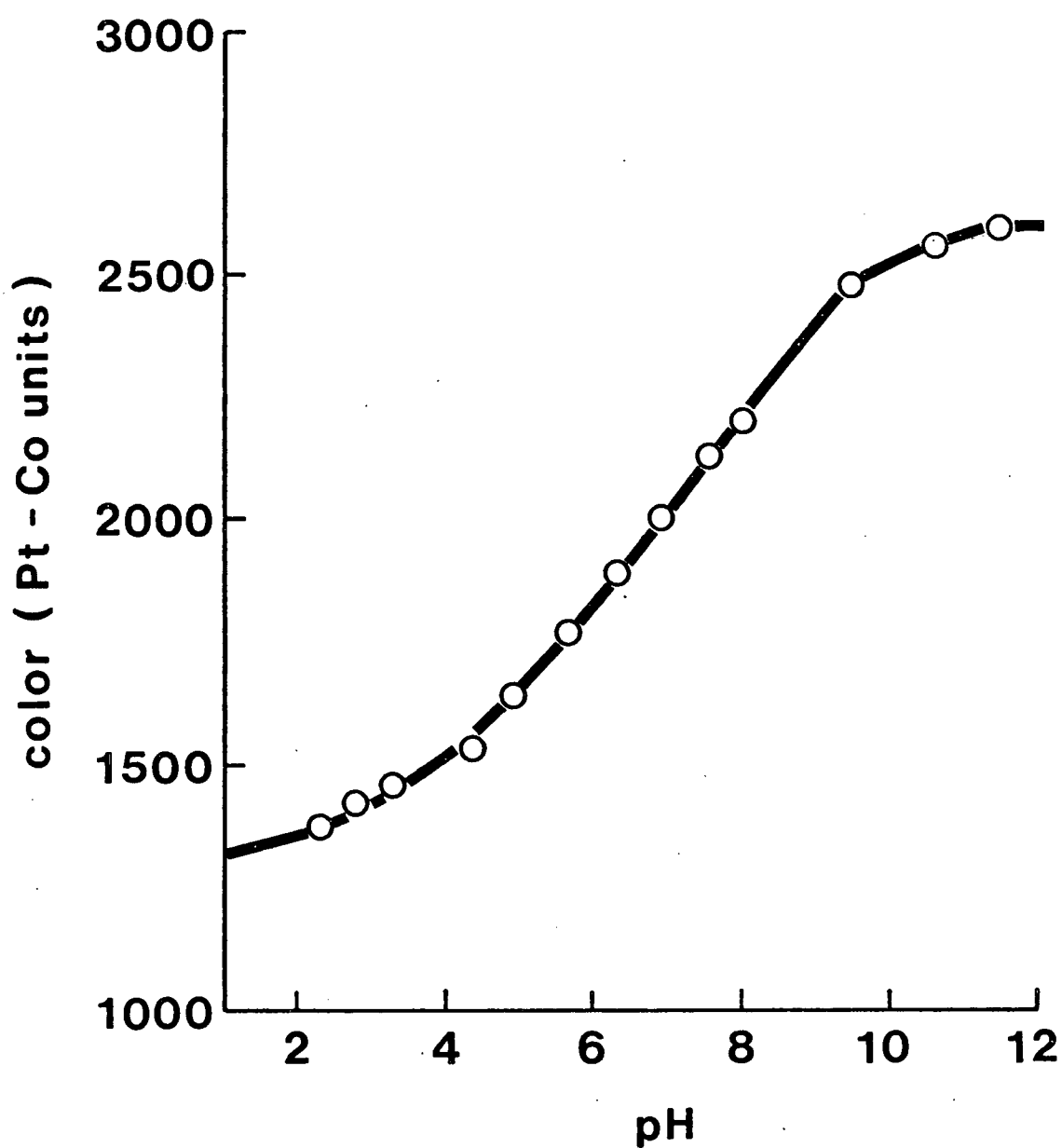
The most important of the previous conclusions (number one) is based on a recent publication by Swanson

et al. (13). These authors have pointed to the presence of a mixture of chromophores in the waste water samples. Since the color of the effluent changes with pH, they suggested, as a plausible explanation, that "the degree of ionization of each chromophore is different at different pH values" (see Figure 10, taken from reference 4). Furthermore, the color bodies were divided into acid-soluble and acid-insoluble groups. Regarding the former it is remarked that "they have low molecular weight, high unconjugated COOH groups, lignin like character, and seem associated with colorless carbon compounds."

It can be observed through Figures 6 and 8 that the percentage of surfactant and solids floated is minimum at 100 ppm and, as is of course, the amount of solids floated (Figure 9). Still, the recovery of some surfactant by flotation at this specific dosage is probably achieved by the presence of some natural surface active species in the effluent and because the coagulation reaction is not completely suppressed. Yet, there are no free surfactant ions in solution as evidenced by the lack of foam. 150 ppm represents the optimum dosage for all the process responses. The process is more "efficient" (Figure 7) and the amount of solids removed by flotation falls within the range of "the amount of possibly floatable solids" (130-160 ppm). At 200 ppm the percentage of surfactant floated remains constant. It seems that the fraction not floated because of Van der Waal interactions is fully replaced by the amount floated as free ions. However, the

figure 10.

COLOR VERSUS pH FOR TOTAL MILL EFFLUENT



process "efficiency" suffers a marked decrease. This is quite understandable since the amount of solids floated (the numerator in the "efficiency" term) is highly affected by the formation of hemimicelles. The drastic change is more easily appreciated in Figure 9 than in Figure 8.

It must be pointed out that the peculiar characteristics exhibited by the process at this pH corresponds quite closely to the ones observed and described by Herschmiller (4) in different aspects of his work. Yet, the effluent used, the set of conditions fixed and the process responses were not the same in his work; also the results obtained were explained using a different approach.

4.2.1.3 pH 5.6

The behavior of the flotation process at pH 5.6 is only a dramatization of what happened at pH 4.6. The same conclusions made before will hold in this case with only one modification; the percentage of attached chromophores is at its highest. Moreover the expectable fraction of surfactant in ionic form is considerably less at this pH (Figure 4). At dosages of 100 and 150 ppm the process only produces a sparse, almost insignificant, light-brown froth. The percentage of surfactant floated increases very little (Figure 6), the process "efficiency" and the percentage of solids

floated remain almost constant. On the other hand, at 200 ppm, a dark brown froth is formed on top of a cream ring, which, again, becomes bigger and paler and finally represents the well known foaming process due to free surfactant ions. It follows that, although an increase in solids floated and process "efficiency" has been suddenly achieved; this will probably be the optimum conditions for the coagulation process since the rest of the chromophores are attached to the nonfloatable complex. Any increase in the surfactant dosage will cause a deleterious effect on the amount of solids removed by flotation. As a rule, the solution becomes more turbid with each increase in the amount of surfactant and there is not a marked improvement at the so-called optimum dosage.

4.2.2 Continuous Experiments

The batch experiments results made it possible to select pH 3.6 and 100 ppm of surfactant as being probably the best parameters for the process. Further batch experiments aimed at diminishing the amount of surfactant per liter of kraft effluent were completely unsuccessful (see Appendix D).

Several preliminary trials were necessary before any positive result could be achieved in the continuous runs. Different methods for mixing the surfactant and the effluent were tried: i) to feed both streams separately into the

flotation column, ii) to add the surfactant to the effluent stream, and then, the mixture, to the flotation column, iii) to set a stirred premixing stage for both streams before they entered to the flotation column. Practically, no results were obtained with the first two procedures. It was also important to keep the air flow rates low since the development of turbulence, at higher values, totally obviated the coagulation-flotation process by redispersing the sublute.

Once the continuous equipment was perfected, it was run using the best batch parameters but various retention times in the column. The results (Table 5) are comparable, in general, to those obtained in the batch runs. The process behaved exactly the same as the corresponding batch experiment. No foam or froth was developed, only a thick dark scum. The treated effluent was virtually colorless. It is clearly noticeable that increasing the flotation time over 15 minutes has a deleterious effect on the process, probably due to redissolution of the precipitate. The percentage of surfactant floated was higher in the continuous run, possibly because a fresh bottle of the reagent was used and, consequently, ageing was not involved.

Table 5

Continuous Experiment Results Obtained at pH 3.6, 100 ppm of
Surfactant and Various Retention Times

Flotation Time (minutes)	% Surfactant Floated	% Solids Floated	<u>Solids Floated Surfactant Floated</u>	Solids Floated (ppm)	Temp. °C
8	98.6	15.06	1.12	110	25°
8	95.0	18.	1.42	133	26°
15	98.6	15.06	1.12	110	25°
15	94.8	17.5	1.35	128	26°
30	94.48	12.62	0.94	93	25°
30	94.5	15.	1.17	111	26°
45	98.22	11.57	0.86	85	25°
45	94.3	12.0	0.94	89	26°

4.3 Studies on the Influence of pH Adjustment and Time Elapsed on the Kraft Mill Waste

4.3.1 Total Solids Content

Neither the samples with their pHs previously adjusted to a certain value, nor the original effluent showed any marked difference in their solids content with time, i.e. within the same batch, since the total amount of solids present could change from batch to batch (Figures 11-A,B,C,D).

4.3.2 Color

While the color of the refrigerated, original effluent remained unaltered during the chosen period of time (Figure 12D), the samples with previously adjusted pH displayed two types of behaviors. Allowing for the expectable color differences between each batch, it could be said that, at pH 3.6, the color value remained practically constant (Figure 12A) but, on the other hand, at pHs of 4.6 and 5.6 there seemed to be a definite decrease of color after the seventh day (Figure 12 B,C). Swanson *et al.* (13) reported the absorption spectra of kraft effluents, at pH 7.6, after storing the samples for 1, 3, 6 and 24 days at room temperature (Figure 13). A marked decrease in color is evident between three and six days of storage.

figure 11.

EFFECT OF STORAGE TIME AND pH ON SOLIDS CONTENT OF KRAFT MILL EFFLUENT

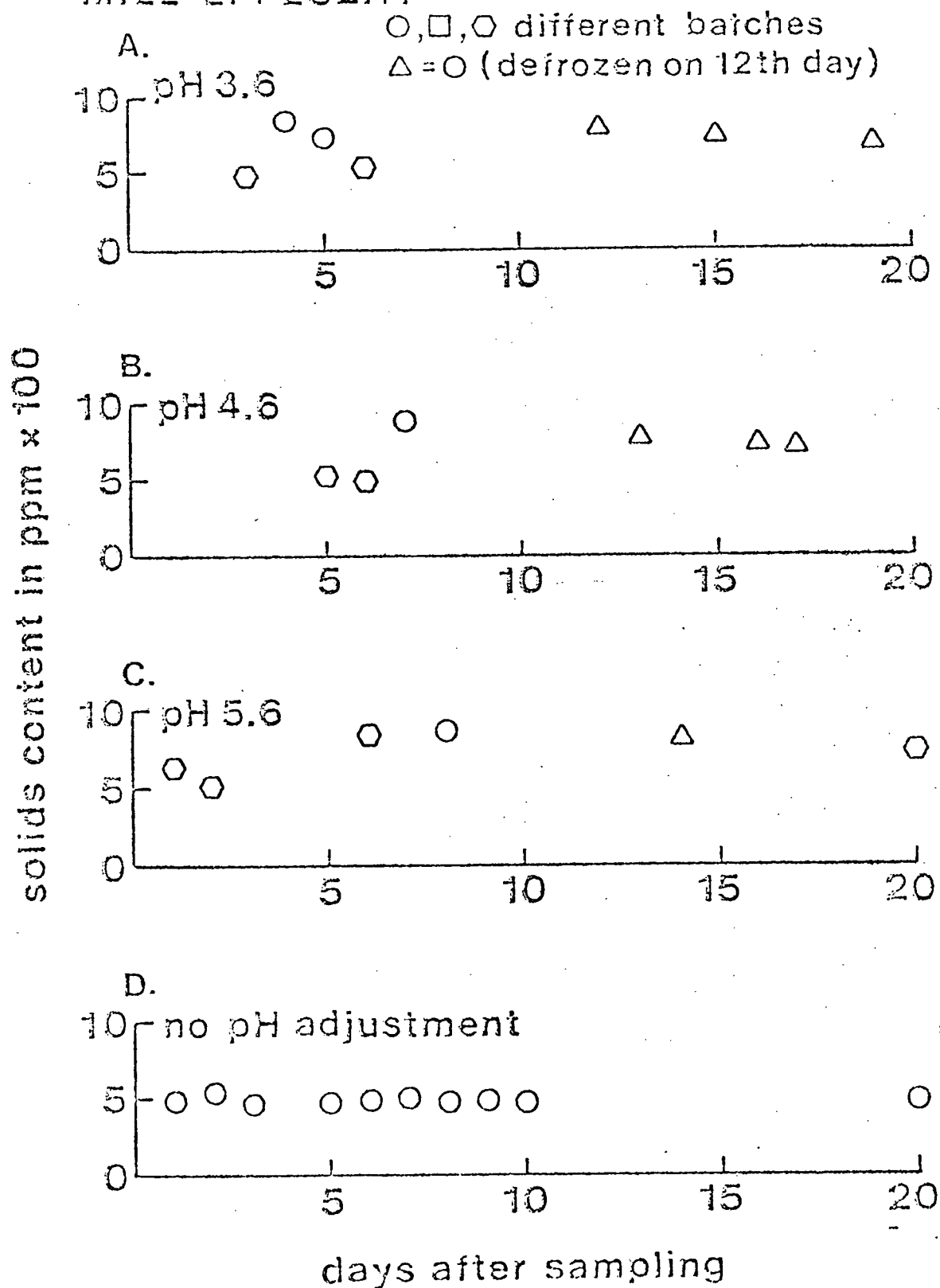


figure 12.

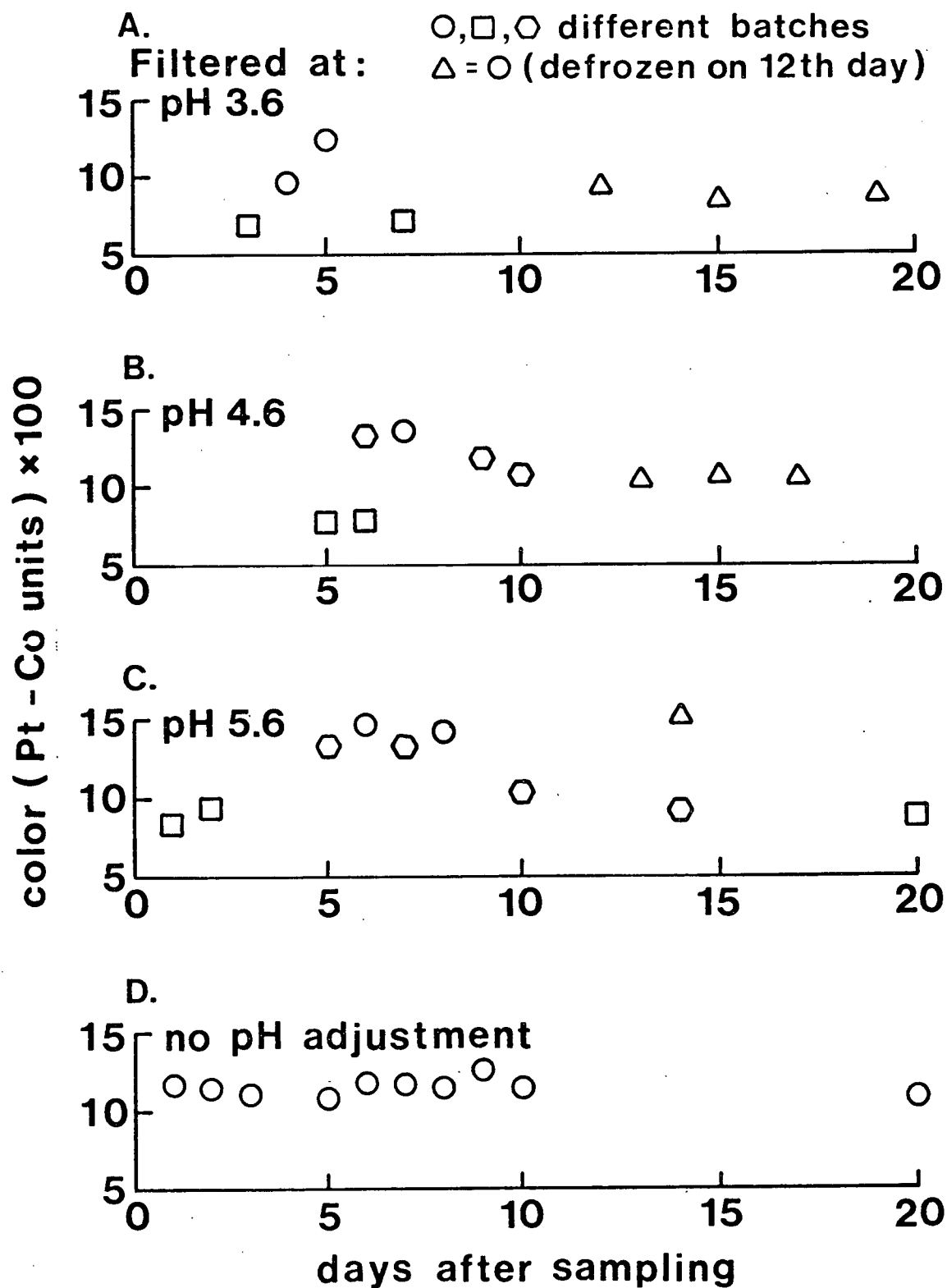
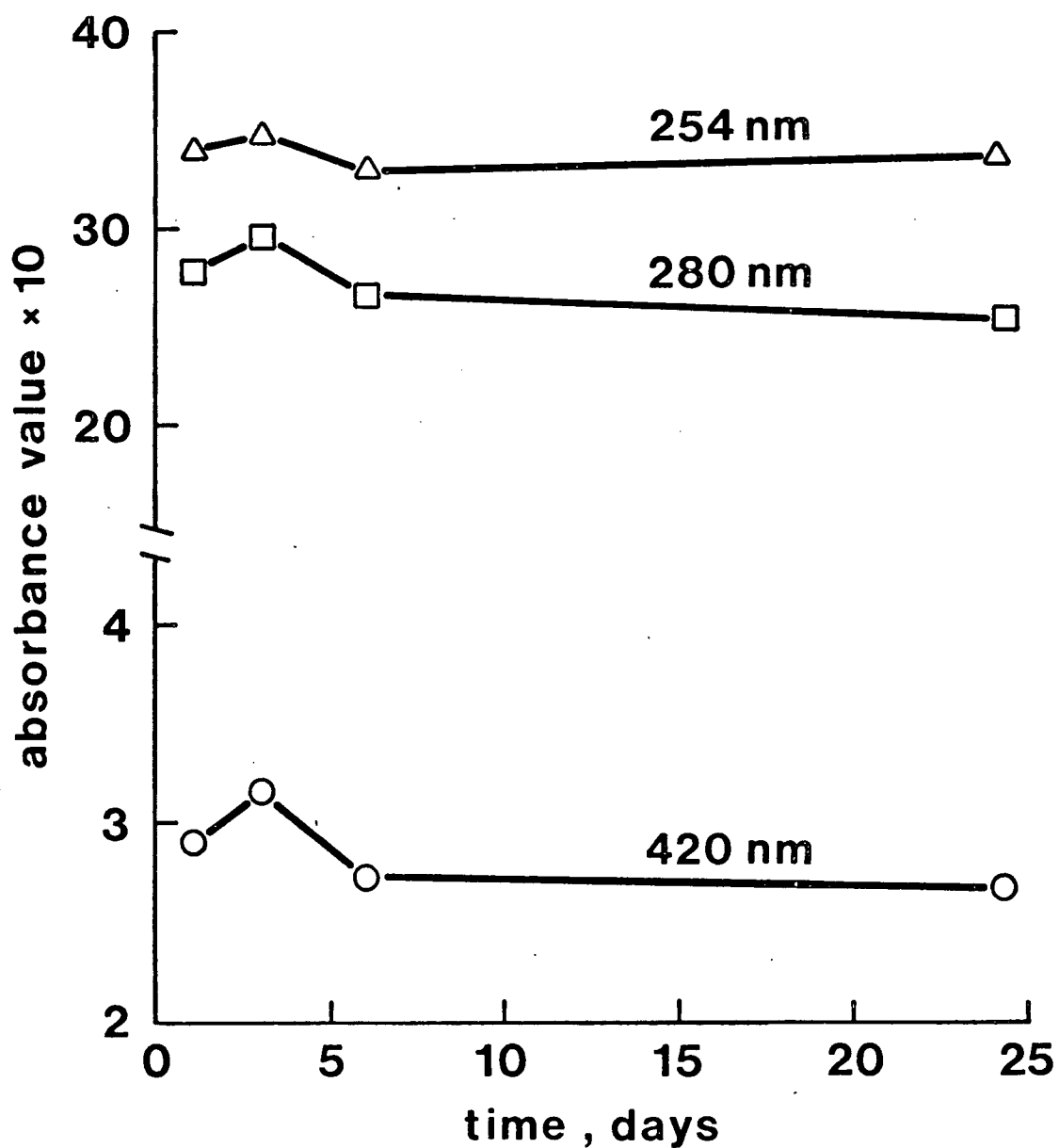
**EFFECT OF STORAGE TIME AND pH
ON COLOR OF KRAFT MILL EFFLUENT**

figure 13.

**EFFECT OF STORAGE ON ABSORB-
ANCE (at pH 7.6) OF UNTREATED
WASTE**



4.3.4 Filterability

The filtration rate of the effluent, which is quite high in alkaline medium becomes much slower at low pH values, especially at 3.6. The possibility of the presence of neutral, insoluble, chromophoric aggregates at this pH has been mentioned already and could probably be the cause for the marked change in the filtration rate. Moggio (63) observed that "the color bodies become increasingly insoluble at low pHs." Brown (64) has also described a similar phenomenon in his experimental work. The color readings, as a rule, are always lower in those samples in which the pH has been adjusted at its lowest value. Therefore, although the color readings are taken at the same pH value for all samples, it is a fact that some color has been left behind during the required filtration stage. It is also noteworthy that, once the flotation process has been accomplished, the fastest filtration rate for the remaining solution is obtained at pH 3.6. This means that most of the colloids and colloid aggregates present (chromophoric or not) have been removed from the solution during the flotation process. Undoubtedly this is in agreement with the quality of the resultant solution. In general, for pH 4.6 and 5.6, the higher the initial amount of surfactant the more turbid the final solution turns. The turbidity of the solution and most of its color is removed during the filtration stage preceding the color test. For that reason,

it is obvious that surfactant and color bodies are bound in a complex, non-floatable aggregate, big enough to be removed by filtration. Figure 14 shows how deceiving the color test can be, if taken as a measure of the process response.

According to it the amount of color removed increases as the dosage of surfactant is raised, regardless of the pH of the effluent. It follows that the presence of interaction is not disclosed. Moreover, the conclusion reached is openly denied by the process behavior since the "worst looking" effluent is obtained when the flotation parameters are set at pH 5.6 and 200 ppm of surfactant.

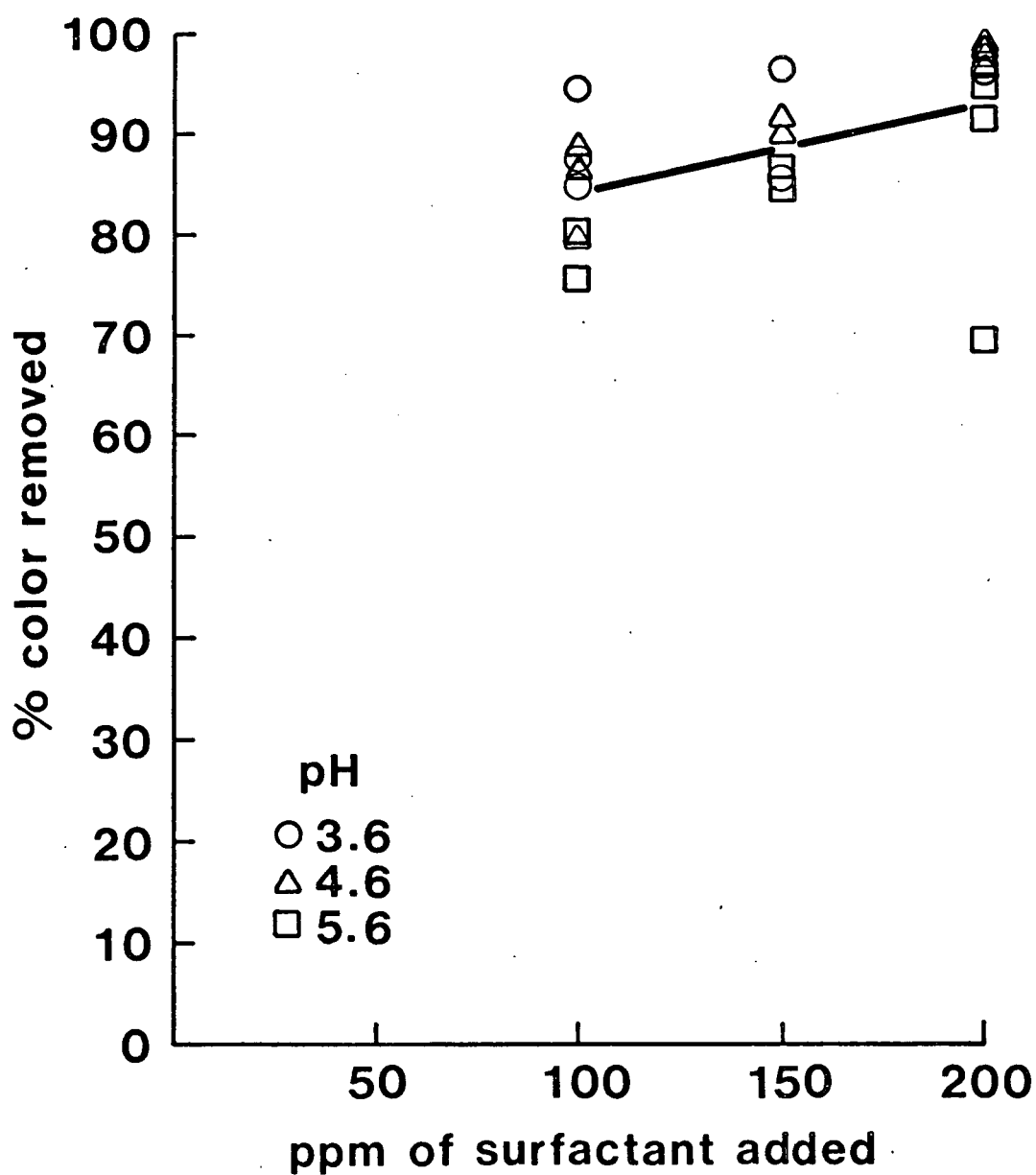
4.4 Studies on the Behavior of Kraft Mill Waste in Various Acidification-Alkalization Sequences

- i) acidification-alkalization-acidification
- ii) alkalization-acidification-alkalization-acidification

A sample from Elk Falls total mill effluent was used in these studies. This total mill effluent was obtained by mixing proportional amounts of the four main outlets from the mill. The pH of the mixed effluent was seven and hence this was the starting point. Concentrated hydrochloric acid and concentrated sodium hydroxide were the acid and alkali used (see Appendix C).

figure 14.

**COLOR REMOVAL FROM KRAFT
MILL EFFLUENT AS A FUNCTION
OF AMOUNT OF SURFACTANT
ADDED AND pH**



Figures 15 and 16 show the behavior displayed by the effluent in the two aforementioned sequences respectively. Although for a different purpose, Prahacs *et al.* (61) investigated the trends followed during the acidification of kraft mill caustic extraction stage effluent. They did not perform a back neutralization. The agreement between both results is really remarkable. Their results are partially reproduced in Figure 17. Since the main objectives of these studies were to gain some knowledge of the behavior of the waste at the pHs under study, the discussion will be focussed in that direction. The most striking feature in both Figures, 15 and 16, is that once the effluent has been brought to a very low pH, the original pattern (i.e. curve AB) is never reproduced during any further alkalization-acidification sequences. From that point on, the typical strong base-strong acid neutralization curve is always obtained. Gathering all the information together, it can be said that

- i) During the first acidification of the effluent from pH 7 to 3, certain chemical specie or species are irreversibly transformed,
- ii) No noticeable precipitate or gas evolution is observed,
- iii) The color of the solution is left unaffected by the change since back alkalization restores the color reading to its full initial value.

figure 15.

BEHAVIOUR OF KRAFT MILL EFFLUENT IN THE SEQUENCE ACIDIFICATION • ALKALIZ- ATION • ACIDIFICATION

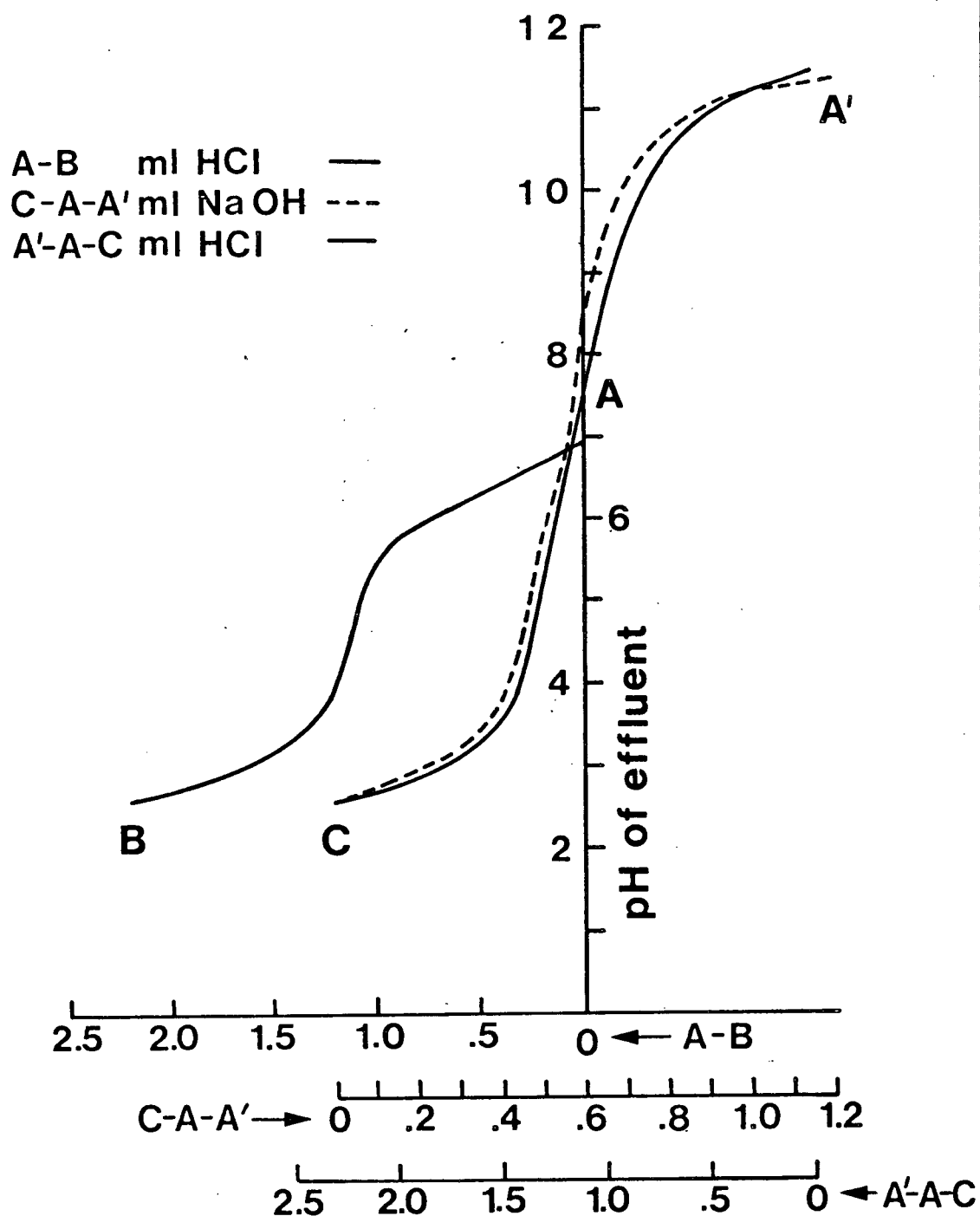


figure 16.

BEHAVIOUR OF KRAFT MILL EFFLUENT IN THE SEQUENCE ALKALIZATION·ACIDIFICATION·ALKALIZATION·ACIDIFICATION

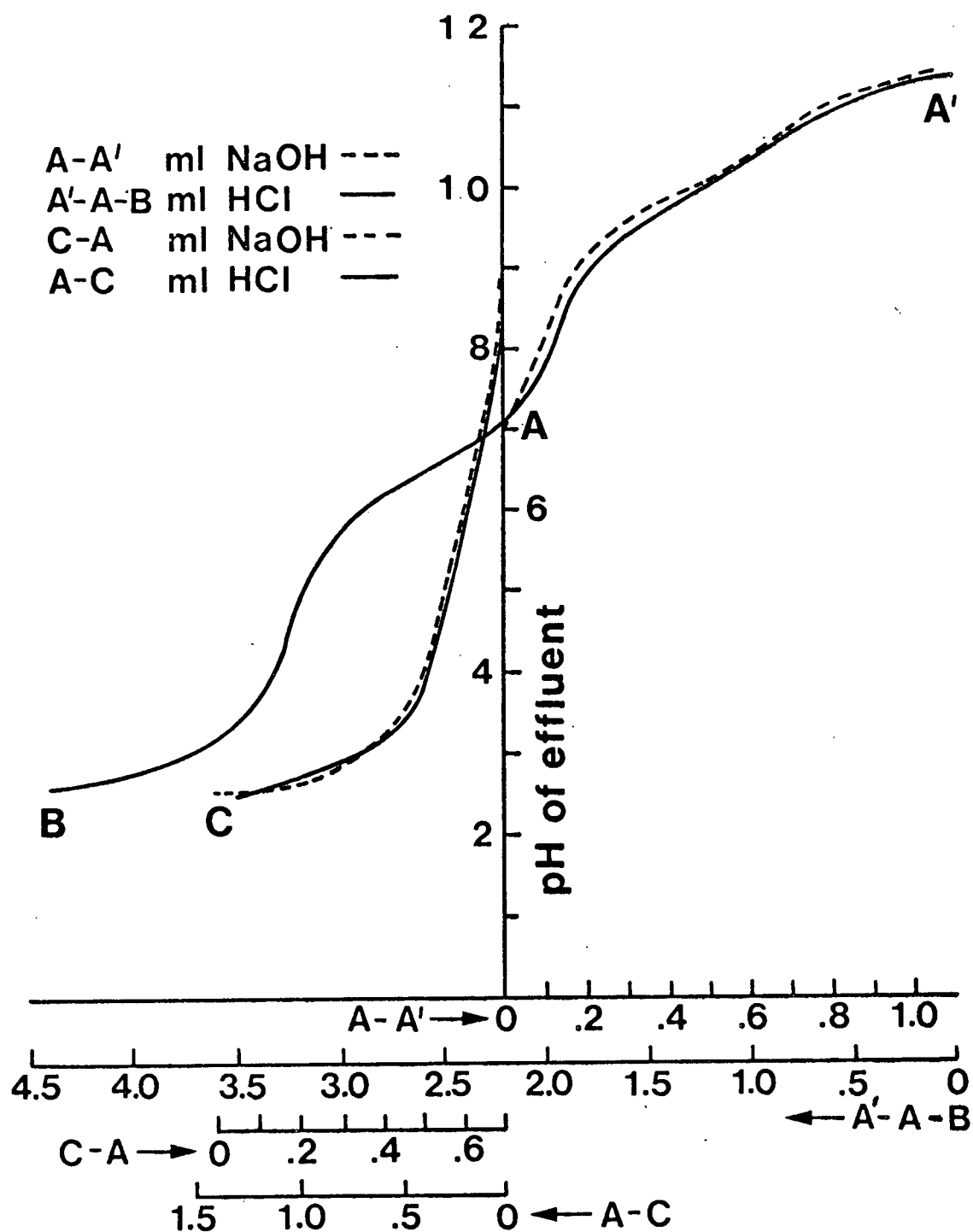
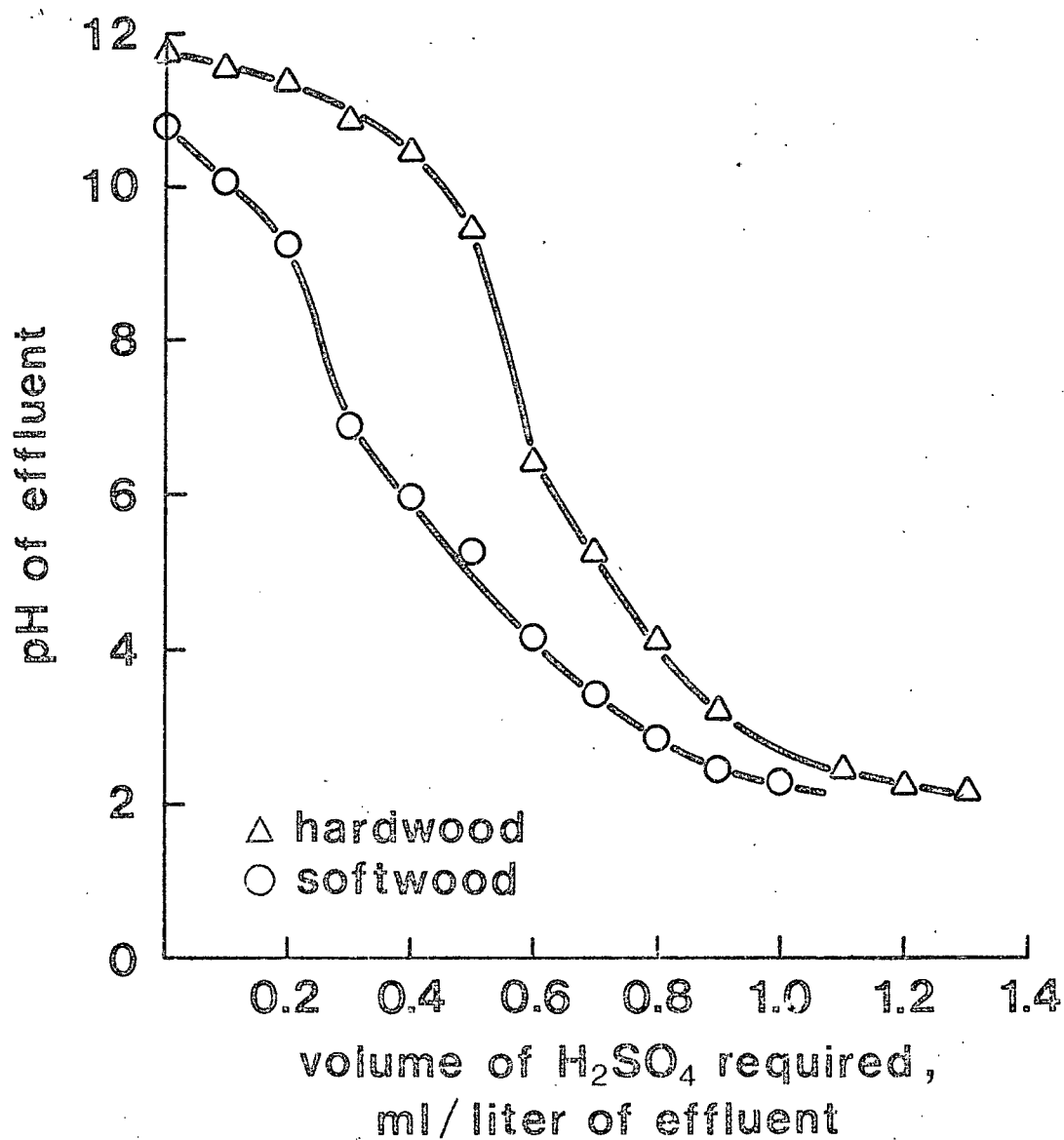


figure 17.

ACIDIFICATION OF KRAFT CAUSTIC
EXTRACTION EFFLUENT WITH 98%
 H_2SO_4



It has been suggested that some types of sugars are originally attached to the color bodies and released, afterwards, in polymeric form at certain pH values (13).

Taking into account how complex the composition of the effluent is and how many possible interactions can be developed between all the different species present, it would be presumptuous to name the factor responsible for such a peculiar behavior.

In agreement with the discussed results, it is possible that an increasing concentration of hydronium ion assists in breaking the bonds that hold the acid soluble chromophores to their associates and, from that moment, they remain in solution as individual species.

4.5 Other Variables of Interest

Before closing this discussion, it must be pointed out that the influence of certain variables was determined during several sets of tentative batch experiments. Previous work carried out by Herschmiller (4) in relation to these specific variables was taken as a good starting point. For that reason those variables were fixed at definite values during the experimental work. This was done with the intention of narrowing the basic study to the most important variables. They shall be mentioned briefly:

Air flow rate and sparger size - It was found that the flotation process performed at its best at low gas flow rate (1.66 cc/sec) and using a fine porosity disperser (4,65).

Introduction of the surfactant - The best results were obtained dissolving the surfactant in 10 cc methanol and introducing it at very slow rates by a syringe. Any attempt to introduce the surfactant in a single dose or in a powder form resulted in very poor results (10).

Premixing time and stirrer speed - The premixing time and the stirrer speed appeared to have a marked effect on the formation of the precipitate. Five minutes of premixing time and a stirrer speed of 950 RPM seemed to make a good combination of both parameters.

Temperature - Rubin and Johnson (65) observed that temperatures in the range from 15° to 34°C do not affect the ion flotation process. Prahacs and Wong (61) found no sensible change in the percentage of color removed from kraft caustic extraction effluent at temperatures varying from 20 to 58°C. The experiments discussed were carried out always with an effluent temperature within 25-35°C. The results obtained did not show any significant temperature dependence.

Chapter 5

CONCLUSIONS

5.1 From the Studies on the Floatability of the Surfactant

1. The percentage of surfactant recovered by flotation is an optimum at pH values varying from 3.6 to 4.6. Outside this range, the tendency of the surfactant ions to associate is maximum.

2. At optimum pH values and in aqueous solution, the presence of aggregates becomes evident at concentrations greater than 72.5 ppm. Nevertheless, the interaction of the surfactant ions among themselves is not a critical factor in the color coagulation process.

3. Under the best conditions, 90% of the surfactant in solution is in ionic form. The rest is probably aggregates that might be readily formed in solution or, more likely, due to ageing of the surfactant.

4. It is possible to use the percentage of surfactant recovered by flotation as a means to determine the presence of its aggregates in aqueous solution. This technique still needs further improvement.

5.2 From the Studies on the Flotation Process

5.2.1 Batch Experiments

1. It has been disclosed the presence of significant interaction between the pH of the waste and the amount of surfactant added. Consequently, the behavior of the flotation process depends entirely on the combined values assumed by these variables.

2. It is possible to select pH 3.6 and 100 ppm of surfactant as the best parameters for the process within the studied ranges. At these conditions it was observed that:

- a) the amount of solids that could be possibly floated varied from 130-160 ppm,
- b) the process responses were at their best values, i.e. 90% surfactant floated, 1.57 ratio of solids floated to surfactant floated and 21.5 of total solids floated,
- c) the reproducibility of the results was highly satisfactory,

- d) two simultaneous processes seemed to take place:
 - i) aggregation of the acid insoluble chromophores,
 - ii) an instantaneous coagulation reaction between the acid-soluble, negatively charged chromophores and the cationic surfactant ion
- e) the complex species formed by the described processes were immediately removed by flotation in the form of a dark, thick scum. Neither froth nor foam was present. In general both appeared to be related with an inefficient performance of the process.

3. The flotation process was found to be sensitive to air flow rate, sparger size, means of introducing the surfactant, stirrer speed and premixing time. However, no significant temperature dependence was found in the range of 25 to 35°C.

5.2.2 Continuous Experiments

1. The possibility of running the coagulation-floatation process continuously has been fully demonstrated.

2. The process behavior and results of the continuous runs are comparable to those obtained at the corresponding batch experiments.

3. The mixing of the surfactant and effluent requires a separate stirred premixing stage in order to achieve positive results.

4. The development of turbulence at high air flow rates obviates the flotation-coagulation process by redispersing the sublimate.

5. An increase of the flotation time above fifteen minutes has a deleterious effect on the process, presumably because of redissolution of the precipitate.

5.3 From the Studies on the Effluent Behavior

1. During the storage of the refrigerated original sample, no sensible change in color has been detected. Yet, if the color test is preceded by a pH adjustment, the final color readings are being affected via the filtration stage. There is also some evidence of time effects at pHs 4.6 and 5.6. For that reason, it has been proven the inaccuracy of the color test for expressing flotation results. Regarding the total solids content no marked difference was introduced by storage or pH adjustment, besides the normal increases due to the chemicals added.

2. During the acidification of the effluent from pH 7 to 3 certain chemical specie or species are irreversibly transformed. The true mechanism involved is not known. It is suggested the releasing of the acid soluble chromophores from their associates as partially responsible for such behavior.

Chapter 6

FURTHER WORK

The present work has proven the feasibility of a continuous coagulation-floatation process for removing the color bodies from kraft mill effluents. Yet the process, at its present stage, is not commercially competitive with other proposed techniques due to the high cost of the surfactant. Therefore, further studies are required regarding its industrial possibilities. It is suggested that any future work undertaken in this process should have the following aims:

1. To modify the process using dispersed or entrained air as the aeration source. This would eliminate the use of fine sparger nozzles and its consequently plugging.
2. Either to find a cheaper and/or more efficient surfactant or to develop a surfactant recovery process for its recycle. A suggested recovery process would be to

dissolve the colored sublate in a caustic solution. This should break up the surfactant-chromophore complex leaving a quaternary ammonium hydroxide and a soluble color compound. The quaternary ammonium hydroxide could be solvent extracted from this alkaline solution. Acidification of the extract and removal of the solvent would complete the system. However, the described recovery process is purely in the realm of educated speculation.

3. To determine the toxicity of the clear effluent since it is not known how the remaining surfactant contributes to it.

4. To characterize the kraft effluent color bodies before and after the treatment in order to gain a better understanding of the involved mechanisms.

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APPENDIX A

ANALYSIS OF VARIANCE OF THE DESIGNED SET OF BATCH EXPERIMENTS

A.1 General Review (66,67)

A.1.1 Two-factor Experiments

To present general formulas for the analysis of variance of a two-factor experiment using repeated observations, the case of n replications of the treatment combinations determined by a levels of factor A and b levels of factor B will be considered. The observations may be classified by means of a rectangular array in which the rows represent the levels of factor A and the columns represent the levels of factor B. Each treatment combination defines a cell in the array. Thus there are ab cells, each cell containing n observations. Denoting the k th observation taken at the i th level of factor A and the j th level of factor B by y_{ijk} , the abn are shown in the following table.

The observations in the (ij) th cell constitute a random sample of size n from a population that is assumed

Table A1
Two-Factor Experiment with n Replications

A	B				Total	Mean
	1	2	b		
1	y_{111}	y_{121}	. . .	y_{1b1}	$T_{1..}$	$\bar{y}_{1..}$
	y_{112}	y_{122}	. . .	y_{1b2}		
	.	.		.		
	.	.		.		
2	y_{11n}	y_{12n}		y_{1bn}	$T_{2..}$	$\bar{y}_{2..}$
	y_{211}	y_{221}	. . .	y_{2b1}		
	y_{212}	y_{222}	. . .	y_{2b2}		
	.	.		.		
.	.	.		.	$T_{a..}$	$\bar{y}_{a..}$
	.	.		.		
	.	.		.		
	.	.		.		
a	y_{21n}	y_{22n}		y_{2bn}	$T_{a..}$	$\bar{y}_{a..}$
	y_{a11}	y_{a21}	. . .	y_{ab1}		
	y_{a12}	y_{a22}	. . .	y_{ab2}		
	.	.		.		
Total	.	.		.	$T_{...}$	$\bar{y}_{...}$
	y_{a1n}	y_{a2n}	. . .	y_{abn}		
	$T_{.1.}$	$T_{.2.}$. . .	$T_{.b.}$		
	$\bar{y}_{.1.}$	$\bar{y}_{.2.}$. . .	$\bar{y}_{.b.}$		

to be normally distributed with mean μ_{ij} and variance σ^2 .

All ab populations are assumed to have the same variance σ^2 .

- where:
- $T_{ij\cdot}$ = sum of the observations in the (ij)th cell
 - $T_{i\cdot\cdot}$ = sum of the observations for the ith level of factor A
 - $T_{\cdot j\cdot}$ = sum of the observations for the jth level of factor B
 - T_{\dots} = sum of all *abn* observations
 - $\bar{y}_{ij\cdot}$ = mean of the observations in the (ij)th cell
 - $\bar{y}_{i\cdot\cdot}$ = mean of the observations for the ith level of factor A
 - $\bar{y}_{\cdot j\cdot}$ = mean of the observations for the jth level of factor B
 - \bar{y}_{\dots} = mean of all *abn* observations

A.1.2 Two-Factor Analysis of Variance

The general model for a two-factor experiment is:

$$y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \epsilon_{ijk}$$

where: ϵ_{ijk} measures the deviations of the observed y_{ijk} values in the (ij) th cell from the population mean μ_{ij} .

$(\alpha\beta)_{ij}$ denote the interaction effect of the i th level of factor A and the j th level of factor B

α_i the effect of the i th level of factor A

β_j the effect of the j th level of factor B

μ overall mean

The following restrictions are imposed on the general model:

$$\sum_{i=1}^a \alpha_i = 0, \quad \sum_{j=1}^b \beta_j = 0, \quad \sum_{i=1}^a (\alpha\beta)_{ij} = 0, \quad \sum_{j=1}^b (\alpha\beta)_{ij} = 0$$

The three hypotheses to be tested are:

i) $H_0^I: \alpha_1 = \alpha_2 = \dots \alpha_a = 0$

H_1^I : at least one of the α_i 's is not equal to zero

ii) $H_0^{II}: \beta_1 = \beta_2 = \dots \beta_b = 0$

H_1^{II} : at least one of the β_j 's is not equal to zero

$$\text{iii) } H_0''': (\alpha\beta)_{11} = (\alpha\beta)_{12} = \dots (\alpha\beta)_{ab} = 0$$

$$H_1''': \text{at least one of the } (\alpha\beta)_{ij} \text{'s is not equal to zero}$$

Table A2
Analysis of Variance for the Two-Factor Experiment
with n Replications

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Tabulated F α = level of significance
<u>Main Effects</u>					
A	SSA	(a-1)	$s_1^2 = \frac{SSA}{(a-1)}$	$f_1 = \frac{s_1^2}{s^2}$	$F_\alpha = [(a-1), ab(n-1)]$
B	SSB	(b-1)	$s_2^2 = \frac{SSB}{(b-1)}$	$f_2 = \frac{s_2^2}{s^2}$	$F_\alpha = [(b-1), ab(n-1)]$
<u>Interaction</u>					
AB	SS(AB)	(a-1)(b-1)	$s_3^2 = \frac{SS(AB)}{(a-1)(b-1)}$	$f_3 = \frac{s_3^2}{s^2}$	$F_\alpha = [(a-1)(b-1), ab(n-1)]$
Error	SSE	ab(n-1)	$s^2 = \frac{SSE}{ab(n-1)}$		
TOTAL	SST	abn-1			

The sum of squares are usually obtained by constructing the following table of totals.

Table A3
Total for the Sum of the Observations

A	B				Total
	1	2	. . .	b	
1	$T_{11\cdot}$	$T_{12\cdot}$. . .	$T_{1b\cdot}$	$T_{1\cdot\cdot}$
2	$T_{21\cdot}$	$T_{22\cdot}$. . .	$T_{2b\cdot}$	$T_{2\cdot\cdot}$
.
.
.
a	$T_{a1\cdot}$	$T_{a2\cdot}$. . .	$T_{ab\cdot}$	$T_{a\cdot\cdot}$
Total	$T_{\cdot 1\cdot}$	$T_{\cdot 2\cdot}$. . .	$T_{\cdot b\cdot}$	$T_{\cdot\cdot\cdot}$

and using the following computational formulas:

$$SST = \sum_{i=1}^a \sum_{j=1}^b \sum_{k=1}^n y_{ijk}^2 - \frac{T_{\cdot\cdot\cdot}^2}{abn}$$

$$SSA = \frac{\sum_{i=1}^a T_{i..}^2}{bn} - \frac{T_{...}^2}{abn}$$

$$SSB = \frac{\sum_{j=1}^b T_{.j.}^2}{an} - \frac{T_{...}^2}{abn}$$

$$SS(AB) = \frac{\sum_{i=1}^a \sum_{j=1}^b T_{ij.}^2}{n} - \frac{\sum_{i=1}^a T_{i..}^2}{bn} - \frac{\sum_{j=1}^b T_{.j.}^2}{an} + \frac{T_{...}^2}{abn}$$

$$SSE = SST - SSA - SSB - SS(AB)$$

A.2 Tabulated Analysis of Variance and Sample Calculations

A.2.1 Analysis of Variance for % Surfactant Floated, pH and Amount of Surfactant Added

A.2.1.1 Tabulated Data

Table A4

Tabulated Data for % Surfactant Floated, pH and Amount
of Surfactant Added

Amount of Surfactant Added, ppm	pH		
	3.6 (b ₁)	4.6 (b ₂)	5.6 (b ₃)
(a ₁) 100	90. 90.38	30. 17.	27. 24.5
(a ₂) 150	80.33 87.33	67.66 70.66	24.66 6.66
(a ₃) 200	81.25 81.	75. 51.	25. 32.

A.2.1.2 Table of Totals

Table A5

Total for the Sum of the Observations for % Surfactant
Floated, pH and Amount of Surfactant Added

Amount of Surfactant Added, ppm	pH			
	3.6 (b ₁)	4.6 (b ₂)	5.6 (b ₃)	Total
(a ₁) 100	180.38	47.	51.5	278.88
(a ₂) 150	167.66	138.32	31.32	337.30
(a ₃) 200	162.25	126.	57.00	345.25
TOTAL	510.29	311.32	139.82	961.43

A.2.1.3 Analysis of Variance

Table A6

Analysis of Variance for % Surfactant Floated,
pH and Amount of Surfactant Added

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Tabulated F α = level of significance
<u>Main Effects</u>					
Amount of Surfactant Added	437.83	2	218.92	$s_1^2 = 3.449$	$F(2,9,.95) = 4.26$
pH	11,458.29	2	5729.14	$s_2^2 = 90.26$	$F(2,9,.99) = 8.02$
Interaction	2,286.97	4	571.74	$s_3^2 = 9.00$	$F(4,9,.99) = 6.42$
Error	571.21	9	63.47		
TOTAL	14,754.30	17			

A.2.2 Analysis of Variance for Ratio of Solids Floated/
Surfactant Floated, pH and Amount of
Surfactant Added

A.2.2.1 Tabulated Data

Table A7

Tabulated Data for Ratio of Solids Floated,
pH and Amount of Surfactant Added

Amount of Surfactant Added, ppm	pH		
	3.6 (b_1)	4.6 (b_2)	5.6 (b_3)
(a_1) 100	1.47 1.67	0.80 1.24	0.185 0.53
(a_2) 150	0.875 1.34	1.36 1.25	0.16 0.53
(a_3) 200	0.97 0.802	0.64 0.94	0.88 1.78

A.2.2.2 Table of Totals

Table A8

Total for the Sum of the Observations for Ratio of Solids
Floated/Surfactant Floated, pH & Amount of Surfactant Added

Amount of Surfactant Added, ppm	pH			
	3.6 (b_1)	4.6 (b_2)	5.6 (b_3)	Total
(a_1) 100	3.14	2.04	0.715	5.895
(a_2) 150	2.21	2.61	0.69	5.51
(a_3) 200	1.77	1.58	2.66	6.01
TOTAL	7.12	6.23	4.065	17.415

A.2.2.3 Analysis of Variance

Table A9

Analysis of Variance for % Solids Floated,
pH and Amount of Surfactant Added

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Tabulated F α = level of significance
<i>Main Effects</i>					
Amount of Surfactant Added	0.02	2	0.01	$s_1^2 = 0.117$	$F(2,9,.95) = 4.26$
pH	0.82	2	0.41	$s_2^2 = 4.82$	$F(2,9,.95) = 4.26$
Interaction	2.08	4	0.52	$s_3^2 = 6.12$	$F(4,9,.95) = 3.63$ $F(4,9,.99) = 6.42$
Error	0.766	9	0.085		
TOTAL	3.686	17			

A.2.3 Analysis of Variance for % Solids Floated, pH and Amount of Surfactant Added

A.2.3.1 Tabulated Data

Table A10

Tabulated Data for % Solids Floated, pH and Amount of Surfactant Added

Amount of Surfactant Added, ppm	pH		
	3.6 (b_1)	4.6 (b_2)	5.6 (b_3)
(a_1) 100	24.26 20.49	3.41 4.0	0.58 1.78
(a_2) 150	21.65 20.80	15.66 17.25	0.71 0.819
(a_3) 200	20.08 19.11	13.23 18.23	17.52 11.27

A.2.3.2 Table of Totals

Table A11

Total for the Sum of the Observations for % Surfactant
Floated, pH and Amount of Surfactant Added

Amount of Surfactant Added, ppm	pH			
	3.6 (b_1)	4.6 (b_2)	5.6 (b_3)	Total
(a_1) 100	44.75	7.41	2.36	54.52
(a_2) 150	42.45	32.91	1.53	76.89
(a_3) 200	39.19	31.46	28.79	99.44
TOTAL	126.39	71.78	32.68	230.85

A.2.3.3 Analysis of Variance

Table A12

Analysis of Variance for % Solids Floated,
pH and Amount of Surfactant Added

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Tabulated F α = level of significance
<u>Main Effects</u>					
Amount of Surfactant Added	168.15	2	84.07	$s_1^2 = 17.96$	$F(2,9,.99) = 8.02$
pH	738.48	2	369.24	$s_2^2 = 78.89$	$F(2,9,.99) = 8.02$
Interaction	285.17	4	71.29	$s_3^2 = 15.23$	$F(2,9,.99) = 6.42$
Error	42.12	9	4.68		
TOTAL	1233.92	17			

A.2.4 Sample Calculation

The required calculations shall be illustrated by using the data obtained from % solids floated, pH and amount of surfactant added.

$$\begin{aligned} SST = & 24.26^2 + 20.49^2 + 21.65^2 + 20.80^2 + 20.08^2 + 19.11^2 + 3.41^2 + 4^2 + \\ & 15.66^2 + 17.25^2 + 13.23^2 + 18.23^2 + 0.58^2 + 1.78^2 + \\ & 0.71^2 + 0.819^2 + 17.52^2 + 11.27^2 - \frac{(230.85)^2}{18} \end{aligned}$$

$$SSA = \frac{54.52^2 + 76.89^2 + 99.44^2}{6} - \frac{(230.85)^2}{18}$$

$$SSA = 3128.80 - 2960.65 = 168.15$$

$$SSB = \frac{126.39^2 + 71.78^2 + 32.68^2}{6} - \frac{(230.85)^2}{18}$$

$$SSB = 3699.13 - 2960.65 = 738.48$$

$$\begin{aligned} SSAB = & \frac{44.75^2 + 42.45^2 + 39.19^2 + 7.41^2 + 32.91^2 + 31.46^2 + 2.36^2 + 1.53 + 28.79^2}{2} \\ & - 3128.80 - 3699.13 + 2960.65 \end{aligned}$$

$$SSAB = 4152.45 - 3128.80 - 3699.13 + 2960.65 = 285.17$$

$$SSE = 1233.92 - 168.15 - 738.48 - 285.17 = 42.07$$

$$MSA = \frac{168.15}{2} = 84.07$$

$$MSB = \frac{738.48}{2} = 369.24$$

$$MSAB = \frac{285.17}{4} = 71.29$$

$$MSE = \frac{42.12}{9} = 4.68$$

$$s_1^2 = \frac{84.07}{4.68} = 17.96$$

$$s_2^2 = \frac{369.24}{4.68} = 78.89$$

$$s_3^2 = \frac{71.29}{4.68} = 15.23$$

A.2.5 Conclusions

Since in the three sets of data studied the interaction between the two factors, i.e. pH and amount of surfactant added, is highly significant, it is not sensible to attempt to draw inferences on the main effects for the presence of interaction could mask them. Instead, the data should be analyzed observing the influence of each factor at fixed levels of the other.

APPENDIX B

REGRESSION ANALYSIS APPLIED TO THE DATA OBTAINED

AT pH 3.6

B.1 General Review (68)

B.1.1 Linear Regression

The method of least squares was applied to the data in an attempt to obtain a straight-line relationship between the variables presently under study.

The formulae used for a regression model of the type $y = \beta_0 + \beta_1 x + \epsilon$, were the following:

1) $\hat{y} = b_0 + b_1 x$ predictive model

$$2) \quad b_1 = \frac{\sum x_i y_i - \frac{(\sum x_i)(\sum y_i)}{n}}{\sum x_i^2 - \frac{(\sum x_i)^2}{n}}$$

3) $b_0 = \bar{y} - b_1 \bar{x}$

$$4) \quad \bar{y} = \frac{\sum y_i}{n}$$

$$5) \quad \bar{x} = \frac{\sum x_i}{n}$$

$$6) \quad SS_{TOTAL} = \sum y_i^2 - \frac{(\sum y_i)^2}{n}$$

$$7) \quad SS_{REGRESSION} = \frac{\left[\sum x_i y_i - \frac{(\sum x_i)(\sum y_i)}{n} \right]^2}{\left\{ \sum x_i^2 - \frac{(\sum x_i)^2}{n} \right\}}$$

$$8) \quad SS_{TOTAL} = SS_{REGRESSION} + SS_{RESIDUAL}$$

$$9) \quad s^2 = \frac{SS_{RESIDUAL}}{(n - 2)}$$

$$10) \quad F = \frac{SS_{REGRESSION}}{s^2}$$

$$11) \quad R^2 = \frac{SS_{REGRESSION}}{SS_{TOTAL}}$$

where: y = dependent or random variable

x = independent or fixed variable

β_0, β_1 = parameters of the regression model

\hat{y} = predicted value of y for a given x

b_0, b_1 = estimates of β_0, β_1 based on the observations

$\epsilon = y - \hat{y}$ = residual difference between the actual observation for a given x and the corresponding fitted value obtained by use of the fitted regression equation

n = number of observations

SS_{TOTAL} = Sum of squares about the mean

$SS_{REGRESSION}$ = Sum of squares due to regression

$SS_{RESIDUAL}$ = Sum of squares about regression

s^2 = mean square about regression, it provides an estimate based on $n - 2$ degrees of freedom of the variance about the regression, $\sigma^2_{y \cdot x}$

R^2 = coefficient of determination, it represents the percentage of the variation in the data which is explained by the regression equation.

$SE_E = \sqrt{s^2}$ = standard error of estimate, it means that the band around the regression surface computed as $\hat{y}_i \pm SE_E$ approximately includes 68% of the observation used to estimate the regression coefficients (b_0, b_1)

B.1.2 Examining the Regression Equation

B.1.2.1 Lack of Fit and Pure Error

The sum of squares residual can be broken into the amount due to the variation between the value of y within given values of x , and another component which is normally called the lack of fit contribution. The first component, calculated from repeated points, reflects mere random variation or pure experimental error; while the second component is a measure of the systematic variation brought about by higher order terms. The computations required for testing hypotheses in a regression problem with repeated measurements on the response may be summarized as shown in the table. The computed f values are compared with the 100 $(1 - \alpha)$ % point of the tabulated $F(1, n - 2)$ or $F(k - 2, n - k)$ distribution respectively, in order to determine the relative significance of the ratio tested.

B.1.2.2 Plot of Residuals

In performing the regression analysis certain assumptions about the errors are made, i.e. the errors are independent, have zero mean, a constant variance, σ^2 , and follow a normal distribution. Thus if the fitted model is correct, the residuals should exhibit tendencies that tend to confirm

Table B1

Analysis of Variance for Repeated Measurements on the Response

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f
Regression	$SS_{\text{REGRESSION}}$	1	$SS_{\text{REGRESSION}}$	$\frac{SS_{\text{REGRESSION}}}{s^2}$
Residual	SS_{RESIDUAL}	$n - 2$	$\frac{SS_{\text{RESIDUAL}}}{n - 2}$	
Lack of fit	$SS_{\text{RESIDUAL}} - SS_{\text{PURE ERROR}}$	$k - 2$	$\frac{SS_{\text{RESIDUAL}} - SS_{\text{PURE ERROR}}}{k - 2}$	$\frac{SS_{\text{RESIDUAL}} - SS_{\text{PURE ERROR}}}{s_e^2(k - 2)}$
Pure error	$SS_{\text{PURE ERROR}}$	$n - k$	$s_e^2 = \frac{SS_{\text{PURE ERROR}}}{n - k}$	
TOTAL	SS_{TOTAL}	$n - 1$		

where n = number of observations using k distinct values of x .

the assumptions made, or at least, should not exhibit a denial of the assumptions.

The best and easiest way to examine the residuals is graphical. In practical regression situations a detailed examination of the corresponding residual plots is usually far more informative, and the plots will almost certainly reveal any violations of assumptions serious enough to require corrective action. The most common plots of residuals are:

i) In time sequence, if the order is known. This will indicate whether a long-term time effect is influencing the data.

ii) Against the independent variables. This will reveal:

- a) the constancy of the variance,
- b) error in calculation, i.e. linear effect of x not removed,
- c) need for extra terms, for example a quadratic term in x in the model.

iii) Against the actual value of y . This will test the accuracy of the predictive model. Care must be taken to avoid the use of the predictive model outside the explored x range, i.e. for extrapolating purposes.

Regarding the independence of the errors, it has been stated that in general regression situations the effect of

correlation between residuals need not be considered when plots are made, except when the ratio number of degrees of freedom in residuals/number of residuals is quite small.

B.2 Tabulated Analysis of Variance, Sample Calculation and Plot of Residuals

B.2.1 Analysis of Variance for % Surfactant Floated vs Amount of Surfactant Added at pH 3.6

Table B2

Analysis of Variance for % Surfactant Floated vs Amount of Surfactant Added at pH 3.6

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Tabulated F
Regression	120.50	1	120.5	$\frac{120.5}{6.72} = 17.93$	$F(1, 5.99) = 16.26$
Residual	33.60	5	$\frac{33.6}{5} = 6.72$		
Lack of fit	6.5	1	$\frac{6.5}{1} = 6.5$	$\frac{6.5}{6.77(3-2)} = 0.96$	$F(1, 4, .99) = 21.20$
Pure error	27.1	4	$\frac{2.71}{4} = 6.77$		
TOTAL	154.1	6			

B.2.2 Analysis of Variance for Ratio of Solids Floated/
Surfactant Floated vs Amount of Surfactant
Added at pH 3.6

Table B3

Analysis of Variance for Ratio of Solids Floated/Surfactant
Floated vs Amount of Surfactant Added at pH 3.6

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Tabulated F
Regression	0.69	1	0.69	$\frac{0.69}{0.04} = 17.25$	$F(1, 5.99) = 16.26$
Residual	0.20	5	$\frac{0.02}{5} = 0.04$		
Lack of fit	0.03	1	$\frac{0.03}{1} = 0.03$	$\frac{0.03}{0.042(3-2)} = 0.705$	$F(1, 4, .99) = 21.20$
Pure error	0.17	4	$\frac{0.17}{4} = 0.042$		
TOTAL	0.89	6			

B.2.3 Analysis of Variance for % Solids Floated vs
Amount of Surfactant Added at pH 3.6

Table B4

Analysis of Variance for % Solids Floated vs Amount
of Surfactant Added at pH 3.6

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Computed f	Tabulated F
Regression	6.37	1	6.37	$\frac{6.37}{2.39} = 2.66$	$F(1, 5.99) = 16.26$
Residual	11.93	5	$\frac{11.93}{5} = 2.39$		
TOTAL	18.30	6			

B.2.4 Sample Calculations

The required calculations shall be illustrated by using the data obtained from the relation ratio of solids floated/surfactant floated vs amount of surfactant added at pH 3.6.

B.2.4.1 Calculations Concerned with the
Regression Equation

Table B5

Calculations Concerned with the Regression Equation

Amount of Surfactant Added in ppm	Solids floated Surfactant floated								Days After Sampling
x	y	xy	x ²	y ²	\bar{x}	\bar{y}	\hat{y}	$y - \hat{y}$ (ϵ)	
100	1.47	147.	10,000	2.16			1.56	-0.09	7
100	1.67	167.	10,000	2.79			1.56	0.11	5
100	1.72	172.	10,000	2.96			1.56	0.16	15
150	0.87	130.5	22,500	0.76			1.21	-0.34	3
150	1.34	201.	22,500	1.80			1.21	0.13	4
200	0.97	194.	40,000	0.94			0.86	0.11	12
200	0.80	160.	40,000	0.64			0.86	-0.06	19
$\Sigma 1000$	$\Sigma 8.84$	$\Sigma 1171.5$	$\Sigma 155,000$	12.05	142.9	1.26		$\Sigma 0.02$	

$$b_1 = \frac{1171.5 - \frac{1000 \times 8.84}{7}}{155,000 - \frac{(1000)^2}{7}} = -0.07 \quad (2)$$

$$b_0 = 1.26 - (-0.007 \times 142.9) = 2.26 \quad (3)$$

$$\hat{y} = 2.26 - 0.007x \quad (1)$$

$$SS_{\text{TOTAL}} = 12.05 - \frac{(8.84)^2}{7} = 0.89 \quad (6)$$

$$SS_{\text{REGRESSION}} = \frac{\left[1171.5 - \frac{1000 \times 8.84}{7}\right]^2}{155,000 - \frac{(1000)^2}{7}} = 0.69 \quad (7)$$

$$SS_{\text{RESIDUAL}} = 0.89 - 0.69 = 0.20 \quad (8)$$

$$s^2 = \frac{0.20}{(7 - 2)} = 0.04 \quad (9)$$

$$s = 0.2$$

$$R^2 = \frac{0.69}{0.89} = 77.53 \quad (11)$$

$$f = \frac{0.69}{0.04} = 17.25 \quad (10)$$

B.2.4.2 Calculations Concerned with the
"lack of fit" Test

Table B6

Calculations Concerned with the "lack of fit" Test

Amount of Surfactant Added in ppm x	Solids floated Surfactant floated y	y^2	\bar{y} $\left(\frac{\Sigma y}{n_R}\right)$	Number of Repetitions (n_R)	Degrees of Freedom ($n_R - 1$)	\bar{y}^2	$n_R \bar{y}^2$	$y_i^2 - n_R \bar{y}^2$
100	1.47	2.16	1.62	3	2	2.62	7.87	0.04
100	1.67	2.79						
100	1.72	2.96						
	$\Sigma 4.86$	$\Sigma 7.91$						
150	0.87	0.76	1.10	2	1	1.22	2.44	0.12
150	1.34	1.80						
	$\Sigma 2.21$	$\Sigma 2.56$						
200	0.97	0.94	0.885	2	1	0.783	1.566	0.014
200	0.80	0.64						
	$\Sigma 1.77$	$\Sigma 1.58$			$\Sigma 4$			$\Sigma 0.17$

degree of freedom for pure errors - $\eta - k = 7 - 3 = 4$

$$SS_{\text{PURE ERROR}} = \sum \sum y_i^2 - \eta_R \bar{y}^2 = 0.17$$

$$SS_{\text{LACK OF FIT}} = SS_{\text{RESIDUAL}} - SS_{\text{PURE ERROR}} = 0.20 - 0.17 = 0.03$$

$$s_e^2 = \frac{SS_{\text{PURE ERROR}}}{\eta - k} = \frac{0.17}{4} = 0.0425$$

$$\text{computed } f = \frac{SS_{\text{RESIDUAL}} - SS_{\text{PURE ERROR}}}{s_e^2 (k - 2)} = \frac{0.03}{0.0425(3-2)} = 0.705$$

tabulated $F(1, 4, .99) = 21.20$

B.2.4.3 Plot of Residuals

figure B1.

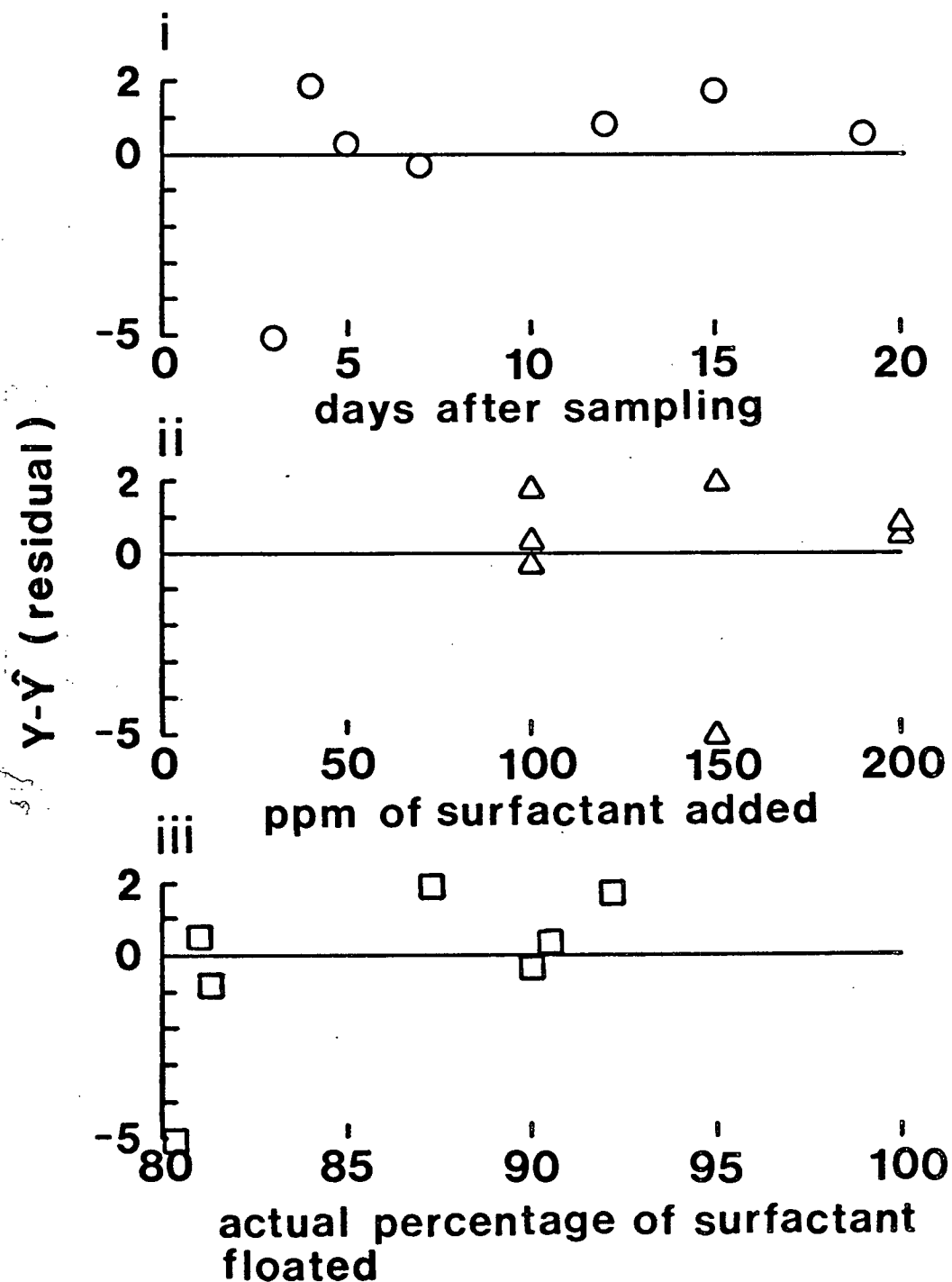
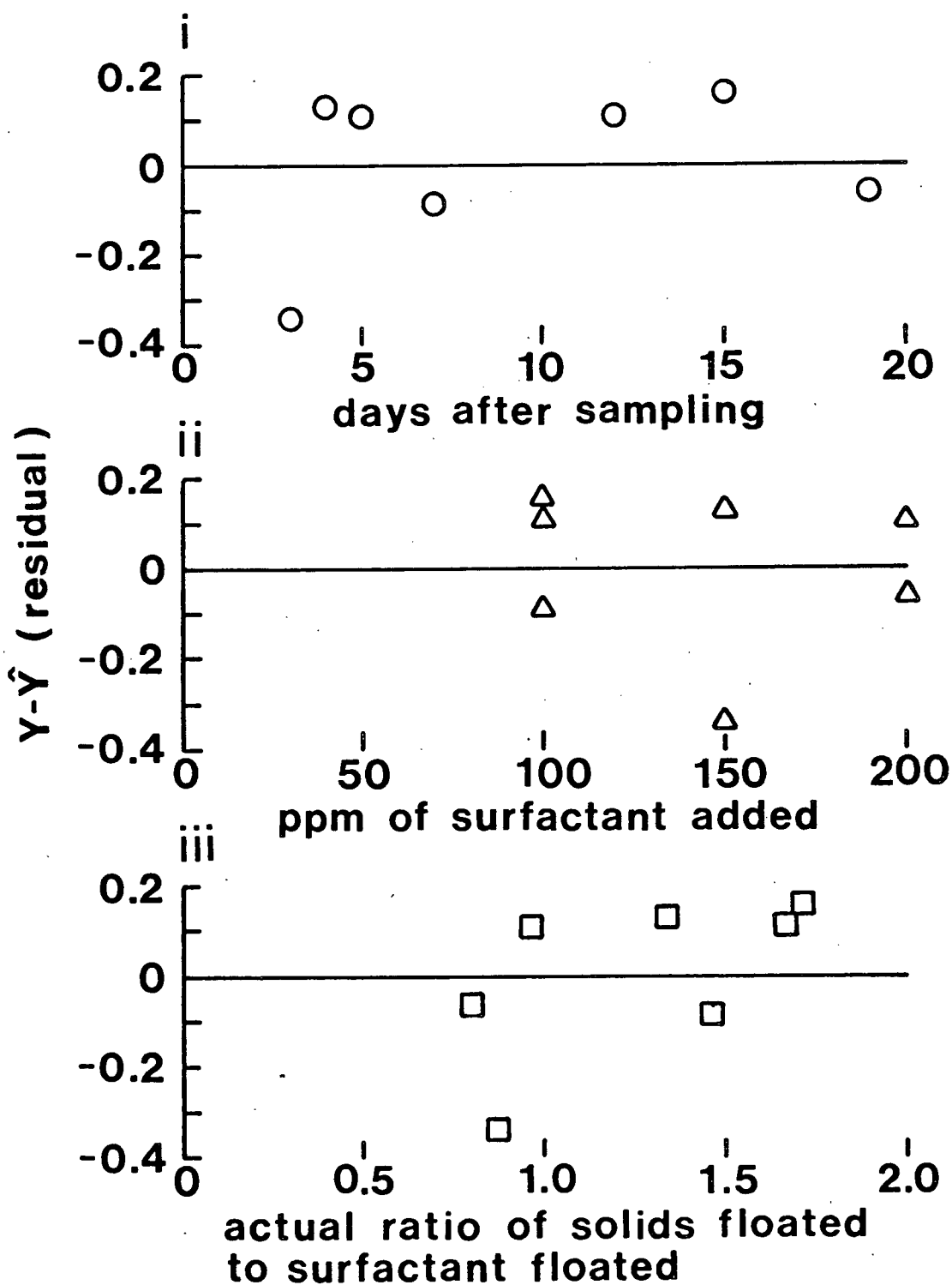
**RESIDUALS OF THE REGRESSION
MODEL OBTAINED FOR THE % OF
SURFACTANT FLOATED**

figure B2.

**RESIDUALS OF THE REGRESSION
MODEL OBTAINED FOR THE RATIO
OF SOLIDS FLOATED TO SURFACT-
ANT FLOATED**



B.3 Conclusions

B.3.1 % Surfactant Floated vs Amount of Surfactant Added

- i) The predictive model is $\hat{y} = 100.247 - 0.099x$
- ii) 78% of the variation in the data is explained by the regression equation
- iii) The hypothesis that a linear regression does not exist can be rejected running a risk of less than 1% of being wrong
- iv) The band around the regression surface computed as $\hat{y}_i \pm 2.59$ approximately includes 68% of the observations used to estimate the regression coefficients
- v) According to the lack of fit test the model is a plausible one which has not been found inadequate by the data
- vi) The mean of the errors is zero
- vii) The plots of residuals reveal neither a time dependence nor any violations of the assumptions made, nevertheless the y values are slightly underpredicted by the model ($\hat{y} < y$)

B.3.2 Ratio of Solids Floated/Surfactant Floated vs
Amount of Surfactant Added

- i) The predictive model is $\hat{y} = 2.26 - 0.007x$
- ii) 77% of the variation in the data is explained by the regression equation
- iii) The hypothesis that a linear regression does not exist can be rejected running a risk of less than 1% of being wrong.
- iv) The band around the regression surface computed as $\hat{y}_i \pm 0.2$ approximately includes 68% of the observations used to estimate the regression coefficients
- v) According to the lack of fit test the model is a plausible one which has not been found inadequate by the data
- vi) The mean of the errors is zero
- vii) The plot of residuals revealed neither a time dependence nor any violations of the assumptions made

B.3.3 % Solids Floated versus amount of surfactant added

- i) The hypothesis that a linear regression does not exist cannot be rejected, therefore it is not advisable to assume a linear association between the dependent and independent variables

APPENDIX C

ANALYTICAL TECHNIQUES AND CLEANING PROCEDURE

C.1 Color Determination

As mentioned, Herschmiller's modified colour test (4) was used without modification; so it will not be reported here.

C.2 Residual Surfactant Determination

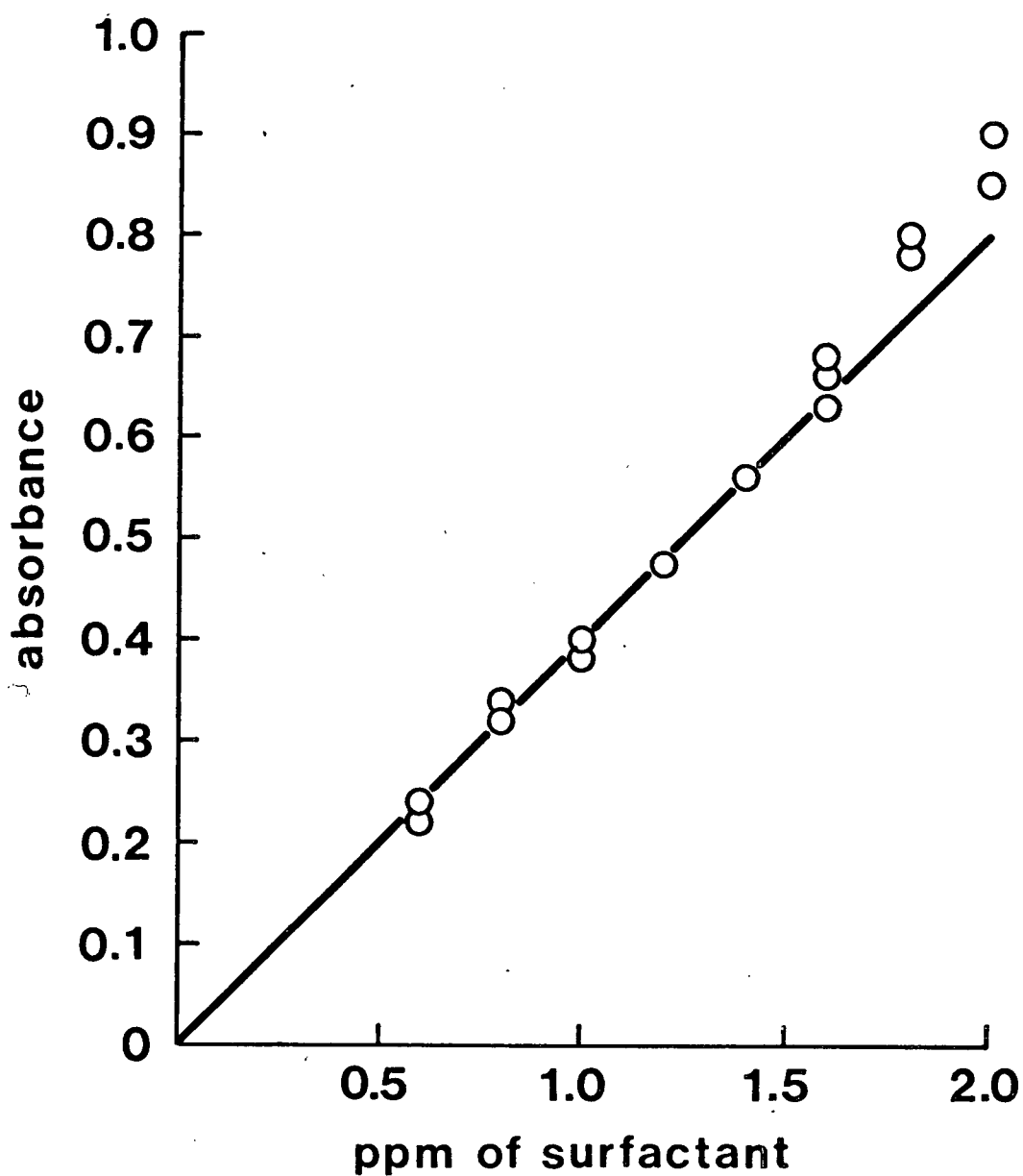
A fairly extensive amount of literature was surveyed on the different techniques proposed for determining the concentration of cationic surface-active agents in aqueous solutions (69,70,71,72,73). The method suggested by Van Steveninck and Mass appeared to be the most promising; therefore it was tried on several tentative flotation runs using the mill effluent and modified accordingly.

An adequate volume of the remaining effluent was diluted to 50 ml. Then, in succession, were added 5 ml of 10% sodium carbonate, two drops of concentrated sodium

hydroxide (prepared by dissolving 50 g of C.P. sodium hydroxide in 50 ml of distilled water), 1 ml of bromophenol blue (freshly prepared daily by dissolving 40 mg of dye in 100 ml of 0.001N NaOH) and 10 ml of 1,2-dichloroethane (spectrophotometric grade). The mixture was hand-shaken for three minutes in a stoppered 125 cc teflon separatory funnel and allowed to settle for 20 extra minutes. Since the optical density of the organic phase changed with time, all the readings were taken exactly at 50-55 seconds after the settling time was over, at 600 m μ . For the same reason, distilled water was used as a blank instead of the extraction solvent and special care was taken to submit all samples to the same timed procedure. The concentration of the cationic surfactant was determined by means of a calibration graph, previously prepared from solutions with known concentrations of surfactant (Figure C1). The deviation from Beer's law became apparent at concentrations above 1.7 ppm.

The accuracy of the technique was established by repeating the experimental runs, with distilled water instead of the mill effluent. Total solids were determined before and after flotation and, hence, the amount of surfactant floated could be estimated and compared with the results of the colorimetric technique. On the average both methods agreed within a 3. % of difference.

figure C1.

**CALIBRATION GRAPH FOR VARIOUS
CONCENTRATIONS OF SURFACTANT**

C.3 Floatable Solids Determination

The first analytical method (4) applied for determining the amount of floatable solids in the mill effluent, had the following questionable assumptions:

- i) All the surfactant present in the solution was floated or removed by filtration
- ii) A strictly stoichiometric reaction took place between the surfactant and the potentially floatable solids present in the effluent
- iii) The filtration stage did not exert any influence upon the amount of potentially floatable solids still present in the effluent at that moment

In order to develop a second approach, it was necessary to determine:

- a) total amount of solids present in the initial solution after its pH adjustment and before the addition of the surfactant
- b) total amount of solids present in the remaining effluent after the experiment was completed
- c) residual amount of surfactant present in the remaining effluent after the experiment was completed

Then:

1. $a +$ amount of surfactant added -
 $b = d$, total amount of solids floated
2. amount of surfactant added - $c = e$,
amount of surfactant actually floated
3. $d - e =$ amount of solids floated from
the effluent, at a fixed pH and with
a certain initial amount of surfactant

No filtration stage was required.

The solids analyses were done according to the standard test for "Residue on Evaporation" (74). Tests were performed with 100 cc aliquots of solution and run in duplicate. The samples were left in the oven at 103°C, for 12 hours; allowed to cool for two hours in a desiccator and weighed. For that purpose a Mettler H10T balance was used. The weights were accurate to the nearest 0.1 mg. Possible decomposition of the quaternary ammonium surfactant during the heating period was also tested for. No observable decomposition occurred.

C.4 Cleaning Procedure

After each experiment the flotation equipment was thoroughly scoured with a brush and recovered methanol. Next the procedure was repeated but this time with a soap-water solution. Finally the equipment was rinsed twice, one with tap water and secondly with fresh methanol.

Pipets, evaporating dishes and other laboratory glassware were soaked in a warm chromic acid-sulfuric acid solution, followed by rinsing with large volumes of tap water. The evaporating dishes were additionally placed in the oven, at 103°C for two hours, then allowed to cool in a dessicator.

The diffuser was cleaned with a soft tooth brush and a mild detergent solution. Afterwards it was rinsed with distilled water and backwashed with fresh methanol.

Before using any new fritted filter, it was washed by suction with hot hydrochloric acid and rinsed with distilled water. This treatment removed loose particles of foreign matter such as dust. Later, the general procedure followed to avoid permanent stain of the frit was to clean it with hot concentrated sulfuric acid plus a few drops of sodium nitrite. Then hot distilled water was passed through the frit until the pH of the wash water remained neutral.

APPENDIX D

Flotation of Kraft Mill Effluent. Tabulated Batch Experimental Results

First Set

pH	Amount of Surfactant Added, ppm	Days After Sampling	Temp. °C	% Surf. Floated	Initial Color (Pt-Co Units)	Final Color (Pt-Co Units)	% Color Removed	Initial Solids, ppm	Solids Floated, ppm	% Solids Floated	Solids floated Surf. floated
5.6	200	5	35	60.5	1320	400	69.7	NA	NA	NA	NA
4.6	200	6	35	78	1330	30	97.7	NA	NA	NA	NA
5.6	150	7	35	43	1340	180	86.6	NA	NA	NA	NA
4.6	200	9	32	80	1175	15	98.7	NA	NA	NA	NA
4.6	100	10	26	51	1075	120	88.8	NA	NA	NA	NA
5.6	150	11	28	25.3	1040	NA	NA	NA	NA	NA	NA
6.6	150	12	28	6.66	1213	370	69.5	NA	NA	NA	NA
6.6	200	13	28	13	1100	220	80	NA	NA	NA	NA
5.6	100	14	25	24.5	920	225	75.5	728	13	1.78	.53

Second Set

pH	Amount of Surfactant Added, ppm	Days After Sampling	Temp. °C	% Surf. Floated	Initial Color (Pt-Co Units)	Final Color (Pt-Co Units)	% Color Removed	Initial Solids, ppm	Solids Floated, ppm	% Solids Floated	Solids floated Surf. floated
3.6	150	4	30	87.3	960	140	85.4	846	176	20.80	1.34
3.6	100	5	25	90.4	1250	140	88	732	150	20.5	1.67
5.6	150	6	29	24.7	1460	225	84.6	848	6	0.71	0.16
4.6	150	7	28	67.7	1360	115	91.5	881	138	15.7	1.36
5.6	100	8	25	27	1410	285	79.8	860	5	0.58	0.18
3.6	200	12	25	81.25	940	35	96.4	784	158	20.1	0.97
4.6	150	13	29	70.7	1050	105	90	771	133	17.25	1.25
5.6	200	14	35	10	1260	105	91.7	819	36	4.39	1.80
3.6	100	15	25	92.1	850	120	86	747	160	21.3	1.72
4.6	200	16	25	75	1070	40	96.4	735	134	18.23	0.94
4.6	100	17	26	30	1050	220	79	703	24	3.41	0.80
3.6	200	19	28	81	870	35	96	680	130	19.11	0.80

Third Set

pH	Amount of Surfactant Added, ppm	Days After Sampling	Temp. °C	% Surf. Floated	Initial Color (Pt-Co Units)	Final Color (Pt-Co Units)	% Color Removed	Initial Solids, ppm	Solids Floated, ppm	% Solids Floated	$\frac{\text{Solids floated}}{\text{Surf. floated}}$
5.6	100	1	25	0	820	NA	NA	647	0	0	NA
5.6	150	1	25	6.66	820	NA	NA	647	5.3	.82	.53
5.6	200	2	25	25	940	NA	NA	508	89	17.52	1.78
3.6	150	3	25	80.3	680	25	96.4	485	105	21.65	.87
4.6	100	5	25	17	765	105	86.3	525	21	4	1.24
4.6	200	6	25	51	785	15	98.2	499	66	13.23	.64
3.6	100	7	25	90	715	40	94.5	544	132	24.26	1.47
5.6	200	20	25	32	880	50	94.3	497	56	11.27	0.88

Fourth Set

3.6	50	8	25	26	NA	NA	NA	681	0	0	0
3.6*	100	9	27	50	NA	NA	NA	1558	126	8.08	2.52

(sample not diluted)

APPENDIX E

BIBLIOGRAPHIC SURVEY ON PROPOSED METHODS FOR REMOVING COLOR FROM KRAFT MILL EFFLUENTS

Moggio, W. A. Color removal from kraft mill effluents. *Proc. 8th Ind. Waste Conf., Purdue Univ. Eng. Bull., Extension Ser.* no. 87: 465-76 (1955).

The problem of color removal from kraft mill effluents has not kept pace with the progress made in the biological stabilization of these effluents, principally because the color-imparting substances exert little or no biological oxygen demand; hence the solution of biological stabilization was considered more pressing. However, color removal is important, because the presence of color is evidence to the public that the stream contains such effluents and, though it does not create stream pollution, may lead to unwarranted and unjust accusations. The color bodies in kraft effluents are primarily lignin compounds whose color increases with increasing pH values; at pH values on the acid side, they become increasingly insoluble. The removal can be accomplished by either biological, physical, or chemical means; the use of hydrated lime offered the greatest promise of eventual success from economic and operation standpoints (*cf.* B.I.P.C. 23: 583-4). In all previous attempts for color removal from kraft-mill effluents, the matter of sludge handling has been the unsurmountable obstacle; hence, hydrated-lime sludge conditioning methods received first consideration. Two multistage methods were developed; both involve the carbonation of the sludge, and one involves further treatment of the carbonated calcium-organic sludge with black liquor, with the result that economical dewatering in standard equipment and recovery of the calcium content of the sludge in re-usable form become possible. Details of the two procedures are given. The development of a satisfactory sludge-handling method does not signify that the complete solution to the color problem has been found; other factors still require extensive investigation. 3 tables, 4 figures, and 3 references.

E.S.

2430. Colour and methods for colour removal. NEMEROW, N. L. *Proc. 11th Industr. Waste Conf., Purdue Univ. Engng Exm Ser.* No. 91, 1956, 584-594. The removal of colour from waste waters is important from an aesthetic point of view, and the author discusses various aspects of the removal of colour. Methods for measuring the intensity of colour are indicated briefly, and the concept of reflected light from a river water and the need for an instrument to measure it, are discussed. The experiences of various investigators in the removal of colour from waste waters are reviewed. These show that colour can be removed by many methods, with various degrees of efficiency. The chemical and physical structural characteristics of coloured compounds which affect colour removal are shown in a table. A bibliography of 29 references is appended.

WINGET, RUSSELL L. The pulp and paper industry pollution abatement program in the United States. *Pulp Paper Mag. Can.* 57, no. 3: 224-6, 230 (Convention issue, 1956).

The function, research activities, problems, and achievements of the National Council for Stream Improvement are described. Major problems center around solids removal, sludge dewatering and disposal, B.O.D. reduction, toxicity, and color removal. Over the past decade, U. S. pulp and paper industry pollution/ton of product has been decreased by over 50%. C.L.B.

372. NEMEROW, NELSON L. Color and methods for color removal. *Proc. 11th Ind. Waste Conf., Purdue Univ. Eng. Bull., Extension Ser. no. 91: 584-94 (June, 1957).*

Because of complaints from the public, the removal of color from waste waters is often more important than the removal of B.O.D. For the measurement of color intensity and quality the spectrophotometer, the filterphotometer, or a color comparator (such as the Hellige comparator) may be used. Both transmitted and reflected light may be measured in sewage and waste waters. The first is useful in determining the efficiency of color removal, whereas the second is measured because it is the light seen by an observer. A review of the literature pertaining to methods used for the removal of color from waste waters is given. Past experience indicates that color may be removed by many methods with varied degrees of efficiency. The chemical structure of the colored compounds is an important factor in the choice of the method of removal. 3 tables and 29 references. J.S.

1034. McINNIS, J. S., MILLS, R. H., and COLLINS, T. T., JR. Color and sulphide problems in water treatment at Hudson Pulp & Paper Corp. *Paper Trade J.* 142, no. 27: 32-5, 38; no. 29: 26-34 (July 7, 21, 1958).

Developments of the water-treating facilities and procedures at the Hudson Pulp and Paper Corp. plant at Palatka, Fla. are discussed. Practical aspects involved in the removal of color and sulfide from water for use in the manufacture of bleached pulp and in drinking-water systems are described. Methods for the removal of organic colorants in water include coagulation, destruction by chlorination and other oxidizing agents, decoloration by adsorption on charcoal and other surface-active materials, filtration, and electrolysis. The most practical of these procedures is coagulation of the negatively charged color bodies with sufficient alum at optimum pH using clay as a weighting agent and a proper coagulant aid. Recent years have seen the development of several excellent coagulant aids which help materially in the reduction of color by broadening the pH range at which floc formation occurs and improving the settling and filtering characteristic of the color flocs formed. The effectiveness of some of these materials (activated silica and Separan) has been shown by mill data. Pilot-plant studies on sulfide removal indicated the important role of sulfur bacteria, in conjunction with aeration, for the removal of sulfide and reduction of chlorine demand. These considerations are important where the water is to undergo a subsequent softening operation followed by chlorination before use in the mill process. The second section of the article includes a detailed literature summary on the subjects of color and sulfide removal in water treatment. 2 tables, 1 figure, and 103 references. R.A.S.

6781. BERGER, HERBERT F., and BROWN, RICHARD I. The surface reaction method for color removal from kraft bleachery effluents. *Tappi* 42, no. 3: 245-8 (March, 1959).

Previous research by the National Council for Stream Improvement and by several kraft mills has shown that color can be removed successfully from combined kraft and bleach effluents by precipitation with lime. The resulting sludge, however, has been extremely difficult to dewater to a dryness suitable for reburning in the kiln. The authors describe laboratory and bench-scale pilot plant experiments in which caustic extract from a bleached kraft mill is treated by application to a precoat of hydrated lime on a rotary vacuum filter. The lime-lignin reaction takes place at the surface of the precoat, forming a film which may be continually doctored off exposing a fresh reactive surface. The lime-organic film is dry enough to be fed to the kiln along with lime mud, and color removal is in excess of 95%. A larger scale pilot plant

has been set up at a southern bleached kraft mill by an equipment manufacturer, and the process is now under evaluation; 6 figures. — R.A.S.

1232. New approaches to pulp and paper mill waste treatment. GRIM, H. W. *Indust. Waster*, 1959, 4, 200-204. The author reports on and discusses research and development work in progress to improve the treatment of pulp and paper mill effluents. The three basic problems being studied are the dewatering and disposal of sludges obtained from sedimentation processes, reduction of colour in bleaching waste waters, and reduction of B.O.D. Developments in the methods employed for dewatering sludge are outlined (see *Wat. Pollut. Abstr.*, 1959, 32, Abstr. No. 2103). Studies show that addition of fly ash to the influent of the sedimentation tank improves sedimentation and increases the rate of dewatering of the sludge; the possibility of applying fly ash as a preliminary coating on filters is being investigated and preliminary tests have given good results. Preliminary pilot tests on an aerobic thermophilic process for the digestion of sludge indicate that substantial quantities of volatile matter can be destroyed in a relatively short time by this method. Exploration of all suggested methods for reducing colour has revealed that the most promising is the lime treatment technique; it was recently discovered that caustic extract from kraft bleaching could be almost completely decolorized by vacuum filtration through a bed of hydrated lime. Previous work carried out to increase the efficiency of B.O.D. removal from the waste waters produced by the paper industry is reviewed. It has been found that aeration and recirculation in stabilization tanks greatly improves oxygen transfer, hence increasing the degree of oxidation occurring per unit of storage time. Graphs are included to illustrate the results obtained.

1149. BERGER, Herbert F. Chemical treatment and water reclamation. Pulp Paper Mag. Can. 65, no. 6: T260-2 (June, 1964).

A chem. process for the redn. of both color and B.O.D. from kraft pulping and bleaching effluents has been devd. It involves slaking lime from the kiln with part of the effluent to be trtd. and adding it to the remaining effluent. Org. cpds., incl. color bodies, are adsorbed on the lime, which is then sepd. from the effluent in a thickener and dewatered on a vacuum filter or centrifuge. The supernatant from the thickener, together with the filtrate from the vacuum filter, is then carbonated with lime-kiln gas at controlled pH in a reactor to reclaim lime in soln. and further decolorize the effluent. CaCO_3 from the reactor is reclaimed on the mud filter in the causticizing system. The filter cake from the lime trmt. contains the added lime still as $\text{Ca}(\text{OH})_2$ and is used to causticize the green liquor. The liquor dissolves the org. cpds. from the lime and they appear in the white liquor produced. After the digester, they end up in the black liquor sent to the recovery furnace,

where they are burned together with org. matter dissolved out of the digested wood. This process gave a better than 90% color removal and a B.O.D. redn. of 40-60%. With some modifications (elimination of the first clarifier), it was found applicable to the trmt. of NSSC effluent as well, though at added expense (need for a lime kiln and slaker). The residual color (300-800 units) of the lime-trtd. effluent is gen. acceptable for discharge into streams, but is too high for water re-use in some processes. Two methods for addnl. color removal were investigated, one based on activated carbon and the other on foam fractionation. The latter required use of an external surfactant to produce a suitable foam and gave uneconomical enrichment ratios for color removal, but might be suitable for B.O.D. redn. and addnl. tall oil recovery from effluents rich in tall oil soaps. The activated-C process, at decreased pH and elevated temp., gave nearly total color removal from effluents of all kraft bleach plant stages, but the economics of the trmt. require further large-scale study and improvement. Total cost of high-degree kraft effluent trmts. for nearly closed water recirculation (incl. biol. trmt., lime decolorization, C adsorption, and desalination by electrodialysis) is still too high, viz., 50 cents per 1000 gal. 8 ref.

C.L.B.

5649. MURPHY, Nelson F., and GREGORY, Dale R. Removal of color from sulfate pulp wash liquors. Proc. 19th Ind. Waste Conf. (Eng. Bull. Purdue Univ. 49, no. 1; Eng. Extension Ser. no. 117): 59-79 (May, 1964; publ. Jan., 1965).

Studies concerning the effectiveness of a high-pressure (600 to 3200 p.s.i.g.)/high-temp. (254 to 400°C.) trmt. (using a Parr Pressure Reaction App.) in the removal of color from the effluent resulting from the caustic extrn. stage of a kraft pulp bleaching process show that under basic conditions (pH 7.5 or 9.3), essentially complete effluent vaporization is necessary for effective decolorization to occur. However, under acidic conditions (pH 3.5 or 5.5), effluent light transmittance of up to 50% (compared to distilled water) was attained with effluent vaporization of only 35%. A transmittance of up to 93% was attained at 100% effluent vaporization. The mechanisms of the decolorization reactions are unknown. Holding time under steady-state conditions had only a small effect on decolorization. Tests indicate that the sludge obtained as a result of decolorization can be removed by filtration. About 3,000 gal. of dark-colored waste are produced/t. of pulp bleached. 10 ref.

L.G.S.

14854. Davis, C. L., Jr.
 TERTIARY TREATMENT OF KRAFT MILL EFFLUENT
 INCLUDING CHEMICAL COAGULATION FOR COLOR
 REMOVAL.
 Tappi 52, no. 11: 2132-4 (Nov., 1969).

To protect estuary waters, the Ga. State Water Quality Control board required clarification, chem. trmt., and biochem. stabilization of kraft linerboard mill waste prior to discharge. The degree of chem. trmt. is defined in terms of APHA color units and is limited to 30 ppm with a max. waste discharge of 10 million gal./day. The 5-day BOD is limited to 800 lb./day, and suspended solids are limited to 10 ppm. A trmt. system to meet these specs. was put into operation in March, 1968 at the Riceboro, Ga. mill of Interstate Paper Corp. In sequence, it involves waste flocculation with lime (37 t./day calcd. as 90% CaO), removal of lime sludge and settleable solids, natural stabilization in an oxidn. basin satd. with Ca hydroxide at pH ca. 12.0, mech. aeration, and controlled discharge. The mill's rated capacity is 400 t./day of unbleached kraft linerboard. Process water requirements (excl. cooling) are 12,500 gal./t. only, about half the ind. av. A prelim. rept. of operating experience and costs is given. Total capital investment for waste trmt. is estd. at \$2,500,000 (10% of mill cost), of which nearly \$500,000 went into the color-removal system. Total first-year cost for operation and admin. of the system (incl. \$269,000 for chemicals) was \$883,700, or \$3.19 per t. of prodn. (assuming 10-yr. linear depreciation). The color-removal installation was supported partly by a \$467,000 grant from the Fed. Water Pollution Control Admin.
 C.L.B.

5853. Marton, J.; Stern, A. M.; Marton, T.
 DECOLORIZATION OF KRAFT BLACK LIQUOR WITH
POLYPORUS VERSICOLOR, A WHITE-ROT FUNGUS.
 Tappi 52, no. 10: 1975-81 (Oct., 1969).

A strain of the white rot fungus, *Polyporus versicolor*, which had been previously adapted to kraft lignin, significantly reduced the color of dild. pine kraft black liquor. The mechanism of the color removal was studied by using 3 kinds of lignin (spruce MWL, pine Indulin AT, and pine black liquor) and several lignin model substances. Lignin was not sufficient as the sole carbon source to support cell propagation; cell growth required an easily metabolizable sugar and other nutrient suppl. The intensity of cell growth and, simult., the degree of decolorization were higher under aerobic than under anaerobic conditions. The aerobically grown cells adsorbed lignin on their surfaces; hence phys. adsorption plays a major role in removing color, rendering the process less attractive from a technol. point of view. Part of the lignin was metabolized and chem. degraded. Under anaerobic conditions, where the rate of decolorization was much lower, phys. adsorption also became less significant. Adsorption did not play an important role for the phenolic lignin models; most of them could be metabolized easily. The reaction prods. were studied by means of differential spectry. and thin-layer chromat. The main steps involved in the aerobic trmt. are of an oxidative nature, in line with a phenol oxidase mechanism advanced recently by Kirk, Harkin, & Cowling. The formation of quinoid intermediates was demonstrated. The reactions of the phenolic models and their potential relations to the behavior of lignin chromophores are discussed. 16 ref.
 C.L.B.

10561. Luner, P.; Dence, C.; Bennett, D.; Kung, F.-L.
MECHANISMS OF COLOR REMOVAL IN THE TREATMENT OF PULPING AND BLEACHING EFFLUENTS WITH LIME. I. TREATMENT OF CAUSTIC EXTRACTION STAGE BLEACHING EFFLUENT.
NCASI Tech. Bull. no. 239: 52 p. (July, 1970).

Commercial spent liquor from the NaOH extn. stage of a softwood kraft bleaching sequence was sep'd. into precipitable and nonprecipitable fractions by trmt. with lime (CaO) or slaked lime (Ca hydroxide). The solids comprising each fraction were subjected to elemental and functional group anal. and mol.wt. detns. as a means of clarifying the mechanism of the lime pptn. process for color removal. Results showed that removal of color from the spent NaOH extn. liquor with lime is a chemical rather than a phys. process and that it is dep. on the presence of enolic and phenolic OH groups and on the mol.wt. of the solids contained in the liquor. Enolic and phenolic OH groups on structures contg. chromophoric groups react with lime and other Ca cpds. under alk. conditions forming insol. Ca salts which ppt. In spent NaOH extn. liquors the phenolic OH content is low, and pptn. results primarily from interaction of lime with enolic OH groups. The mol.wt. of the solids is a determinant factor in the lime pptn. process as it affects the soly. of the resulting Ca salts. 32 ref. W.W.

10562. Luner, P.; Dence, C.; Bennett, D.; Ota, M.
MECHANISMS OF COLOR REMOVAL IN THE TREATMENT OF PULPING AND BLEACHING EFFLUENTS WITH LIME. II. TREATMENT OF CHLORINATION STAGE BLEACHING EFFLUENTS.
NCASI Tech. Bull. no. 242: 24 p. (Dec., 1970); cf. ABIPC 41: abstr. 10561.

As in the case of the previous work on NaOH extn. stage bleaching effluent, these studies demonstrated that removal of colored org. matter from spent chlorination stage bleaching effluent by lime involved Ca salt pptn. which was dep. on (1) the presence of weakly acidic enolic and, to a lesser degree, phenolic OH groups, and (2) on the mol.wt. of the dissolved solids present as a determinant of soly. of the resultant Ca salts. It is possible as well, that during lime neutn. of chlorination stage effluent, hydrolysis of chloro substituents causes further formation of weakly acidic OH groups which react with lime forming insol. Ca salts. 18 ref. W.W.

9227. Sameshima, K.; Kondo, T.
STUDY ON THE COLOR OF PULP INDUSTRY WASTE LIQUORS. I. RELATIONSHIP BETWEEN THE COLOR OF WASTE LIQUOR FROM KRAFT PULP MULTISTAGE BLEACHING AND THE ISOLATED CHLORINOXYLIGNIN.
J. Japan Wood Res. Soc. (Mokuzai Gakkaishi) 16, no. 7: 347-52 (Nov., 1970). [Jap.; Engl. sum.]

Pine and birch kraft pulps were subjected to multistage bleaching by the CEHD sequence, and the color-causing substance in the spent bleach liquors was isolated by acidification to pH 1.0 fld. by centrifugation and dialysis. This substance, tentatively called Cl-oxylignin, contributed ca. 80% to the total color and ca. 45% to the COD of the effluent. It contained only ca. 1.6% carbohydrates (as xylose), showed a shoulder on the UV absorption curve at ca. 285 nm., and gave an IR spectrum charac. of lignin. In comparison with other lignin preps., it displayed marked light absorption in the visible spectrum but no charac. absorption max. Its mol.wt. was rel. high, comparable to that of pine dioxane lignin. The dark color may derive largely from reactions assocd. with lignin demethylation, in which the Ph and CO groups act as chromophores and the COOH group as auxochrome. 18 ref. C.L.B.

1602. Mohanrao, G. J.; Subrahmanyam, P. V. R.
 STREAM AND AIR POLLUTION PROBLEMS RELATED
 TO DISPOSAL OF EFFLUENTS FROM PULP AND PAPER
 INDUSTRY.
 Ippta 8, no. 3: 155-63 (July-Sept., 1971). [Engl.]

This is mainly a rev. regarding stream pollutants. The main water pollutants are high pH, BOD, COD, suspended solids, and coloring matter. BOD and solids may be reduced to reasonable limits by means of activated sludge trmt. and by anaerobic lagoons. The latter are less expensive. Color and COD are difficult to remove. Suspended solids that emanate mainly from machine waters can be reduced initially by intraplant techniques involving savealls, and later by coagulation and sedimentation. Possibly it would be well to reduce BOD and to correct the pH of pulp mill effluents by means of anaerobic lagooning. The anaerobic effluent can be subjected to land disposal or treated by aerated lagooning before discharging into a stream. Air pollutants from kraft mills are also considered briefly. They consist mainly of hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and "particulate pollutants". Their sources are outlined. 30 ref. L.E.W.

1558. Basu, S.
 STUDIES ON CARBONATION OF BLACK LIQUOR FOR
 LIGNIN PRECIPITATION AND ITS SUBSEQUENT SEPA-
 RATION.
 Ippta 8, no. 4: 207-14 (Oct./Dec., 1971). [Engl.]

A study was made concerning the feasibility of removing "ligno-organic" components from black liquor by "carbonation" in rendering the liquor suitable for causticization of Na cpds. to NaOH. The process parameters during carbonation included the degree of turbulence, temp., pressure, time, and final pH. All of these were studied, and the optimum conditions were detd. Pressure carbonation at 4.5 kg./sq.cm. fld. by trmt. with acetone to insure coacervation-flocculation had a pronounced effect on removal of the ligno-organic components, obtained as a lyophilic colloid. Carbonation at atm. pressure was carried out on a small scale. Pressure carbonation was done in an elec. heated 18-liter autoclave provided with arrangements for recirculating the liquor through a heat exchanger. The response of the black liquor to coagulation-coacervation flocculation as a means of lignin removal was found to be correlated with the props. of the original cellulosic raw matl. with respect to lignin content and distribution. 21 ref. L.E.W.

10867. Davis, C. L.
 COLOR REMOVAL FROM KRAFT PULPING EFFLUENT
 BY LIME ADDITION.
 Water Poll. Control Res. Ser. (EPA) no. 12040ENC12/71: 72
 p. (Dec. 1, 1971). [Avail. from NTIS; PB218306] cf. ABIPC
 40: abstr. 6854 and ABIPC 42: abstr. 2729.

1589. Interstate Paper Corp.
 COLOR REMOVAL FROM KRAFT PULPING EFFLUENT
 BY LIME ADDITION.
 Water Poll. Control Res. Ser. (U.S. EPA) 12040 ENC: 117 p.
 (Dec. 1, 1971). [Supt. Doc., GPO, Washington, D.C. 20402;
 \$1.25]

A prototype color removal system using slaked lime was designed, constructed, and operated as an integral part of a tertiary trmt. system for total process effluent from a kraft linerboard mill (Interstate Paper Corp.) at Riceboro, Ga. The lime pptn. process was combined with primary clarification fld. by natural biochem. lake stabilization and mech. aeration. Results showed that the system can operate under widely varying conditions to yield a rel. const. effluent color of ca. 125 ppm APHA color units by dosage of the original effluent (1200 ± 200 ppm color units) with 1000 ± 50 ppm of Ca hydroxide. Assuming a price of \$15.35/t. of 90% CaO lime, this trmt. level costs \$53.73 per million gal. of effluent. Equipment evaln. indicated substantial savings in capital cost for future installations, since performance is directly related to control of lime feed. The Ca was recovered continuously under mill conditions, using a statist. designed program which is described. The total tertiary trmt. system achieved an overall 5-day BOD redn. of 98%; the final discharge averaged 6 ppm BOD. 19 ref. C.L.B.

569. Dalpke, H.-L.
 STUDIES DEALING WITH EFFLUENT TREATMENT BY
 THE USE OF ACTIVATED CARBON.
 Papier 26, no. 1: 4-10 (Jan., 1972). [Ger.; Engl. & Fr. sum.]

The removal of biologically harmful substances (characd. by 5-day BOD detns.) from mill effluents is known to be essential in preserving (or restoring) waterways. Besides biol. purification, a no. of chem. and phys. purification processes have been suggested for redg. 5-day BOD. One of these involves the adsorptive action of activated C. The author gives exptl. data obtained in a series of 4-stage lab. expts. involving effluent trmt. in 4 C-contg. cylinders, and covers the theoret. basis for van der Waals adsorption. Apparently, the effluent studied could be decolorized completely at a specific flow rate of 1.5 liter/hr./kg. C. Such trmt. also removed the residual fibers completely, and lowered the 5-day BOD level to not over 25 mg. O/liter. The technique is shown in appropriate illustrations. 2 ref. L.E.W.

2855. Subrahmanyam, P. V. R.; Sachan, P. C.; Mohanrao, G. J.
ASPECTS OF COLOR REMOVAL FROM PULP AND
PAPER MILL EFFLUENTS.
Ippta 9, no. 1: 20-3 (Jan./March, 1972). [Engl.]

Lignin is described as an "aesthetic pollutant", and its "nonbiodegradability" is discussed. For the removal from effluents of color due to lignin, chemical methods like massive lime trmt., biol. methods like activated sludge trmt. and the utilization of various fungi, and phys. methods like adsorption by activated carbon or soils have been suggested. Lab. studies by the present authors, using 8 different soils, are described in detail. It is shown that color redn. is directly proportional to soil cation-exchange capacity. The requirement of land for trg. pulp-mill effluents is also calcd., assuming a steady rate of percolation and a given rate of evapn. 12 ref.
L.E.W.

4154. Leszczynski, C.
DECOLORIZATION OF KRAFT MILL EFFLUENTS.
Przegląd Papier. 28, no. 3: 88-9 (March, 1972). [Pol.]

Colored substances in the effluents from kraft mills, consisting mainly of lignin derivs. and tannins, are not degraded in the activated sludge purification process. Although these substances are not toxic to aquatic organisms in concns. presently found in waters, they are harmful by inhibiting the penetration of sunlight into the water, increase the costs of trmt. of water, and prevent the use of the waters for recreational purposes. For these reasons, many methods have been proposed for decolorization of effluents prior to their disposal into natural waters, incl. pptn. with metal salts, adsorption on activated C, reverse osmosis, etc. Among these methods only trmt. with lime was found suitable for ind. purposes. The process, devd. and patented in the USA, consists essentially in mixing the effluents with lime, sepg. the ppt. contg. the colored substances by sedimentation, dewatering it to a dryness of 40-60%, and using it in the causticization plant. The process has been introduced in three U.S. mills, notably the Riceboro (Ga.) mill of the Interstate Paper Corp., the Georgia-Pacific Corp. mill in Woodland (Maine), and the Continental Can Co. mill in Hodge (La.). The decolorization procedures and their efficiency at the three mills are described. Also mentioned are pilot plant studies carried out by the International Paper Co. and the American Can Co. on lime decoloration of bleaching effluents, and on modifications of kraft pulp bleaching processes to reduce the load of colored substances in effluents. 13 ref.
J.S.

7415. Dytnerskii, Yu. I.; Svittsov, A. A.; Romanenko, Yu. K.; Zhilin, Yu. N.; Semenov, V. P.; Trupchaninova, O. V.
 USE OF REVERSE OSMOSIS AND ULTRAFILTRATION
 FOR THE PURIFICATION OF EFFLUENTS.
 Bunnazh. Prom. no. 7: 22-4 (July, 1972). [Russ.]

Purification of mill effluents by the methods of reverse osmosis and ultrafiltration was studied in the lab. of the Baikal pulp mill. Some results are reported of expts. carried out on effluents which have been purified chem. and biol., on nonpurified effluents, and on black liquor evapn. condensates. In both purification methods CA membranes of domestic prodn. were used. The results of these preliminary expts. indicate that purification is more effective

compared to the presently used methods, and that the purified effluents can be used as recycle process water. The advantage of ultrafiltration over reverse osmosis is a high efficiency at rel. low pressures (3-10 kg./sq.cm.). On the other hand, reverse osmosis removes dissolved mineral cpds.; until now such removal has been the most complex problem in effluent purification. J.S.

- 453(U). Lavrinenko, I. K.; Solyanik, P. A.; Vilenskii, V. I.
 PURIFICATION OF PAPER MILL EFFLUENTS BY
 MICROFILTRATION.
 Vodosnabzh. Kanaliz. Gidrotekh. Sooruzh., Resp.
 Mezhd. Nauch.-Tekh. Sb. no. 15: 40-4 (1972). [Russ.]

It was shown that it is possible to use microfilters for the purification of paper mill effluents and of process water used by such mills. From: Ref. Zh., Khim. no. 24: abstr. 1557 (Dec. 25, 1972). D.M.C.

- 9719(R). Tyler, M. A.; Fitzgerald, A. D.
 A REVIEW OF COLOR REDUCTION TECHNOLOGY IN
 PULP AND PAPER MILL EFFLUENTS.
 CPPA Tech. Sect. Proc. 1972: D116-23; discn.: D123-5.

Over 60 lit. repts. on effluent trmts. for color removal were studied to assess the status of ind. practices. Lime trmt. is the most established method, achieving 65% color removal from bleached kraft effluent at a capital cost of \$1-1.5 million and operating costs of \$1.0-1.5 per ton of pulp. Coagulation with alum gives similar results at similar costs, but requires improved systems for handling the difficultly dewatering sludge. Adsorption on activated C accomplishes complete color removal, but at high operating costs. Switching from Cl to oxygen bleaching of kraft pulp would reduce effluent color by 60-65% and save ca. \$2 per ton of pulp in chem. consumption. Capital costs for such a conversion are estd. at \$2 million. 8 ref. C.L.B.

3028(M). Gould, M.

NEW LIME PROCESS FOR REMOVAL OF COLOR FROM
KRAFT MILL EFFLUENT AT GEORGIA-PACIFIC
[CORP.'S] WOODLAND, MAINE, MILL.
TAPPI Envir. Conf. 1972: 141-7.

The patd. effluent-decoloring process described involves trmt. of alk. extn. waste from a kraft bleach plant with ca. 2000 ppm. of lime before entering a solids-contact clarifier. Reaction of lime with color bodies precipitates a settleable sludge which is continuously removed from the clarifier. The lime sludge underflow is then mixed with prefiltered lime mud and dewatered on a conventional belt filter. The dewatered sludge is fed directly into the lime kiln where the color bodies are burnt off and the lime is recovered. The full-scale trmt. plant (installed after pilot-plant trials) removes ca. 90% of the color and ca. 45% of the BOD from the effluent of the alk. extn. stage, and recovers ca. 80% of the lime used. Mill experiences, incl. process parameters, costs, and maintenance, after the 1st yr. of operation are indicated. C.L.B.

1613. Oswalt, J. L.; Land, J. G., Jr.

COLOR REMOVAL FROM KRAFT PULP MILL EFFLUENTS BY MASSIVE LIME TREATMENT.
Envir. Protection Technol. Ser. EPA-R2-73-086: 109 p.
(Feb., 1973).

A demonstration plant was installed and operated to determine whether trmt. with 20,000 ppm lime could effectively and economically decolor kraft pulp mill effluents, notably the black effluent from the alk. extn. stage of the bleach plant, and the reddish-brown effluent from the final unbleached pulp washing stage. The impact of massive lime trmt. on a hypothetical 1000 t./day bleached kraft integrated mill is described. Using all the lime normally available in such a mill would allow trmt. of 4 million of the 29 million gal. of total effluent. This would remove 72% of the total effluent's color, reducing the residual color to ca. 740 APHA units at an estd. cost of \$1.80/t. of pulp, incl. depreciation, insurance, and taxes. 10 ref. C.L.B.

1630. Swanson, J. W.; Dugal, H. S.; Buchanan, M. A.; Dickey, E. E.
KRAFT EFFLUENT COLOR CHARACTERIZATION BEFORE AND AFTER STOICHIOMETRIC LIME TREATMENT.
 Envir. Protection Technol. Ser. EPA-R2-73-141: 75 p. (Feb., 1973). [GPO, Supt. Doc., Washington, D.C. 20402; \$1.00]

The NCASI lime trmt. process was found to remove an av. of ca. 86% of the color, 57% of the total org. C, and 17% of total sugars from unbleached kraft mill effluents collected at Riccboro, Ga., over a 15-month period and processed at Appleton, Wis. No appreciable change in chloride content was noted. The wt.-av. mol.wts. of the untrd. acid-insol. fractions varied from less than 400 to ca. 30,000; the mol.wts. of the untrd. acid-sol., lime-trd. acid-insol., and lime-trd. acid-sol. fractions varied from below 400 to ca. 5000. The study showed that color bodies having an apparent mol.wt. below 400 are not removed, but those having mol.wts. above 5000 are completely removed. In the 400-5000 mol.wt. range, partial removal takes place. Based on IR spectry., the acid-insol. color bodies of high mol.wt. seem to contain a high proportion of CO groups, probably conjugated with an aromatic ring, while the low mol. acid-sol. fractions seem to contain nonconjugated COOH groups assocd. with carbohydrates. Color bodies are aromatic cpds., partly degraded lignin, having a neg. charge and existing primarily as sol. Na salts in aq. solns. The color bodies which are not removed by lime trmt. have low mol.wt., high unconjugated COOH groups, ligninlike character, and seem assocd. with colorless C cpds. 18 ref. C.L.B.

11801. Gould, M.
COLOR REMOVAL FROM KRAFT MILL EFFLUENT BY AN IMPROVED LIME PROCESS.
 Tappi 56, no. 3: 79-82 (March, 1973); cf. ABIPC 41: abstr. 10544; 43: abstr. 3028, 8487.

1626. Spruill, E. L.
COLOR REMOVAL AND SLUDGE RECOVERY FROM TOTAL MILL EFFLUENT.
 Tappi 56, no. 4: 98-100 (April, 1973).

A lime trmt. color removal system, with recovery of lime and fibrous sludge integrated into the kraft lime processing system, has been constructed for trmt. of total mill effluent at the unbleached kraft mill of Continental Can Co., Hodge, La. With about 1000 ppm of lime, color redn. of 80-90% has been achieved in kraft effluent, with lower effectiveness on neutral sulfite chem. wastes. Good centrifugal dewatering and lime kiln incineration of sludges have been recorded. Settling and thickening of color sludge have been excellent, but carbonation-stage settling has been more variable. 8 ref. C.L.B.

1632(M). Timpe, W. G.; Lang, E. W.
 ACTIVATED CARBON TREATMENT OF UNBLEACHED
 KRAFT EFFLUENT FOR REUSE: PILOT PLANT
 RESULTS.

TAPPI Envir. Conf. (San Francisco), May 1973: 203-18.

An earlier lab. study at St. Regis Paper Co.'s R&D Div. (Pensacola, Fla.) established the degree of effluent trmt. achievable with activated C alone and combined with other methods. It also helped to pick the best of 24 activated C preps., and ascertained that MeOH and other low-mol. org. cpds. are not removable by activated C. The present rept. gives exptl. and operating data for a 30 gal./min. pilot plant in which 3 different pretrmts. (clarification, clarification plus lime trmt., and biooxidn. plus clarification) preceded the adsorptive removal of effluent components in 2 different systems. One system utilized 4 std. downflow granular C columns, the other involved multistage countercurrent agitation (FACET system, short for "fine activated carbon effluent trmt."). The lime/C sequence achieved color removals to below 100 APHA color units and TOC removals to less than 100 mg./liter. It was the most econ. of the 3 sequences studied. Optimum chem. dosages were 320-600 mg. of CaO/liter plus 2.5 lb. of C/1000 gal. For successful trmt. with activated C, the unbleached kraft effluents must contain ca. 80 mg. of Ca/liter. The other 2 sequences yielded rel. low adsorption rates, probably due to coagulation of colloidal color bodies on the C surface. The FACET system was found to be tech. sound and capable of farther devt. to provide trmt. at lower capital cost than with conventional C columns. 17 ref. C.L.B.

1640(M). Wright, R. S.
 COLOR REMOVAL FROM KRAFT PULP MILL EFFLU-
 ENTS BY MASSIVE LIME TREATMENT.
 TAPPI Envir. Conf. (San Francisco), May 1973: 229-35.

Massive lime trmt. by the NCASI-devd. process will remove over 90% of color bodies from effluents of the final unbleached kraft pulp washing stage and of the alk. extn. stage in bleach plants. These 2 effluents contain 65-75% of the total color load produced in the mfr. of bleached kraft pulp. Using all the lime normally available in a typical bleached kraft mill, ca. 14% of the total effluent can be trd. By trg. the most highly colored effluents, 72% of the mill's total color load can be removed. The introduction of massive lime into the mill's liquor causticizing operation will dil. the white liquor and lower its concn. by ca. 15%. Hence the total liquor vol. handled throughout the mill will increase and require increased capacity of chem. prepn. and recovery equipment. For a given pulp prodn., lime kiln fuel requirements increase 6.4%. Moreover, the carryover of org. cpds. by the massive lime sludge into the cooking liquor system can intensify foam problems. Buildups of Cl and other matls. have no apparent effect on the chem. recovery cycle. A typical 1000 t./day kraft mill may spend ca. \$1.80/t. of bleached pulp for massive lime trmt. of 4,000,000 gal. effluent, without adverse effect on pulp bleachability or final prod. quality. C.L.B.

5110. Sanks, R. L.
ION-EXCHANGE COLOR AND MINERAL REMOVAL
FROM KRAFT BLEACH WASTES.
U.S. EPA, Envir. Prot. Technol. EPA-R2-73-255: 201 p.
(May, 1973). [Supt. Doc., GPO, Washington, D.C. 20402;
\$2.35]

Laboratory evalns. of 20 ion-exchange resins and 7 carbons for removing color and minerals from kraft bleach plant effluent showed that the resins were equal to carbon for decoloring the combined waste. With few exceptions, resins were unsuited for decoloring wastes from each stage separately. Except for success in the use of weak wash to regenerate Amberlite XAD-8 resin, utilization of mill liquors for regeneration was unsuccessful. Sulfuric acid, NaOH, and ammonia were good regenerants, but lime was poor. Single stage ion-exchange produced water adequate for unbleached pulping while two-stage desalination produced water adequate for bleached pulping. The costs for desalination incl. amortization over a 10 yr. period are estd. to vary from \$1.38/1000 gal. (for the nonoptimized lab. process) to \$0.42/1000 gal. (with estd. 90% cation regeneration efficiency, 85% anion regeneration efficiency, and 87% prod. recovery). 63 ref. W.W.

(See also abstr. no. 5615, 5642)

5649. Croom, H. C.; Owens-Illinois Inc.
SYSTEM FOR REMOVING COLOR FROM PAPER MILL
LIQUID WASTE.
U.S. pat. 3,736,254. issued May 29, 1973. 7 claims.

Liquid pulping effluent is mixed with an aq. slurry of lime and lime mud composed principally of calcium carbonate, under alk. conditions. The mixt. is subjected to clarification sepn. of formed precipitants. The liquid effluent overflow is carbonated by bubbling carbon dioxide gas through it to ppt. calcium carbonate and residual color-imparting entities and to effect adjustment of the pH to approx. neutral. The decolorized liquid is ready for discharge.

F.J.L.

8534. Pulp & Paper International.
COLOR REMOVAL PROCESS.
Pulp Paper Intern. 15, no. 5: 69 (May, 1973).

PPRIC has successfully tested a new method for decolorizing pulp mill effluents which was originally developed and patented at the Centre Technique of France. The principal color-carrying effluent streams from a pulp mill are contacted with high molecular weight amines dissolved in a water immiscible solvent. The process is said to remove 90-98% of the color, 45-85% of the COD, and 30-70% of the BOD from the effluents. The amines can be regenerated and recirculated to the process. Small scale tests in a kraft mill gave results as good as laboratory trials. Assuming economic feasibility studies give favorable results, the process will be retested on a larger scale.

P.B.H.

- 1590(M). Johnson, J. S., Jr.; Wintern, R. E.; Moore, G. E.
HYPERFILTRATION (REVERSE OSMOSIS) OF KRAFT
PULP MILL AND BLEACH PLANT WASTES.
TAPPI Envir. Conf. (San Francisco), May 1973: 237-43.

Kraft mill effluents (brown sock wash water, decker and screen room wastes, and bleach plant effluents) were subjected to high-pressure hyperfiltration (R.O.) through dynamic membranes of polyacrylate on a hydrous Zr(IV) oxide substrate; to moderate-pressure ultrafiltration using low-salt-rejection membranes comprising single layers of hydrous Zr(IV) oxide or of neut. org. polymers; and to low-pressure filtration. Devatering of weak black liquor was also attempted. Compared to conventional detachable CA membranes, fluxes were considerably higher, and decontamination seemed adequate for reuse of many filtrates. Moreover, filtration could be conducted at the temp. of the process, and the membranes could be regenerated or removed and reformed in situ. 24 ref. C.L.B.

10265. Kemmer, F. N.; Nalco Chemical Co.
COLOR REMOVAL PROCESS.
Can. pat. 929,712. Issued July 10, 1973. 4 claims.

This process for decolorizing paper mill waste with lime is similar to that described previously in U.S. pat. 3,578,587; cf. ABIPC 42: abstr. 4034. F.J.L.

7911. Fremont, H. A.; United States Plywood-Champion Papers Inc.
COLOR REMOVAL FROM KRAFT MILL AQUEOUS EFFLUENTS.
U.S. pat. 3,758,405. Issued Sept. 11, 1973. 10 claims.

A system is provided for removing color bodies from aq. effluents from kraft pulp mfr. such as first stage caustic extn. filtrate. The system involves adjusting the pH of the effluent to about 9, subjecting the effluent to ultrafiltration to form an aq. permeate and a retentate contg. all the color bodies in a solids concn. of at least 15%, and thermally oxidg. the retentate to oxidize the color bodies to colorless inorg. salts and gases which can be safely disposed of. F.J.L.