# FOAM SEPARATION OF KRAFT MILL EFFLUENTS

by

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# ABSTRACT

A laboratory investigation into foam separation processes, as applied to kraft pulping and bleaching effluents is described. Two methods, foam fractionation and ion \* flotation were tested in the laboratory.

The procedures developed concentrated primarily on the removal of effluent colour because this property lent itself most readily to the available analytical methods, and because effluent colour removal presents one of the greatest waste water treatment problems facing the industry today.

The foam fractionation technique was not successful. Substantial colour removals were obtained, but it was subsequently shown that the mechanism of removal was really an ion flotation.

Positive results were obtained with the use of the ion flotation process for removal of effluent colour. At optimum conditions, the recovery of flotable material and the corresponding removal of effluent colour were in excess of 95 per cent. Variation of surfactant dosage

ii

showed that below a critical level no colour was removed. As concentrations increased above this value the amount of colour removed increased rapidly, reaching a high removal level beyond which increases in surfactant concentration were of little value. The rate of flotation recovery was found to be significantly affected by the air sparge rate and the sparger pore size, both parameters which would determine the area available for adsorption. The pH of the flotation cell solution had a marked effect on the system. Optimum pH was clearly defined as 5.1. Removal of material other than just the chromophoric fraction was apparent. Biological oxygen demand data, while not extensive, demonstrate a significant reduction in the bio-degradable portion of the effluent.

The possible future development of the process into a viable candidate for industrial application is discussed.

iii

# TABLE OF CONTENTS

																								Page
ABSTRAC	т	• .•	•	•	•	•	•	•	•	•	•	٠	•	•	•	•	•	•	•	•	•	•	•	ii
LIST OF	TAB	LES.	•	•	•	•	•	•	•	•	•	•	•	٠	•	•	•	٠	•	٠	٠	•	•	ix
LIST OF	FIG	URES	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	х
ACKNOWL	EDGE	MENT	S.	•	•	•	٠	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	٠	xiii

# Chapter

1	INTRODUCTION	I
2	BASIC BACKGROUND KNOWLEDGE OF THE PULPING, BLEACHING, AND EFFLUENT SYSTEMS	1
	General	1
	Kraft Pulping	1
	Lignin, the Colour Producer	5
	Chromophores Derived from the Pulping Process	5
	Chromophores Derived from the Bleaching Process	7
	Properties of the Various Chromophores 12	2
	Summary	1
3	MILL EFFLUENT COLOUR REMOVAL TECHNOLOGY 15	5
	The Relative Dominance of Hydrated Lime 19	5

# <u>Chapter</u>

	Other Alternatives
	Activated Carbon
	Aluminium and Iron Salts 17
	The Grenoble Process
	Summary
4	ADSORPTIVE BUBBLE SEPARATION METHODS 21
	General
	The Classification System
	Foam Fractionation
	Froth Flotation
	Ore Flotation
	Low Gas-flow-rate Methods
	Ion Flotation
	Precipitate Flotation
	Other Froth Flotation Methods
	Reported Separations
	Summary
5	ION FLOTATION
	Introduction
	Surface Activity
	Micelles
	Other Parameters Affecting Ion Flotation 35
	Stability of the Froth
	The Collector-Colligend Ratio

6

	Introduction of Surfactant	37
	Choice of Collector	37
	Bubble Size and Characteristics	38
	Air Sparge Rate	38
	рН	39
	Ionic Strength	40
	Concentration of Colligend	40
	Temperature	41
	The Kinetics of Ion Flotation	41
	Summary	42
E	EXPERIMENTAL APPARATUS	43
	Foam Fractionation Apparatus	43
	Ion Flotation Apparatus	46
I	EXPERIMENTAL PROCEDURE	48
	Foam Fractionation - Batch Operation	48
	Foam Fractionation - Continuous Operation	49
	Ion Flotation - General	51
	Analytical Tests and Procedures	5 <b>3</b>
	Colour Determination	53
	Biological Oxygen Demand	53
	pH, Measurement and Calibration	53
	Stirrer Speed Calibration	54
	Flotable Solids Determination	54

# <u>Chapter</u>

		Cle	anin	ng P	roc	ced	ure	es.	•	•	•	•	•	•	•	•	•	•	•	55
		Ele Zet	ctro a Po	ophc oter	oret itia	tic al	Mc Mea	obi asu	li re	ty mer	an nt	d/ ·	or	•	•	•	•	•	•	55
		Rot	amet	er	Cal	lib	rat	tio	n.	•	•	•	•	•	•	•	•	•	•	56
8	RESULT	rs A	ND D	) I S (	CUSS	510	Ν.		•	•	•	•	•	•	•	•	•	•	•	57
	Gei	nera	.1 -	the	e Et	ffl	uer	nt.	•	•	•	•	•	•	•	•	•	•	•	57
	Fo	am F	ract	ior	nat	ion	( E	Bat	ch	) F	≀es	u 1	ts	•	•	•	٠	•	•	60
	Foa	am F	ract	cior	nat	ion	((	Con	ti	nuc	ous	)	Re	su	1t	s	•	•	•	63
	Ioi	n Fl	otat	ior	n Re	esu	lts	5.	•	•	•	•	•	•	•	•	•	•	•	67
		Gen	eral	i	• •	•	•	• •	•	•	•	•	•	•	•	•	•	.•	•	67
			The	Col	lle	cto	r-(	Co1	1 i	ger	١d	Ra	ti	0	•	•	•	•	•	70
			Co11	lect	tor	Mi	ce	l1e	F	orr	nat	ic	n	•	•	•	•	•	•	74
			pH.	•	• •	•	•		•	•	•	•	•	•	•	•	•	•	•	75
			Bubb	le	Si	ze	•		•	•	٠	• •	•	•	•	•	٠	•	•	80
			Air	Spa	argo	e R	at	e.	•	•	•	•	•	•	•	•	•	•	•	81
			Co11	lect	tor	Pr	e-i	nix	T	ime	э.	•	•	•	•	•	•	•	•	85
			BOD	5 Re	emo	val	•		•	٠	•	•	•	•	•	•	•	•	•	88
			Kine	etio	cs (	of	th	e F	10	ta	tic	n	Re	ecc	ve	ery	1.	•	•	92
			The	Ιοι	n F	lot	at	ion	_S	ys <sup>.</sup>	ten	1 8	as	Pa	irt	t				0.5
			ot a	an :	Ind	ust	ri	al	١r	ea	tme	ent	5 8	rc	) C 6	255	5.	•	•	90
9	CONCL	USIC	DNS.	•	• •	•	•	• •	٠	٠	•	•	•	•	•	•	•	•	•	99
10	RECOM	MENE	DATIO	DNS	F0	R F	UR	THE	R	ST	UDY		•	•	•	•	•	•	•	101
REFERENCE	ES	• •	• •	•	••	•	•	• •	•	•	•	•	•	•	•	•	•	•	•	104
NOMENCLAT	FURE.	•••		•		•	•		•	•	•	•	•	•	•		•	•	•	109

APPENDICES	· · ·	Page
A	The Modified Colour Test	. 111
B	Summary of Ion Flotation Data	. 119
С	Flotation Recovery Results	122

viii

# LIST OF TABLES

<u>Table</u>		Page
1	Typical Batch Operation Foam Fractionation Data	. 61
2	Typical Continuous Operation Foam Fractionation Data	• 64
3	Biological Oxygen Demand Removal Data	. 90

# LIST OF FIGURES

Figure		Page
1	General Types of Chromophoric Structures Present in Kraft Pulping Wastes	8
2	Possible Sites of Degradative Attack by ClO $_2$ and Cl $_2$ on Lignin	10
3	Formation of o-Benzoquinonoid Unit during Chlorination	11
4	Generalized Formation of o-Quinone during Pulp Bleaching	11
5	Schematic Diagram of the Grenoble Process for Purification of Kraft Pulp Mill Effluents	20
6	Classification Scheme for the Various Adsorptive Bubble Separation Methods	22
7	Four Modes for Continuous Foam Fractionation	25
8	Schematic Diagram of the Foam Fractionation Experimental Apparatus	. 44
9	Schematic Diagram of the Ion Flotation Experimental Apparatus	. 47
10	Colour versus pH for First Caustic Extraction Stage Effluent	58
11	Colour versus pH for Total Mill Effluent	. 59

Х

<u>Figure</u>

12	Schematic Drawing of Scum Formation 69	)
13	Percent Colour Removal versus Surfactant Dosage	I
14	Percent Flotation Recovery versus Surfactant Dosage	}
15	Percent Colour Removal versus pH 76	5
16	Percent Flotation Recovery at Various pH Values	3
17	Zeta Potential versus pH for Flotation Cell Effluent	}
18	Percent Flotation Recovery at pH 5.1 for Two Sparger Porosities 82	2
19	Percent Flotation Recovery at pH 4.5 for Two Sparger Porosities 83	3
20	Percent Flotation Recovery at Various Air Sparge Rates	1
21	Foam Volume versus Air Sparge Rate 86	5
22	Foam Volume versus Surfactant Dosage 87	7
23	Absorbance versus Wavelength for Run 3 91	1
24	Plot of Mln([M-R]/M) versus Time for Runs 16 and 20	3
25	Plot of log(M-R) versus Log(time) for Runs 16 and 20	4
26	Proposed Ion Flotation Process for Purification of Pulp Mill Effluents 90	6

# <u>Figure</u>

A1	Absorbance versus Wavelength for Various Concentrations of First Caustic Extraction Stage Effluent	•	•	•	•	112
A2	Absorbance versus Concentration of First Caustic Extraction Stage Effluent	•	•	•	•	113
A3	Absorbance versus Wavelength for Various Strengths of the Pt-Co Standard Solution	•	•	•	•	115
A4	Absorbance versus Colour Concentration .	•	•	•	•	118

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xiii

## CHAPTER 1

# INTRODUCTION

Pulp and paper wastewater treatment, in its present form, involves the removal of settleable solids and the stabilization of the biodegradable organic fraction of the mill effluents. The methodology for removing the settleable solids and disposing of the voluminous sludge which is produced and for reducing the biologically available organics have now been developed to a substantial degree. Biological treatment does not, however, significantly affect certain properties such as effluent colour. This fact underlines the need for at least a third step in the conventional treatment scheme; a tertiary stage to remove, or partially remove, the colour containing, relatively non-biodegradable portion of the effluent.

Historically [1], this fraction has been considered to be relatively innocuous to aquatic life. Natural water, it was argued, is usually coloured and turbid and dilution is usually sufficiently high that the added material would

not alter the natural state appreciably. However, recent work [2] has shown that the reduced penetration and the altered spectrum of the light, which does penetrate to a certain depth, may affect aquatic growth.

The non-biodegradable portion of the pulp mill effluent is comprised primarily of wood extractives and lignin degradation products which are formed during the pulping and bleaching stages. A large portion of this material is chromophoric. Because of the limitations and relative complexities of the range of analytical procedures involved, the purification techniques ultimately employed were, for the most part, related to just the removal of this chromophoric portion.

Foam fractionation has been used to remove soluble organic compounds and individual cations and anions from aqueous solution by complex formation with surfactants [3]. The technique makes use of the surface-active properties, induced or natural, of the solute which cause it to accumulate at gas-liquid interfaces. The material can then be raised to the surface by introducing gas bubbles and can subsequently be collected in a more concentrated form by drainage of the foam.

Although kraft pulping wastes contain some natural surface active components [30], these were not thought to

be related to the bulk of the chromophoric substances. Thus, removal of the surface active components would not necessarily remove the chromophoric substances to any appreciable degree. Available information [4] indicates that the chromophores are largely lignin derived and in the degradation processes quinonoid type compounds are usually involved. This fact, coupled with the fact that the effluent behaves, in a sense, as a pH indicator, leads to the conclusion that, at least under alkaline conditions, a substantial portion of the chromophoric material possesses a negative charge. Based on this conclusion the present research study was undertaken, using the foam fractionation technique and a cationic surfactant as the foundation upon which to build.

Experimentation with the foam fractionation system revealed that the presumed mechanisms were invalid and further indicated that the research effort should be shifted to an ion flotation technique, again using a cationic surfactant. This technique proved to be successful. In itself, this presented another problem. Would it be better to investigate a few specific areas, in depth, or to explore the technique as widely as possible? In a review of all considerations, the latter course of action was chosen.

## CHAPTER 2

# BASIC BACKGROUND KNOWLEDGE OF THE PULPING, BLEACHING, AND EFFLUENT SYSTEMS

### General

In order to attempt to understand the mechanics of any separation it is necessary to have as much information as possible about the chemical and physical nature of the component which is to be removed and about the chemical and physical nature of the environment from which it is to be separated. For the chromophoric agents (colour producing bodies) of the kraft pulping and bleaching processes, this task is extremely complicated.

#### Kraft Pulping

No discussion of the kraft pulping and bleaching wastes can develop without some attention to the basic characteristics of the pulping process. The kraft pulping process normally employs a strongly alkaline sodium hydroxide and

sodium sulfide cooking solution or "liquor." The sodium hydroxide attacks all components of the wood, including cellulose, to varying degrees. The sodium sulfide increases the rate of attack on the lignin, while buffering the effect of the sodium hydroxide on the cellulose [5]. According to Hägglund [6], lignin first takes up sulfur in the solid phase, followed by molecular splitting which forms additional free hydroxyl groups, thereby producing soluble lignin fragments. Sulfidization of the reactive groups in the lignin molecule reduces or prevents the tendency to repolymerize, thus promoting and retaining solubility. Because kraft pulping is a topochemical reaction (i.e. proceeding in successive steps in different areas of the wood substance) the innermost layer of lignin, the lignin of the cell wall is attacked last and very slowly. The technical cook, therefore, yields in a soluble form, lignin which has undergone a degree of degradation ranging from a little to a great deal.

#### Lignin, the Colour Producer

Lignin is, then, the major constituent of the wood which the process transforms into a soluble form, along with varying amounts of carbohydrates and other extractives. Lignin and/or its degradation products are responsible for

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most of the colour in the pulping and bleaching effluents [7]. Lignin is a highly branched or cross-linked, highly reactive, polymer with a subunit of a molecular weight of approximately Two of the reactions which lignin will undergo, reac-840. tions which are particularly important with respect to the pulping process itself, sulfonation and hydrolysis, have been discussed. Other reactions include those important in bleaching and, ultimately, in the final determination of the characteristics of the effluents, namely halogenation and oxidation. All these reactions, then, are the means by which the structural units which determine the effluent colour are produced. Despite the considerable amount of work which has been performed with the intention of identifying the specific chromophoric groups responsible for colour, the matter has not yet been completely resolved. For the most part, irrespective of liquor origin (i.e. pulping or the various bleach stages), structures producing colour consist of aromatic and guinonoid nuclei and carbonyl and ethylenic groups [5].

### Chromophores Derived from the Pulping Process

Hartler  $et \ allest allest a number of lignin derived chromophores which have been isolated from effluents of the pulping operation. These include,$ 

. . . aliphatic double bonds conjugated with the aromatic ring, quinonemethides, quinones, chalcone structures, and heavy metal complexes with catechol structures.

The structures shown in Figure 1 are illustrative of these types. These structures, it must be noted, could be present in the forms shown or as components of larger structures.

### Chromophores Derived from the Bleaching Process

When pulp is bleached the lignin or its degradation products are further degraded, but under conditions which are much less harsh than those of the pulping operation. Therefore, the colour imparted to bleach plant effluents is a combination of pre-existing chromophores and additional, perhaps different, chromophoric groups which have been created in the bleaching process itself.

Studies [8] conducted at the State University of New York College of Forestry indicate that the colour of chlorination stage effluents can be traced to the formation of o-benzoquinoid units, probably as intermediaries. Studies [8] with model compounds have shown that the condensation product of such an intermediary is the corresponding catechol (1, 2-dihydroxybenzene) derivative. Other reactions, in addition to a condensation, are possible. In fact, some



DIHYDROXYSTILBENE TYPE



QUINONEMETHIDE TYPE

0

II H C

HC

11

OCH<sub>3</sub>

OCH<sub>3</sub>

# STILBENEQUINONE TYPE



oxidations resulting in rupture of the quinone ring would be expected to yield low molecular weight, colourless fragments [9,10].

A large body of evidence [11,12,13,14] indicates that what is probably true of the chlorination stage is also true, in general, of the other bleach stages. Sarkanen et al. [11,12], in a two-part study, suggested that chlorine dioxide and sodium chlorite in their oxidative reactions with guaiacyl type compounds cause, (a) some ring opening, and also (b) formation of p-benzoquinone structures. Other, not identified, oxidative reactions were also said to occur. The formation of the p-benzoquinone derivatives was observed in bleach liquor reactions of lignin model compounds containing a wide variety of side chains, leading to the conclusion that an extrapolation to lignin itself could be Figure 2 details the possible sites of degradative made. attack by ClO<sub>2</sub> and Cl<sub>2</sub> on lignin. Figure 3 illustrates the formation of an o-benzoquinonoid unit during chlorination and the alternate reaction. Bailey and Dence [13] report that alkaline hydrogen peroxide oxidizes the various side chain substituents of lignin very actively, resulting in the formation of methoxyhydroquinone and subsequently p-benzoquinone.



FIGURE 2 Possible Sites of Degradative Attack by CIO<sub>2</sub> and Cl<sub>2</sub> on Lignin



FIGURE 3 Formation of o-Benzoquinonoid Units During Chlorination



FIGURE 4 Generalized Formation of o-Quinone During Bleaching

In summary, the chemicals used in bleaching have been shown to convert lignin to o- or p-quinonoid type structures which can then undergo further reactions. Figure 4 is a generalized picture of this procedure. Again, as noted previously for the case of the chromophoric groups produced during the pulping operation, the end products of the above reactions could be present in the forms shown or incorporated into larger molecular fragments.

### Properties of the Various Chromophores

The colour producing fragments were once commonly regarded as being in the collodial state. Recently, published data for the chlorination stage effluent [8] and for the caustic extraction effluent [4] have tended to dispute this supposition, proposing instead that the fragments are composed of material of a very wide range of molecular weight, but are completely soluble. The average molecular weight for material in the chlorination effluent has been reported to be about 1500 [8]. The molecular weight of the ether extractable material in this effluent (approximately onethird, by weight) is roughly one-tenth of the value given for the total residue. Loras [16], in gel permeation studies, found two principal fractions with average molecular weights

greater and smaller than 5000. The results for acidified black liquor yielded average molecular weights of 1600 [4,8]. Reported results [4] for caustic extraction stage effluent again showed two fractions; the first an average molecular weight of 500, the second an average of 200.

Clarke and Davis [15], in their coagulation studies of chlorination stage wastes, indicate that some colloids are involved. Although the dispute as to whether or not colloidal materials are present is not fully resolved, it could well be derived from a difference in classification. Some of the larger macromolecules could well have a molecular weight of 50,000, for which Rezanowich, Yean, and Goring [17] have calculated a diameter of 50 Å, an estimate which has been afforded some experimental verification. A particle of this size would be visible under an electron microscope and is classified by some investigators as colloidal [41].

The chromophores, or at least a significant portion of them, show a markedly different absorbance in different hydrogen ion concentrations. The absorbance of the effluent increases with increasing pH, a not too surprising result considering the existence of structural fragments of the quinone-methide type. This fact also leads to the conclusion that negatively charged sites exist, at the very least, under alkaline conditions.

## Summary

In summary, the chromophoric fraction of the total mill effluent consists of a complex mixture of soluble ligninderived fragments with structures similar to those detailed previously and which, at least under restricted pH conditions, carry a negative charge.

## CHAPTER 3

# MILL EFFLUENT COLOUR REMOVAL TECHNOLOGY

### The Relative Dominance of Hydrated Lime

Most early efforts at removing colour from kraft mill wastes were simply adaptations of methods known to be successful in removing colour from natural waters. The National Council of the Paper Industry for Air and Stream Improvement has published a large quantity of material related to these investigations. In all more than 30 coagulants and adsorbents were screened. The National Council determined that hydrated lime offered the best prospect for a commercially viable process for three reasons [18,19]:

- 1. It was readily available and relatively cheap.
- 2. Recovery techniques were highly developed, in fact, they were available at virtually every mill.

3. Kraft mill operating personnel possessed the background and knowledge necessary to operate the overall process.

A variety of problems have plaqued adaption of the hydrated lime processes and despite some considerable progress [1,4,8] the industry is still not willing to accept it as the only Early difficulties [18,19] involved problems enanswer. countered in dewatering the gelatinous, lime-organic sludge produced by the "minimum dose" process. An attempt at using a hydrated lime precoat on a vacuum filter failed because of filter precoat cracking problems [22,23]. The use of a massive dose of lime to reduce the influence of organic matter on sludge dewaterability, coupled with the fact that the sludge remains reactive as an alkaline reagent led to a scheme for incorporating the colour removal process into the recausticizing stage of liquor recovery. Laboratory studies and mill pilot plant trials have proven, generally, to be favourable [24]; colour removals of about 90 per cent were obtained.

#### Other Alternatives

#### Activated Carbon

Research and pilot plant efforts are presently continuing in the various adaptations of the lime process, as well as in other areas. The attractiveness of activated carbon decolourization has been enhanced by improved regeneration techniques and by the development of markets for by-products [25].

## Aluminium and Iron Salts

Although efforts to remove colour from pulp mill wastes using alum as the primary coagulant have been reported [2,18] to be non-competitive for commercial application, there has been renewed interest in this area. Clarke and Davis [15] have reported on recent work in which aluminium and ferric salts were investigated for the removal of colour and total organic carbon from chlorination stage waste liquors. They point out that for optimum removal, dosage and pH must be rigidly controlled. Silica and organic polyelectrolyte additives were not found to have any significant effect on removal, although they tended to promote better flocculation.

Smith and Christman [20] have investigated alum and ferric chloride coagulation of unspecified kraft and sulfite mill wastes. In addition to pH and dosage data, the results of sedimentation studies, at optimum conditions, were reported for both the alum and ferric chloride-kraft wastewater systems. Tejera and Davis [21] have investigated the use of aluminium and ferric salts for the removal of colour and total organic carbon from kraft mill caustic extraction wastes. They noted that both coagulants are about twelve times more effective for this waste than for the chlorination wastes studied earlier [15]. In the three cases cited above, the sludge resulting from the coagulation process has been listed as voluminous and, in some cases, slow-settling. More work is definitely needed in order to determine an efficient means of circumventing this problem.

#### The Grenoble Process

Recently, the Pulp and Paper Institute of Canada has published information [26] concerning their progress in developing the French "Grenoble" process [42] into a commercially viable alternative. In this process, high molecular weight amines are dissolved in an organic solvent (e.g. isooctane, paraffin oil, or kerosene) and agitated with the colour-bearing effluent. The two phases are separated and the colour extract stream is regenerated with a strongly alkaline solution. The method has been shown to be capable of 90 to 99% removal of colour and 30 to 75% removal of BOD and COD, in a single stage. The major problem encountered

has been the formation of relatively stable dilute emulsions of the amine-solvent phase in the purified aqueous underflow, resulting in many cases, in high chemical losses. Figure 5 is a schematic representation of the process.

#### Summary

Despite the promise shown by the various available methods, no one method can be said to have achieved a level of performance which precludes research effort into others. Each method has advantages and disadvantages and even with further development the over-riding importance of individual situation economics is likely to leave scope for new methods. In fact, the possibility of process change, especially in the bleach sequence, and the desirability of increased recycling of process waters to cut down on the overall cost of effluent treatment ensure the maintenance of this assumption.



FIGURE 5 Schematic Diagram of the Grenoble Process for Purification of Kraft Pulp Mill Effluents

## CHAPTER 4

## ADSORPTIVE BUBBLE SEPARATION METHODS

## General

Interest in bubble separation techniques and, hence the body of literature on the subject, has grown tremendously in the last 10 to 15 years. It was not until recently, however, that an effort was made to standardize the rather chaotic proliferation of terminology [27]. Because two rather different and often misnamed techniques are to be considered in this work, brief coverage of the methods and the nomenclature is necessary.

#### The Classification System

The proposed system of classification [28] is outlined in Figure 6. Adsorptive Bubble Separation Methods is the generic name given for all the techniques. Those methods which involve a foam or a froth are referred to as foam separation methods. Those methods which, in the absence of


FIGURE 6 Classification Scheme for the Various Adsorptive Bubble Separation Methods

foam, achieve a separation by virtue of the surface activity of the constituents are termed, quite appropriately, nonfoaming adsorptive bubble separation methods. Just as all separation techniques are based on differences in properties, so also are the bubble separation methods. In this case, the difference is surface activity. Thus surface-active, or surface-inactive substances where surface activity has been induced by an appropriate additive, can be separated from solution, or from one another, on this basis.

The collection of a solute at the gas-liquid interface, under equilibrium conditions, can be described by the Gibbs equation [29].

$$d\gamma_{i} = -RT \sum \Gamma_{i} d(\ln a_{i})$$
 (1)

where  $\gamma_i$  is the surface tension of the i<sup>th</sup> component;  $a_i$ is its activity; R is the gas constant; T is the absolute temperature; and  $\Gamma_i$  is the surface excess concentration of compound i at the interface, in units of mass per unit area.

The rendering of a surface-inactive component surface active, by addition of a suitable chemical, can be

achieved in a number of ways [30]: by chelation, by hydrogen bonding, and by various physical attractions, including ionic attraction, electrostatic attraction, and physical adsorption.

# Foam Fractionation

Foam fractionation is based on the selective adsorption of one or more solutes on the surface of gas bubbles which rise through a solution. The bubbles then form a foam on top of the main body of liquid. Since the foam is relatively richer in the adsorbed material, removal of the overhead foam results in a partial separation of the components. The bubbles can be produced by agitation or by release of dissolved gas but it is more usual to produce them by deliberate sparging. The process can be operated batchwise or continuously, in the simple mode or in a number of higher Theoretical treatment, which is analagous to the modes. distillation methods, can be developed [28,31,32]. Figure 7 illustrates four modes for continuous foam fractionation. In general [30], the operation is affected by the gas-toliquid feed ratio, residence time of the foam and the liquid in the process, the amount of reflux (internal and external) and its position, feed position, bubble size, and temperature.



FIGURE 7 Four Modes for Continuous Foam Fractionation

#### Froth Flotation

# Ore Flotation

Froth flotation, as shown in Figure 6 involves a large number of subdivisions. Ore flotation is a solid-solid separation. Ore particles are separated from gangue particles through selective attachment at the surface of rising bubbles [34]. A very well developed and specialized body of literature exists. In fact, this branch of the technology is still, probably, much ahead of the other techniques.

# Low Gas-flow-rate Methods

More important, for this study, are the new foam separation techniques for removal of low concentrations of surface inactive materials from aqueous dispersions. In contrast [35] to ore flotation and foam fractionation, these methods utilize lower rates of gas flow and produce smaller volumes of foam without tall columns or violent agitation of the continuous phase. The separation occurs only at the gas-liquid interface and not in the foam phase. Ion flotation and precipitate flotation are two such techniques.

# Ion Flotation

Sebba introduced the first of the low gas-flow-rate foam separation techniques in 1959 [36]. Sebba's ion flotation is based, in part, on work by Langmuir and Schaefer [37] which described the adsorption of metal ions onto an insoluble monolayer of stearic acid. In ion flotation a surfactant ion, or collector, of opposite charge to the ion to be removed is added to the latter in stoichiometric amounts and in such a way that it exists as a simple ion and not as a micelle. The collector reacts with the inorganic [36] or organic [38] ion to form an insoluble soap, which is raised to the surface to form a froth which collapses into an insoluble scum.

#### Precipitate Flotation

Baarson and Ray were among the earliest investigators to report on the precipitate flotation technique [39]. This technique involves precipitating the material which is to be removed before addition of the collector. While this is usually accomplished by pH adjustment, the process is not so restricted. (Other techniques have been used, including the use of two hydrophilic ions which precipitate to form a solid with a hydrophobic surface [42].) Since the condensed phase is a flocculent material, the overall charge on the material to be removed is reduced, thereby requiring surfactant to react only with ions on the outermost layer to produce the hydrophobic surface. The net result is that much less than the stoichiometric amounts of collector are required. A detailed study, in which several of the variables of both ion and precipitate flotation are compared, has been published by Rubin *et al.* [35]. Additional information is available in a later publication [40].

# Other Froth Flotation Methods

Other subdivisions of froth flotation [28] include macroflotation, the removal of macroscopic particles; microflotation, the removal of microscopic particles, especially micro-organisms or colloids; molecular flotation, the removal of surface inactive molecules through the use of a surfactant which yields an insoluble product and adsorbing colloid flotation, the removal of dissolved substances that are first adsorbed on colloidal particles.

# Reported Separations

A wide diversity of systems are separable by the adsorptive bubble methods. In 1962 Rubin and Gaden [3]

compiled a list which included 18 metals, 14 dyes, 4 organic anions, 21 fatty acids and detergents, 22 proteins and enzymes, and some miscellaneous inorganic and organic sub-In 1968 Lemlich [28] compiled a list of applications stances. which were reported in the time between his and Rubin's compilation. A partial summary of the types of systems detailed in Lemlich's paper would include: the separation from water of various surfactants; the removal of various inorganic ions such as orthophosphate, fluorozirconate, dichromate etc.; the removal of phenol and various other phenolic compounds; the removal of various pH indicators and dyes; the removal and, in some cases, separations of various trace radioactive metal cations, such as  $Cs^+$ ,  $Sr^{2+}$ ,  $Ce^{2\pm}$ ; the removal of a wide variety of other metals from solution, e.g. ferrous iron, ferric iron, silver, lead and copper; the separation of a variety of heavy metal ions; the analytic tests developed by utilizing the various techniques; the removal of various proteins from solution; the separation and removal of various enzymes; the concentration of various microorganisms; the removal of various inorganic colloids such as ferric oxide, stannic oxide, kaolin clay, and ferrocyanide complexes; the removal of detergents from municipal wastewater; the removal of a wide variety of organic and metallic pollutants from industrial wastewater; and the removal of tall oil from kraft black liquor.

# Summary

That the foam separation methods offer promise for removal, particularly for small amounts, of material from liquid is very evident from the foregoing. The methods, in such instances, often provide a means of separation which might be impossibly difficult by the more conventional techniques. In any case, the adsorptive bubble separation methods have gained enough stature to prevent their being neglected in the solution of most separation, concentration, or purification problems.

# CHAPTER 5

# ION FLOTATION

# Introduction

Despite the fact that the technique which was ultimately used in this work is more correctly a specialized case of precipitate flotation, it is usual to include it under the ion flotation classification [42]. The specification is really quite arbitrary and although Pinfold [42], in a recent publication would seem to prefer to call the present technique precipitate flotation of the "third" type, he remains consistent with the earlier convention [28].

As mentioned previously, ion flotation was first introduced by Sebba in 1959 [36] and involves, in its simplest form, the addition, in stoichiometric amounts, of a surfactant ion of opposite charge to the ion that is to be concentrated, and subsequent passage of gas through the solution. (It is possible for the surfactant (collector) to be uncharged and to attach itself to the surface-inactive ion (colligend) by co-ordination.) The froth formed by the passage of gas

subsequently collapses to produce a scum which contains the collected ion in a concentrated form. This collector-colligend product is known as a sublate. Normally, the flotation is performed in very dilute solutions (as low as 10<sup>-5</sup> moles per liter in collector or colligend). Rising concentrations can, however, lead to precipitation of the sublate before the passage of gas through the solution; and, hence, to the overlap of nomenclature with precipitate flotation. The ion flotation process, indeed all the adsorptive bubble separation methods, depends on that property of a molecule known as surface activity.

# Surface Activity

Ion flotation involves the liquid-gas interface, with the liquid of principal interest being water. Water, a highly polar substance, is an exceptionally good solvent for a salt-like or polar solute. When a surface active molecule such as dodecanol,  $C_{12}H_{25}OH$ , which is insoluble or hydrophobic at one end, but polar or hydrophilic at the other is placed in water it tends to orient itself so as to be more stable thermodynamically. One of the two possibilities for this condition is for the hydrophilic group to be accepted into the water and the hydrophobic group to be squeezed out, into the air. In fact, this property is shown by a fairly

extensive group of substances and the ability to concentrate at the air-water interface is the basis for what is referred to as "surface activity." The non-polar part of the molecule is usually an alkyl or alkylaryl chain. It need not be so restricted, however, and fluorocarbons or other substituted hydrocarbons could also form part of the non-polar structure. It must be of sufficient size so that it cannot be drawn into and accommodated by the water structure. The polar part of the molecule can be derived from a wide range of groups; the more common ones are hydroxyl; carboxylic, sulphonic, phosphoric, or other acid groups; the thiol or mercaptan group; primary, secondary, or tertiary amines; and the quaternary ammonium ion.

For a complete discussion of surface activity any one of a number of excellent texts on surface chemistry could be consulted [43,44]. The present discussion will be terminated with mention of the original findings of Langmuir and Schaefer [37], upon which ion flotation was, in part, based. Stearic acid was spread on water containing as little as 5 x  $10^{-8}$  moles per liter of copper or 2 x  $10^{-8}$  moles per liter of aluminium ions. Upon compressing the monolayers of surfactant between floating barriers, characteristic "crumple patterns" developed. The resulting scum was shown to contain the heavy metal salt. This property of the relatively fixed monolayer of surfactant to attract oppositely

charged ions, or counterions, was reported with interest, but it was not until over twenty years had passed before the observation was converted from a laboratory curiosity into a workable process.

#### Micelles

The second way in which surfactant ions can attain a thermodynamically more stable state, providing the concentration is sufficiently high, is by grouping together so that the hydrocarbon chains are close together and thus directed away from the water and the charged hydrophilic ends are in contact with it. Such a grouping is called a micelle. A fundamental and detailed treatment of the subject can be obtained by referring to the work of Shinoda [45].

Sebba repeatedly states [46] that micelles have a detrimental effect on ion flotation because single ions of surfactant are required in order that the amphipathic nature of the ion can be utilized. In addition, he states that single ions are needed to produce a froth of the required stability. Recently, Rubin *et al.* [35] have questioned Sebba's stress on the absence of micelles. They have noted that aged collector solutions, which contained micelles, gave the same removals as others which had been freshly prepared. Pinfold [42] has suggested that the only deleterious effect of micelles is an increased requirement for collector.

The key to the matter is probably the relative rates at which the micelles are formed or dispersed. Although few specific data are available, Sebba [46] suggests that the rate of formation is a relatively slow process. Others [42] have shown that micelles disintegrate very rapidly. These facts will prove to be of some importance in discussing the results of the present work.

Notwithstanding the present dispute on the importance of micelles, it is still considered prudent to take precautions to ensure their absence. Sebba [46] suggests that the simplest way in which to prepare the surfactant for ion flotation is to dissolve the material in a slightly polar solvent; such as one of the lower alcohols — methyl, ethyl or propyl alcohol, or in ketones such as acetone. Because ion flotation is very rapid the surfactant ions will have been removed to the surface before micelle formation can take place.

#### Other Parameters Affecting Ion Flotation

#### Stability of the Froth

In ion flotation, persistent froths are a handicap, and the object of the technique is to produce a froth that will, at the same time provide support for the sublate and

break relatively easily. A detailed treatment of the subject of froth stability can be gained by consulting the general references [43,44]. Some of the factors which affect froth stability are: the type of collector; the concentration of the collector and the sublate; temperature; flotation cell characteristics; and the pH of the solution.

#### The Collector-Colligend Ratio

Although the establishment of the collector-colligend ratio is impossible for the present work because of lack of knowledge of the composition and molecular weight, or rather, the distribution of molecular weights of the colligend, this factor is worth noting. Generally, since the sublate formed in ion flotation is a chemical compound, the ratio of collector and colligend must be at least a stoichiometric one. In a concentrated system such as the one studied in this work, in which the colligend is precipitated before flotation, this ratio can be expected to be closely adhered to. If. for a more dilute system, the mode of collection depends on the surfactant and colligend ions meeting at a bubble surface, the residence time must be sufficient to allow this. In practice, excess collector will probably be needed.

# Introduction of Surfactant

The introduction of the surfactant to the system can be made in one dose or by a series of small doses during the course of the experiment. Various results have been reported for the two methods, ranging from little change [47] to a marked improvement [48] in the flotation. The results are probably compatible because for two different systems the improved stoichiometric efficiency and the possibility of insufficient froth production and hence redispersion of the sublate could be expected to be of different magnitudes.

#### Choice of a Collector

The choice of collector is one of the most difficult problems involved in the ion flotation technique, usually because of insufficient knowledge as to the exact nature of the colligend ion in the solution. Generally the collector should be chosen according to the following guidelines:

- (i) the collector must, usually, be of opposite charge to the colligend ion;
- (ii) the final sublate should be insoluble or only slightly soluble in water;
- (iii) because of the undesirability of the presence of micelles, the shortest chain collector should be preferred;

- (iv) the collector must be inexpensive or at least compatible with a recovery stage if the process is to be a commercial application;
  - (v) since the collector will be wasted from the process, in at least small concentrations, the effluent concentration should have no deleterious effects on the environment.

#### Bubble Size and Characteristics

There is little useful information on this parameter in the literature. It is clear however, that the smallest bubble size is desirable, and thus a sparger of the finest porosity should be used. The practical constraint, of course, is the work required to produce the smaller bubble. Although actual bubble size is related to the pore diameter of the diffuser, other complicating factors prevent direct calculation of bubble areas. Two such parameters are the fact that the diffuser contains a distribution of pore sizes and that the solution usually contains a number of components, a fact which will affect surface tension and hence the bubble size. Photographic techniques are required [42] if the correlation is to be of moderate sophistication.

#### Air Sparge Rate

In general, the published work on the ion flotation technique is divided into two schools of thought; Sebba  $et \ al$ .

have used very small bubbles, slow gas flow rates, and have produced small volumes of foam; Grieves *et al.* have used coarser bubbles, higher flow rates, and have produced correspondingly greater volumes of foam. While the larger volume of foam would have the advantage of supporting the sublate more effectively and preventing redispersion, the separation would not be as good, nor the power or other operating costs as attractive. The determining factor, of course, would be the re-entry of the sublate into the bulk of the solution. The optimum rate, therefore, would seem to be that rate at which the bubbles just break through the surface quietly, reducing re-entry to a minimum. It would also be logical to assume that this criterion would be better met by Sebba's regime.

# pН

The nature of both the collector and the colligend can change markedly with pH. Therefore, this parameter would seem to be one of the most important ones that must be controlled. Sebba [46] lists a number of effects which might occur due to a change in pH:

> (i) the charge of the colligend ion, or for that matter, the surfactant ion might be altered;

- (ii) the nature of the process, and hence the stoichiometric efficiency, might be changed;
- (iii) the stability of the froth, which supports the sublate, might be changed;
  - (iv) the adjustment of pH to extreme values and, hence, the large alteration of the ionic strength might suppress flotation; and
    - (v) the solubility of the sublate might be affected.

Sebba [46] concludes that control of pH within a narrower range than is the normal practice in industry is often required.

#### Ionic Strength

The presence of neutral salts affects the process in a number of ways; they can lower the critical micelle concentration; they can result in the formation of complexes with the colligend ion; and they can provide the colligend with competition for the available collector.

#### Concentration of Colligend

The colligend concentration range most effective for ion flotation has been reported [42] to be about 10<sup>-5</sup> to 10<sup>-3</sup> moles per liter. This range has been suggested as an area of practical application because below 10<sup>-5</sup> moles per liter the solution is so dilute that a stable foam might not develop and above 10<sup>-3</sup> moles per liter the amount of sublate to be handled and the possibility of complexes forming may make operation difficult. Sebba [46] suggests that if flotation is not proceeding well in a concentrated solution that a dilution can often have a beneficial effect.

#### Temperature

Temperature effects have been almost completely ignored in the literature. Although study of this parameter is probably warranted, no attempt will be made to do so in the present work.

#### The Kinetics of Ion Flotation

Kinetic studies of the process have been largely neglected. Grieves *et al.* [48] have published the results of the kinetics of the flotation, in a cell with a coarseporosity frit, of  $FeFe(CN)_6^{2--}$ ions, using a cationic collector.

Rubin *et al.* [35] found that the foam fractionation of  $Cu^{2+}$  ions, in a cell with a fine-porosity frit using

sodium. dodecylsulfate as a collector could be represented as a reversible first order reaction, viz.

$$\ln\left[\left(M'-R'\right)/M'\right] = kt/M'$$
(2)

where R' and M' are fractions of colligend removed at time t and under steady state conditions, respectively. Rubin [53] has used the equation,

$$log(M-R) = logA - mlogt$$
 (3)

where m and A are constants and R and M are the fractions removed at time t and ultimately, respectively, in the kinetic study of a precipitate flotation system.

#### Summary

Ion flotation systems are still relatively novel and the research effort can hardly be classed as large; most of the available theoretical considerations have been derived from relatively few individuals. However, a number of aspects have been identified as important and gradually the process is proceeding into a stage where increasing activity can be expected to yield a workable technology.

# CHAPTER 6

# EXPERIMENTAL APPARATUS

#### Foam Fractionation Apparatus

The foam fractionation trials were conducted in a plastic three inch (ID) four foot high cylindrical column, as shown schematically in Figure 8. The system was designed for use in all modes, batch and continuous, of foam fraction-The liquid level was maintained by means of a simple ation. hydrostatic head, overflow column. Three one-inch diameter foam removal ports were provided at 15 inches, 27 inches, and 39 inches from the bottom flange of the column. Two liquid feed positions were located opposite to the first two foam removal ports and one was placed four inches from the column bottom. Regulated laboratory air was dried and split into two streams; the first stream provided pressure on top of the waste and surfactant storage tanks; the second stream passed through a rotameter and was introduced to the column through a sparger. The sparger consisted of a suitably constructed fine (200 mesh) screen. The pressurized



FIGURE 8 Schematic Diagram of the Foam Fractionation Experimental Apparatus

waste and surfactant tanks delivered their contents via rotameters to a mix-tank - head tank and subsequently to the column. Additionally, the waste line included an inline filter upstream of the rotameter.

The foam removal system consisted of a squirrel cage fan air blower which drew the foam from the column with a vacuum assist. Collapsed foam flowed into a seven inch diameter cylindrical vessel, from which a DCL-Micro Pump boosted it to a head tank. The reflux portion of the collapsed foam flowed through a rotameter to a three pronged liquid distributor atop the column. All liquid streams were measured by rotameters, as mentioned; provision also existed for timed sample collection.

The system was quite versatile with a wide adjustment of liquid height, foam height, and hence retention time, within the limits of the four foot column. The rotameters were ranged so that gas flux rates from 0.2 scfm/sqft to 3.4 scfm/sqft and liquid flux rates from 0.2 gpm/sqft to 1.5 gpm/sqft were attainable. These values allowed gas-toliquid flow ratios from 0.13 to 17.0 scf/gal and liquid retention times up to 120 minutes to be studied. According to Rose and Sebald [31] these levels would cover the range of practical value.

#### Ion Flotation Apparatus

The flotation system, shown schematically in Figure 9, consisted of a suitably regulated, dried and measured air stream connected to a flotation cell. The flotation cell consisted of a large pyrex glass bottle from which the bottom had been removed. The cell was about 16 centimeters 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 was held in place by means of a rubber bung. The diffuser consisted of a 5.4 centimeter diameter Corning fritted glass filter of known pore size. Two different diffusers were available; one with a nominal-maximum porosity of 10-15 microns, the other with a nominal-maximum porosity of 4 - 5.5 microns. The diffuser was positioned 11.5 centimeters from the top of the vessel. Gas rates of from 0.5 to 20 ml/sec of air were attainable.

The excess foam was removed with a vacuum arrangement. Provision for initial stirring of the surfactant, or pH-adjustment chemicals, was available in the form of a G.K. Heller Co. Laboratory stirrer and controller. Provision for pH measurement was also made. All experiments were of a batch nature, using an experimental volume of 2.5 liters.



FIGURE 9 Schematic Diagram of the Ion Flotation Experimental Apparatus

# CHAPTER 7

# EXPERIMENTAL PROCEDURES

#### Foam Fractionation - Batch Operation

The object of the batch operation was to evaluate whether or not the foam fractionation process was feasible before construction of a continuous flow system was undertaken. Experiments were performed using Canadian Forest Products Ltd. - Port Mellon first caustic extraction stage liquor as a feed solution and either one of two long chain amines as the surfactant.

Because colour removal was the property of prime interest, the standard colour test [49] was investigated and modified. An account of this modified test procedure is included in Appendix A.

Prior to an experimental run, the column was washed out with raw effluent. Two liters of raw effluent were then poured into the column. A portion of the raw effluent was held back for the colour test. The pH of the batch runs was not adjusted. The resulting liquid height was simply

recorded, and remained the same for all runs. A foam height of 12 inches was selected and was also held constant. The air was adjusted to a pre-determined rate and the surfactant was injected. This event was recognized as time zero. Following the buildup of the 12 inch head of foam, the air was adjusted to a value which produced a reasonably dry foam, with minimal internal coalescence. As the surfactant was removed from the solution the air flowrate was increased in order to maintain the required head of foam. Samples of the foamate were collected periodically for colour analyses. The apparatus was shut down when a maximum air rate would produce no further foam. Samples of the residual liquid were then withdrawn.

Colour analyses were performed and per cent colour reduction, based on the bottoms or residual liquid, was computed.

# Foam Fractionation - Continuous Operation

Following construction and testing of the continuous flow system, a study was commenced with an objective of establishing the effect of the primary variables; liquid flow rate, air flow rate, and foam height on colour removal. The first two experiments were performed using the caustic

extraction stage liquor used in the previously described runs. Subsequently it was decided to shift emphasis to the combined or total mill effluent and a sample was obtained from MacMillan-Bloedel Limited's Harmac Division. Because of the possibility of biological action, the effluent was stored at a temperature of 4° centigrade.

Surfactant solution was prepared to the required concentration by dissolving weighed quantities of the surfactant in distilled water. Rotameter settings were adjusted to the pre-selected values, liquid height was set, the foam drawoff port (and hence foam height) was selected, and the system was started up. The system was allowed about six residence times to come to a steady state before the first set of samples was taken from the raw effluent, the underflow, and the foamate streams. All flows were checked by timing a measured volume and a liquid balance was performed. A second set of samples was taken and the system was shut down.

Colour analyses were performed and concentration changes were expressed as enrichment,  $X_T/X_F$ , and as bottoms concentration reduction,  $X_B/X_F$ . The fractional colour removal from the feed stream was  $[1 - B/F \cdot X_B/X_F]$ . The meaning of the symbols is outlined in the Nomenclature.

#### Ion Flotation - General

All ion flotation experiments were performed as batch runs in the simple apparatus detailed in Chapter 6. The wastewater used, in all but the first three runs, was Canadian Forest Products Limited - Port Mellon Division combined mill effluent. The waste was stored in a refrigerated room which was maintained at a temperature of 4° centigrade. Two lots of about 100 liters were used over the course of the four month study. Prior to each experimental run, the temperature of the effluent was adjusted to 22° centigrade, then 2.45 liters were poured into the flotation cell. The stirrer was controlled at a speed of 200 rpm and pH adjustment, if necessary, was made.

The collector solution (unless otherwise stated) was prepared by dissolving a weighed quantity of didodecyldimethylammonium bromide (obtained from Eastman Kodak Co.) in 50 ml of low water content (0.10%) methanol. The collector solution was added, slowly, to the stirred effluent. Mixing was continued for a predetermined length of time, the expiry of which signalled the removal of the stirrer, the release of flotation air into the cell, and time zero.

A series of 29 flotation runs was performed in order to evaluate both filtered colour removal and total

floatable solids recovery under a wide variety of conditions. Parameters studied included:

- (i) surfactant or collector dosage,
- (ii) pH,
- (iii) sparger porosity and hence, indirectly, bubble size,
  - (iv) surfactant premix time,
    - (v) air sparge rate, and
  - (vi) ionic strength and colligendcollector charge.

In addition, a number of other areas of interest were briefly surveyed. These included:

- (vii) biological oxygen demand removal,
- (viii) foam volume,
  - (ix) collector micelle formation,
    - (x) the effect of methanol,
  - (xi) effluent aging, and the
  - (xii) kinetics of the flotation recovery.

Time and scope of the project did not permit study of the following:

- (i) temperature effects,
- (ii) choice of collector, or
- (iii) froth stability.

#### Analytical Tests and Procedures

### Colour Determination

As mentioned, the modified colour procedure is fully covered in Appendix A, so it need not be reported here.

#### Biological Oxygen Demand

The  $BOD_5$  tests were performed at the British Columbia Research Council and their test procedure was used, without modification. The Council's procedures follow a standard  $BOD_5$  test procedure [49].

An acclimatized kraft mill seed is maintained by the Council, and it was used in both series of tests.

#### pH Measurement and Calibration

The pH measurements and adjustments were performed with a Corning Model 10, pH meter. Buffer solutions of pH 4.00, 7.00, and 10.0 were used in the ranges 1.5 to 5.5, 5.5 to 8.5, and 8.5 to 12.0 respectively. The instrument was standardized before a set of readings was taken; drift was negligible.

# Stirrer Speed Calibration

The Heller motor controller was calibrated using a Jones Motrola Corp. hand tachometer. Repeated tests showed that the calibration was accurate and reproducible to within 5 to 10 per cent.

#### Floatable Solids Determination

The solids tests performed on the system were done according to the standard test for "Residue on Evaporation" [49]. Total floatable solids was taken to be, for a system in which dosage was stoichiometric, the difference between the "Residue on Evaporation" of the solution at time zero minus 15 seconds (when the initial sample was taken in all cases) and the "Residue on Evaporation" of a filtered sample which was taken after the run was completed. In all cases, the completion of the flotation run was signalled by the fact that a stable froth could no longer be produced. The filters used were Corning, Gooch Type with a "Fine" fritted disc and were capable of removing, completely, the turbidity of the solution, partial removals of floatable solids were judged on the same basis.

Tests were performed with 50 ml aliquots of solution in order to get a sufficient amount of solids for an

accurate weight. Weights were taken on a Sartorius Model 2603 balance and were accurate to the nearest 0.4 mg.

#### Cleaning Procedures

The extremely greasy, fine precipitate produced in the process necessitated specialized flotation cell, glassware, and fritted ware cleaning procedures. Following a flotation run, the flotation cell and the associated equipment were scoured with methanol and rinsed with water. Laboratory glassware was scoured twice with methanol, then washed in a soap-water solution, followed by rinsing with large volumes of water. Glassware, used in weighing, was additionally dried by cloth, placed in a 205° F oven for 15 minutes, then allowed to cool for 30 minutes in a dessicator. Fritted ware, the diffusers and the filters, were soaked overnight in a chromic acid-sulfuric acid solution and then backwashed to whiteness with tap water.

# Electrophoretic Mobility and/or Zeta Potential Measurement

Electrophoretic mobility was measured with a Zeta-Meter. Procedures are outlined in the operating manual of the manufacturer, Zeta-Meter Inc. The system consists of an

illuminator, an electrophoresis cell, and an electrical control unit. A binocular microscope was used for observation of the particles. Additional information and the procedure can be gained by consulting the manual [50].

#### Rotameter Calibration

The manufacturer's calibration curves were checked for liquid service by timing a measured volume of the fluid in question. Since a number of checks yielded no departure from the supplied curves, no further calibration was undertaken.

Since calibration curves were unavailable for air service they were prepared, as needed, using a Wet Test Meter manufactured by Precision Scientific Co., Chicago, U.S.A.

# CHAPTER 8

# RESULTS AND DISCUSSION

#### General - the Effluent

Previously, it was mentioned that the effluent behaves, in a sense, as a pH indicator because its colour changes with pH. Figures 10 and 11 illustrate this property for a first caustic extraction stage and a total or combined mill effluent. Note that the familiar "S" shape of the colour versus pH curve is much more noticeable for the more dilute, total mill effluent.

In Chapter 7, it was noted that the effluent was stored at a temperature of 4° centigrade. This precaution was necessary because the effluent, particularly the total mill variety, is very active biologically, at room temperature. Appreciable biological action was observed in samples which were left at room temperature in about 5 to 6 days. In addition, although it proved to be a much slower process, some lightening in colour was noted in samples stored at room temperature. Test results revealed no such colour


FIGURE 10 Colour versus pH for First Caustic Extraction Stage Effluent



FIGURE 11 Colour versus pH for Total Mill Effluent

change and no appreciable biological action in the effluent which had been stored at 4° centigrade.

## Foam Fractionation (Batch) Results

Table 1 illustrates the results of typical batch operation. Note that in the first run no surfactant was used. With maximum aeration, a foam height of only three inches was obtained. This result is to be expected because the caustic extraction effluent has little natural surface activity compared with the total mill effluent, which contains the resin acids from the pulping operation. No colour removal is reported because the foam could not be made to rise to the removal port.

With a dosage of  $1 \times 10^{-3}$  moles per liter of noctylamine hydrochloride colour reductions of 22 and 35 per cent were realized. Note that the highest reduction was obtained at an increased air sparge rate and a longer foaming time.

The results of the batch runs, while not spectacular, seemed to indicate that the construction of a continuous flow system was warranted. As noted, all batch runs were made with first caustic extraction stage effluent. This fact

Τa	p	1 e	1

Typical Batch Operation Foam Fractionation Data

RUN NO.	1	2	3
Effluent Type	lst Caustic Extraction Stage	lst Caustic Extraction Stage	lst Caustic™ Extraction Stage
Original pH	11.15	11.15	11.15
Column pH	11.15	11.15	11.15
Surfactant Concentration	None 	n-oamine HCL <sup>*</sup> 1 x 10 <sup>-3</sup> M	n-oamine HCL* l x 10 <sup>-3</sup> M
Liquid Volume	1950 ml	1950	1950
Liquid Height	13 inches	13 inches	13 inches
Foam Height	3 inches	12 inches	12 inches
Foaming Time	25 min.	70 min.	150 min.
Air Sparge Rate start finish	102.5 cucm/sec 102.5 cucm/sec	13.3 cm³/sec 61.5 cm³/sec	22.7 cm³/sec 71.2 cm³/sec

\*aged surfactant n-octylamine hydrochloride

(CONTINUED)

RUN NO.	1	2	3
Feed Colour (Pt-Co Units)	-	13,400	13,000
Bottoms Colour (Pt-Co Units)	-	10,500	8,500
% reduction in Bottoms Colour	-	22%	35%

Table 1 (continued)

is especially significant in view of later results concerning the actual mechanism of the removal process.

## Foam Fractionation (Continuous) Results

Despite some considerable effort in perfecting the equipment from a process standpoint, the study of the continuous flow system never really got past the initial stages. Table 2 illustrates four typical continuous mode experimental runs. The early runs (No.'s 1 & 2) were performed with first caustic extraction stage effluent and aged surfactant solutions (in that they had been made up, in water, some time previously) of n-dodecylamine hydrochloride. Because of the rather low colour removals and the difficulty in observing what was happening in this highly concentrated solution, a sample of total mill effluent was obtained. Originally, it was anticipated that the less concentrated solution might lead to a better performance, a fact which is quite often cited in the literature [46]. What actually happened proved to be much more dramatic. The first two trials (No.'s 3 and 4 - Table 2), with a n-octylamine dosage of 1 x  $10^{-3}$  moles per liter, revealed a much better separation, compared with the previous results. A third trial, with a didodecyldimethyl ammonium bromide dosage of  $1 \times 10^{-3}$  moles

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Typical Continuous Operation Foam Fractionation Data

	····	······································		
RUN NO.	1	2	3	4
Effluent Type	Port Mellon lst C.E. Stage	Port Mellon lst. C.E. stage	Harmac total mill	Harmac total mill
Column pH	11.2	11.2	4.8	4.8
Surfactant Concentration	n-ddamine HCL <b>*</b> 1 x 10 <sup>-4</sup> M	n-ddamine HCL* 1 x 10 <sup>-4</sup> M	Octylamine HCL 10 x 10 <sup>-4</sup> M	Octylamine HCL 10 x 10 <sup>-4</sup> M
Aerated Liquid Volume	2.04 L	2.04 L	2.04 L	2.04 L
Foam Height	12 inches	12 inches	12 inches	24 inches
Combined Feed Flow (F)	55 ml/min	27.5 ml/min	105 ml/min	58 ml/min
*aged surfactant n-dodecylamine hydrochloride (CONTINUED)				

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(CONTINUED)

Table 2 (continued)

RUN NO.	1	2	3	4
Residence Time	37 min	74 min	19 min	35 min
Bottoms Flow (B)	49 ml/min	25 ml/min	61.5 ml/min	46 ml/min
Recycle (R)	-	-	-	2 ml/min
Air Flow	42.6 cm³/sec	57.6 cm³/sec	44.2 cm³/sec	27.9 cm³/min
Colour (Pt-Co) Combined Feed (X <sub>F</sub> )	10,100	10,100	2,100	2,100
Colour (Pt-Co) Bottoms (X <sub>B</sub> )	9,600	9,200	1,170	1,040

(CONTINUED)

RUN NO.	1	2	3	4
Removal $\left(1 - \frac{B}{F} \times \frac{X_B}{X_F}\right) 100\%$	16%	18 %	68 %	61 %
Remarks	Some coalescence of foam (i.e. internal reflux at this air rate)	Coalescence minimal notice a precipitate (?) adhering to walls of column at top of foam	Large part of removal just due to bulk re- moval of liquid	Note smaller foam volume

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# Table 2 (continued)

per liter, resulted in a virtually colourless solution. The removal process was not, however, a result of the presumed foam fractionation technique. It was very clearly a coagulation, with the quaternary ammonium surfactant acting as the coagulating chemical. In retrospect, it became clear that the foam fractionation technique probably never had The intense colour of the more highly concentrated operated. caustic extraction effluent had masked the actual mechanism. In fact, a precipitate had been noticed in the earlier runs but its significance had not been appreciated (see run 2 -Table 2). This precipitate had been observed adhering to the walls of the column near the foam removal port. At that time, it was assumed to be very fine particulate material which was derived from the raw effluent.

Thus, the initial results of the continuous foam fractionation revealed, without a doubt, that the mechanism was not as supposed. As a direct consequence of these results, the research effort was shifted to the ion flotation technique.

## Ion Flotation Results

## General

Preliminary trials established the mechanism of the removal process as ion flotation, or as previously mentioned,

67·

precipitate flotation of the third type. The sublate or collector-colligend product was formed immediately following the addition of the collector to the flotation cell. With the passage of air through the solution and the subsequent froth formation and its partial collapse, the insoluble scum was buoyed to the surface and removed. The sublate particles were, in most cases, not visible in the froth until it collapsed. Figure 12 is a diagrammatic representation of this phenomenon. Appendix B provides a summary of the ion flotation experiments. Runs 1 through to 3 were performed with Harmac total mill effluent. Runs 4 through to 29 were performed with Port Mellon total mill effluent. The surfactant used, in all cases, was didodecyldimethyl ammonium bromide. It is rather an unfortunate choice in that an alkyl 14-carbon molecule would likely have been more suitable. However, the extremely poor chemical supply situation and the fact that the surfactant was available as a result of the earlier foam fractionation experiments made it the only choice. In all but three experimental runs, runs 4, 5, and 6, the surfactant was dissolved in 50 ml of methanol. Combined with 2.45 liters of effluent, the solution was approximately 2.5 mole per cent methanol, a value well below that which would produce solubilisation effects [51].







# The Collector-Colligend Ratio

The unknown composition and molecular weight, or rather the unknown distribution of molecular weights, of the colligend make calculation of the collector-colligend mole ratio impossible. However, since all runs were performed with total mill effluent, the colligend concentration can be considered to have been approximately constant and the collector dosage divided by the effluent colour removed can be used as an approximate equivalent ratio. Figure 13 is a plot of per cent colour removal versus surfactant dosage. As illustrated, a dosage of about 6 x 10<sup>-4</sup> moles per liter of surfactant was sufficient to affect virtually complete removal of the chromophoric material. The original effluent colour was about 2100 ppm on the Pt-Co scale or 2100 units of colour per liter. Thus a collector-colligend ratio of about 2.8 x 10<sup>-5</sup> moles of surfactant per 100 units of effluent colour is required.

The data used in plotting Figure 13 were extracted from experimental runs in which all parameters except dosage were maintained constant. The fact that even at the very low surfactant dosage of 1.0 x  $10^{-4}$  moles per liter a stable, loaded foam was produced, indicates that the sublate probably remains surface active. This deduction is supported by the





assumption that the dosage is very much below what could be considered a stoichiometric one and therefore uncombined surfactant molecules probably do not exist. Since the colour test, by definition, involves filtration of the samples to remove all traces of the turbidity or the sublate, the flotation recovery is perhaps a more valid measurement of how well the process works. Accordingly, Figure 14 shows the per cent flotation recovery as a function of surfactant dosage. Note that a maximum recovery is reached at a dosage of 6.0 x  $10^{-4}$  moles per liter and that an increase in surfactant concentration to 8.0 x  $10^{-4}$  moles per liter actually causes a decreased recovery. A complete summary of the flotation recovery results is contained in Appendix C. That the presence of excess collector will often inhibit flotation has been widely reported [51,48]. Pinfold [42] explains this phenomenon by suggesting that the sublate particles

> . . . probably become coated with a layer of surfactant as the concentration of the latter is raised. As this layer will be arranged with the long-chain groups of the collector in contact with the hydrophobic surface of the precipitate and the ionic groups oriented towards the water, the arrangement renders the particles more hydrophilic, and they float less easily.



FIGURE 14 Percent Flotation Recovery versus Surfactant Dosage

In addition, the increased amount of collector could lead to a competition between the sublate and the surfactant ions for a place on the bubble surface, thereby further impairing the flotation efficiency.

#### Collector Micelle Formation

As noted, micelle formation was inhibited in the standard way, by dissolving the surfactant in methanol. Three runs, numbers 4, 5, and 6, were performed in which no methanol was used. Except for the fact that a much longer pre-mix time (up to 30 minutes) was required in order to dissolve the surfactant, the runs were not noticeably different from other equivalent ones in which methanol was used.

Based on Shinoda's data [45] the critical micelle concentration (CMC) for didodecyldimethyl ammonium chloride is  $1.8 \times 10^{-4}$  moles per liter. Since the effect of a different hydrophilic group is not large, the CMC of the surfactant used, didodecyldimethyl ammonium bromide, can be expected to be very nearly  $1.8 \times 10^{-4}$  moles per liter. A number of factors might, however, bring about a change in the CMC; added salts such as NaCl would lower the CMC and added methanol would tend to raise the CMC of the surfactant in question. Based on the results of the three experimental runs described above and upon the fact that the sublate is formed immediately, and the free surfactant concentration therefore greatly reduced in a matter of less than a second, collector micelle formation was not considered to be a factor. This is thought to be true despite the fact that the dosages used would ordinarily result in micelle formation in an aqueous solution.

The question of micelle formation in the sublate has not been satisfactorily resolved. Perhaps the slightly less than complete flotation recovery was due to some sort of sublate micelle formation and a corresponding reduction in the surface activity of the precipitate.

## pН

As noted, pH can have a marked effect on the flotation system because of the large number of ways in which it can affect the nature of both the collector and the colligend. On the basis of colour removal, i.e. sublate precipitated and either removed by the flotation process or by the subsequent filtering of the analytical test procedure, pH appears to be unimportant. Figure 15 illustrates this. However, on the basis of flotation recovery of the sublate,



pH control proved to be very critical. Figure 16 illustrates this point. Note that the best recovery is obtained at a pH of 5.1. The recovery at 4.5, while ultimately reaching a similar level has a considerably slower rate of removal. At pH 5.6 recovery is also significantly worse. Note that these experimental runs were performed with a surfactant dosage of 8.0 x  $10^{-4}$  moles per liter, a dosage slightly higher than the optimum. Flotation was found to be almost totally suppressed when the pH was adjusted to extreme values (refer to experimental runs 9 and 10, Appendix B).

The interpretation of the previous results is very likely related to the charge which the colligend possesses. While it might be possible to measure the electrophoretic mobility of the larger molecular fragments which make up the chromophoric fraction with the help of laser optics, it was not possible to do so with the available equipment. The zeta potential was measured, however, as a function of pH, for various flotation cell solutions. All solutions were derived from experimental runs performed at a surfactant dosage of 8 x 10<sup>-4</sup> moles per liter. Figure 17 details the results of such measurements. Thus, assuming that the addition of the same concentration of cationic surfactant would alter the particle charge by a similar amount, at least in

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FIGURE 16 Percent Flotation Recovery at Various pH Values



FIGURE 17 Zeta Potential versus pH for Flotation Cell Solution,

Surfactant Dosage 8x10<sup>-4</sup> Moles/Liter

the region of pH 4 to pH 10, then the original zeta potential might be expected to have been more negative by a constant increment. Thus, in the region of optimum flotation, the colligend needs less surfactant to satisfy electrical neutrality. Therefore the quantity of surfactant required would be less and precisely the right amount of surfactant would be available to produce a stable froth and so prevent redispersion of the sublate. In the lower pH range excess available surfactant could also have a deleterious effect. The recovery rate curves of Figure 16 tend to support this explanation. The lower than optimum pH curve (pH 4.5) has a slower initial rate, during which time the excess surfactant is wastefully removed. The higher than optimum pH curve (pH 5.6), while it maintains the same initial rate as the optimum, has a lower ultimate recovery because a froth of the required stability cannot be maintained.

While the above explanation would seem to be possible, much more work is needed before it can be accepted as fact.

## Bubble Size

In experimental runs 11 through to 29 two spargers of known nominal, maximum pore diameter, were used. The

per cent flotation recovery rate curves are compared at two different pH values, at the optimum of 5.1 and at a lower pH of 4.5, for the two spargers, in Figures 18 and 19 respectively. In each case, the finer sparger and, hence, smaller bubble size affected an improved recovery rate. This result is not surprising because the smaller bubble size yields an increased area for adsorption of the surface active material.

#### Air Sparge Rate

A second parameter determining the area available for adsorption is the air sparge rate. Increasing the volume of air would also be expected to increase the rate of recovery. Figure 20 would seem to illustrate that this is not the case. However, an air sparge rate of slightly lower than 1.5 ml per sec was not sufficient to cause flotation. Thus, the air requirements reach a maximum or optimum value very rapidly and further increases in air sparge rates caused re-dispersion of the sublate. The fact that the material being floated is already a solid might cause this amplification of a commonly reported effect [42]. Also related to the air sparge rate is the volume of foam



FIGURE 18 Percent Flotation Recovery at pH 5-1 for Two Sparger Porosities



FIGURE 19 Percent Flotation Recovery at pH 4.5 for Two Sparger Porosities



FIGURE 20 Percent Flotation Recovery at Various Air Sparge Rates

produced. Increasing the air rate, at a constant surfactant dosage, greatly increases the amount of foam produced as Figure 21 illustrates.

This property of the system would be of industrial importance because, at an optimum rate of removal, it would be desirable to minimize foam production and aeration power requirements. Note that the original flotation cell volume was the usual 2.5 liters. Thus, at the optimum air sparge rate, the volume of foam produced represents about 2.6 per cent of the original solution. This figure can be contrasted to the 10 to 20 per cent, and even higher, foam production of the foam fractionation runs.

Foam production is also related to the dosage of surfactant. Figure 22 is a plot of foam volume as a function of surfactant dosage. Generally, as surfactant dosage decreases, so too does the volume of foam produced. The slight minima at a surfactant dosage of between 4 x  $10^{-4}$  and 5 x  $10^{-4}$  moles per liter can be rationalized by the observations of the next section.

## Collector Pre-mix Time

Normally, following the addition of the surfactant solution to the effluent the flotation cell solution was



FIGURE 21 Foam Volume versus Air Sparge Rate



FIGURE 22 Foam Volume versus Surfactant Dosage

stirred for two minutes. In a number of experimental runs an additional three minutes was allowed. This additional time appeared to have marked effect over a narrow surfactant dosage range (3 x  $10^{-4}$  to 6 x  $10^{-4}$  moles per liter). In this range the formation of larger than normal particles was observed, possibly by a simple coagulation mechanism. In addition, the rate of removal was much faster and the characteristics of the froth were markedly different. As mentioned, in normal operation the froth became visibly loaded with sublate upon its partial collapse. In the coagulation régime, the floated material became, almost at once, a dense black, oily scum. No sure explanation can be offered for the existence of this régime, although it is certainly related, in some way, to the charge possessed by the precipitate.

The coagulation, also, probably results in a net decrease in surface active material in the solution. The minima in the foam volume versus surfactant dosage curve, referred to in the preceding section, is probably a result of this decrease.

## BOD<sub>5</sub> Removal

As mentioned previously, a number of runs were performed in which no methanol was used to dissolve the surfactant.

Although these experiments were conducted primarily to evaluate the effects of methanol on the system, the absence of methanol provided a chance to test  $BOD_5$  removal.

BOD<sub>5</sub> removal in the presence of methanol would not have been particularly meaningful because of the large  $BOD_5$ of the methanol itself. Table 3 details the operating parameters of two flotation runs and the results of the  $BOD_5$ tests. BOD<sub>5</sub> removal, for the identical conditions, was 18and 30 per cent. Whether or not the  $BOD_5$  removal is totally related to the ion flotation itself or occurred simply because the effluent was aerated and the resulting foam removed is a matter of some doubt. Previous work at Rome, Goergia [30], using no surfactants, indicates that the naturally surface active, BOD<sub>5</sub> producing fraction can account for 12 per cent of the total  $BOD_5$ . Removals of 6 per cent were reported and were related to a 50% reduction in the tall oil content of the effluent. Thus, it is likely that the removals experienced were a consequence of the natural surface activity and the ion flotation technique.

Identification of additional types of materials which were removed in the course of the flotation process was beyond the scope of the work, as outlined previously. However, the absorbance versus wavelength spectra produced as a result of the colour test put forward an interesting area for speculation. As shown in Figure 23, a tracing of such a

T	a	b	1	е	3
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Biological Oxygen Demand Removal Data

RUN NO.	4	6
Surfactant Concentration (moles/liter)	10 x 10-4	10 x 10 <sup>-4</sup> *
Air Sparge Rate (cm³/sec)	7.9	7.9
Pre-Mix Time (min)	23	29
Flotation Removal (%)	99	99
Colour Reduction (%)	96	97
рН	5.1	5.1
Foam Volume (ml)		510
BOD₅ Waste	200	220
BOD $_5$ Cell Residual Solution	140	180
BOD <sub>5</sub> Reduction	30%	18%



FIGURE 23 Absorbance versus Wavelength for Run 3

scan for flotation run number 3, a large quantity of material which absorbs in the ultraviolet region (< 400 nm) is removed. Admittedly, some of the molecules which absorb in the visible region will also absorb in the ultraviolet. However, the large reduction in absorbance cannot be due to just this fraction alone.

## Kinetics of the Flotation Recovery

An attempt was made to fit flotation data to a reversible, first order reaction. The equation used was described in Chapter 5 and was used by Rubin *et al.* [35]. Mln [(M-R)/M] was plotted versus time in Figure 24 for the data of flotation runs numbers 16 and 20. R and M were taken to be the fraction of the sublate removed at time t and ultimately, respectively. These data were selected because they were illustrative of runs in which parameters affecting the rate of removal were studied. The reversible first order reaction equation did not fit the data very well, even as an approximation. A plot of log(M-R) versus log time (Figure 25) was also performed for runs 16 and 20.

$$\log(M-R) = \log A - m \log t \tag{3}$$

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FIGURE 25 Plot of Log(M-R) versus Log(time) for Runs 16 & 20

fairly well, but because it is a logarithmetic relationship and relatively insensitive to changes, this may not be significant. Because removals are rapid and virtually complete within a few minutes, it was concluded that better techniques would be required in order to get meaningful kinetic data.

#### The Ion Flotation System as Part of

#### an Industrial Treatment Process

The collector recovery step of the "Grenoble Process," described in Chapter 3, and presented in Figure 5, is partially applicable to the ion flotation system. A proposed ion flotation treatment process for the purification of pulp mill wastes is presented in Figure 26. In the process, collector from the recovery stage is mixed with the effluent and recycled to the flotation cell. The purified underflow is taken off to sewer or for recycle. In either case, further treatment will probably be necessary. The collapsed froth is directed to the collector recovery system. An organic solvent of sufficient chain length that it is insoluble in water (iso-octane or parafin oil) is added to the collapsed froth, followed by the addition of a concentrated caustic solution, likely white liquor from the pulp mill chemical recovery system. The resulting two phases are separated; the



FIGURE 26 Proposed Ion Flotation Process For Purification of Pulp Mill Effluents

surfactant containing organic phase is retained for further processing and the highly coloured caustic solution is returned to the mill recovery system. The surfactant is separated from the organic solvent and produced in a form suitable for recycle.

The proposed system has a number of advantages:

- a dilute oil-in-water emulsion is not wasted
  with the purified underflow as in the
  Grenoble Process,
- b. no troublesome sludge requires dewatering and disposal,
- c. some credit for aeration is gained for the subsequent BOD₅ removal system,
- d. all chemicals used are part of closed loop systems; only make-up amounts are required,

e. horsepower requirements will be quite small,

f. only small volumes of collapsed froth need be handled, making recovery system tankage requirements modest.

Clearly, before the proposed system is ready for application or even for a pilot plant trial, much further work will have to be performed.

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### CHAPTER 9

### CONCLUSIONS

a. The mechanism of removal was established as ion flotation or perhaps, more logically, precipitate flotation of the third [42] type.

b. Flotation recovery and colour removal were found to be in excess of 95 per cent, at optimum conditions.

c. The flotation system was found to be sensitive to pH, bubble size, air sparge rate, collector dosage, and collector pre-mix time.

d. An attempt at relating the ion flotation rate of recovery data to a reversible, first order reaction was not successful. Rate of recovery data did fit an equation of the form:

log(M-R) = log A - mlogt

e. An ion flotation treatment process, with recovery of all process chemicals, was proposed for the purification of kraft pulp mill effluents.

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#### CHAPTER 10

### RECOMMENDATIONS FOR FURTHER STUDY

There are many problems to be solved both in the theory of the flotation process and in the application of the theory to the kraft pulp mill effluent system. If the present research has been useful, such usefulness will be found in the definition of a convenient starting point for further study. Because of the potential social importance of the proposed purification system, the research effort should be directed towards preparing the system for a pilot plant evaluation.

The areas of most immediate interest, therefore, are:

a. A fairly wide range of cationic surfactants should be reviewed and the most suitable ones selected for batch flotation trials. The surfactants ultimately selected should be commercially available or readily produced by commercial means.



b. The possibility of modifying the process to a true precipitate flotation should be considered. This modification could enhance the desirability of the process from an economic point of view, providing the precipitating chemical is less expensive than the surfactant, which is usually the case. This study would almost certainly involve including the coagulation regime mentioned in the section on Collector Pre-mix Time in Chapter 8. This régime was, almost certainly, more a precipitate flotation than an ion flotation.

c. A fundamental study of the charge carried by the chromophoric molecular fragments in the raw effluent should be attempted. While the success of this study cannot be predicted, positive results would lay the basis for a more thorough understanding of the flotation mechanisms. Particle mobility measurements should also be used as a routine test in the flotation trials.

d. A better method of following the kinetics of flotation recovery must be developed. Perhaps the radioactive tagging or even simple turbidity measurements would prove to be more adequate. When the method is developed, study of the kinetics of removal of the ion flotation or the true

precipitate flotation system should be related to: bubble size and air rate, temperature effects within the range that could be applicable for an actual process, and the other significant parameters.

e. Following adequate completion of the above four items, a bench laboratory scale continuous flotation cell should be developed. After specification of the actual unit operations of the surfactant regeneration stage, design of a pilot plant system could be contemplated and preliminary economic analysis performed.

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# NOMENCLATURE

R	:	the ideal gas law constant.
Т	:	the absolute temperature.
<sup>a</sup> i	:	the activity of the ith component.
Γi	:	the surface excess concentration of the ith component.
R'	:	fraction of colligend removed at time t.
М'	:	fraction of colligend removed at steady state.
t	:	time, in minutes.
k	:	constant defined in equation (2).
Х <sub>т</sub>	:	colour of the collapsed foam, or foamate.
X <sub>B</sub>	:	colour of the bottoms.
F	:	volumetric flow rate of the feed stream.
В	:	volumetric flow rate of the bottoms stream.

	R	:	volumetric flow of reflux stream.
	BOD <sub>5</sub>	:	the five day biological oxygen demand, defined in reference [49].
	СМС	:	critical micelle concentration, defined in reference [45].
	nm	:	nanometer (10 <sup>-9</sup> meters).
	R	:	fraction of colligend-collector product removed at time t.
	М	:	fraction of colligend-collector product ultimately removed.
	A	:	constant, defined in equation (3).
	m	:	constant, defined in equation (3).
•	efflu	uent:	refers to the applicable pulp mill waste water stream.

#### APPENDIX A

### THE MODIFIED COLOUR TEST

Absorbance spectra, for the visible region, are similar for the acid, caustic, pulping, and, of course, the total mill effluents. Figure Al shows that absorbance of the caustic extraction effluent increases with decreasing wavelength over the visible region. In the ultraviolet, a dilution of about 50 reveals a pronounced shoulder between 250 and 275 nm.

In order to check the effluent's behaviour with respect to Beer's Law, samples of caustic extraction effluent were diluted by factors of 2.5, 5.0, 10.0, 20.0, 25.0, 35.7, and 50.0. Figure A2 illustrates the close adherence to Beer's Law over the absorbance range 0.2 to 1.2.

Although there has been some work [52] on the development of colour estimation procedures more directly applicable to kraft pulp mill effluents, these methods have not yet been fully demonstrated. Therefore, the colour



FIGURE A1 Absorbance versus Wavelength for Various Concentrations of First Caustic Extraction Stage Effluent



standard selected was the widely used cobalt and platinum salt solution. Figure A3 shows the absorbance spectra for three concentrations of the standard solution. Because meaningful (i.e. the hue of the solution is roughly the same as the standard) absorbance measurements of the kraft mill effluent can be made at any wavelength between 450 and 550 nm, the precise wavelength of the first maxima of the Pt-Co standard was chosen. This wavelength was established as 455.7 nm. The choice of wavelength also proved especially convenient for another reason; with a 40 mm path length, a dilution of ten for the untreated caustic extraction effluent and a dilution of two for the total mill effluent produced an absorbance in the desirable 0.5 to 1.1 range. Thus, the effluent colour procedure can now be summarized.

#### Preparation of Colour Samples

1. The sample was filtered through a Corning, Gooch Type fritted disc filter. The fritted disc was classified as 'Fine,' corresponding to a nominal, maximum pore diameter of 4, 5.5 microns. The porous filters proved to be capable of completely removing the turbidity of the solution and the use of filter aids was therefore not necessary.



FIGURE A3 Absorbance versus Wavelength for Various Strengths of the Pt-Co Standard Solution

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2. If the samples required dilution, they were next diluted followed by pH adjustment to pH 7.6  $\pm$  0.02 with either concentrated NaoH or NC1.

### <u>Colour Measurement</u>

1. The Unicam SP.800B scanning spectophotometer was set up to operate from 275 to 600 nm. The baseline absorbance was set using a distilled water blank. Details of operation can be found in the machine operating manual.

2. The absorbance spectrum of the sample was produced, using a 50 mm light pathlength. Following completion of the colour sample scans, the applicable spectrum of a holmium filter was run, in order to determine the wavelength accurately.

3. The absorbance of the colour sample was determined at 456 nm and converted to Pt-Co units from the calibration graph.

4. The dilution correction, if any, was made.

#### Preparation of the Calibration Graph

1. The 1000 colour unit standard was prepared by dissolving 2.492 gm of potassium chloroplatinate  $(K_2Pt Cl_6)$  and 2.000 gm of cobaltous chloride (Co Cl\_2  $\cdot$  6H\_20) in distilled water containing 100 ml of concentrated hydrochloric acid. The volume was adjusted to one liter. This standard contained 1000 mg per liter as Pt, hence the common convention of using the terms 'Pt-Co colour units' and 'ppm as Pt-Co' interchangeably.

2. Colour standards, at various concentrations of Pt-Co, were prepared by volumetric dilution.

3. The absorbance of each standard was measured against distilled water at 456 nm as in the preceding case.

4. An expanded version of Figure A4 was prepared using the results of the previous measurement.



### APPENDIX B

## SUMMARY OF ION FLOTATION DATA

Run No.	Me0H	Surfactant Conc. x 10 <sup>-4</sup> (moles/1)	Diffuser Specifi- cation	рH	Pre-mix Time (min)	Air Sparge Rate (cm³/sec)	Colour Reduction (percent)	Ultimate Flotation Recovery (percent)	Foam Vol. (ml)
1	1	5.0	NA	8.14	0.5	NA	94.3	NA	NA
2	√	10.0	NA	7.71	0.5	NA	99.2	NA	177
3	1	10.0	NA ·	7.7	0.5	NA	99.3	100	340
4	None	10.0	NA	5.1	23	7.9	95.9	99	NA
5	None	5.0	NA	5.15	10	7.9	NA	NA	NA
6	None	10.0	NA	5.15	29	7.9	96.0	99	530
7	1	5.0	NA	5.15	7.0	7.9	96.0	57	NA
8	√	8.0	NA	5.15	2.0	7.9	97.2	98	185
9	1	8.0	NA	2.14	2.0	7.9	92.0	<10%	NA
10	1	8.0	NA	12.0	2.0	7.9	95.0	<50%	NA
11	↓ ↓	8.0	Med.	1.57	2.0	7.2	85.0	NA	NA

(CONTINUED)

Run No.	МеОН	Surfactant Conc. x 10 <sup>-4</sup> (moles/1)	Diffuser Specifi- cation	рН	Pre-mix Time (min)	Air Sparge Rate (cm³/sec)	Colour Reduction (percent)	Ultimate Flotation Recovery (percent)	Foam Vol. (ml)
12	1	8.0	Med.	7.68	2.0	7.2	97	76	150
13	1	8.0	Med.	9.8	2.0	7.2	93	72	180
14	1	8.0	Med.	5.61	2.0	7.2	NA	77	120
15	1	8.0	Med.	4.51	2.0	7.2	98	86	260
16	1	8.0	Med.	5.1	2.0	7.2	98	91	140
17	1	10.0	Med.	5.1	2.0	7.2	NA	NA	NA
18	1	10.0	Med.	5.1	2.0	7.2	NA	NA	510
19	1	8.0	Fine	4.5	2.0	7.2	NA	91	330
20	1	8.0	Fine	5.14	2.0	7.2	NA	90	170
21	1	8.0	Fine	5.1	2.0	2.4	NA	91	90
22	1	8.0	Fine	5.1	2.0	1.5	NA	97	65
23	1	8.0	Fine	5.1	2.0	17.1	NA	89	245

APPENDIX B (Continued)

(CONTINUED)

Run No.	МеОН	Surfactant Conc. x 10 <sup>-4</sup> (moles/l)	Diffuser Specifi- cation	рН	Pre-mix Time (min)	Air Sparge Rate (cm³/sec)	Colour Reduction (percent)	Ultimate Flotation Recovery (percent)	Foam Vol. (ml)
24	√	6.0	Fine	5.1	5.0	2.4	NA	93.5	75
25	1	4.0	Fine	5.1	5.0	2.4	NA	90	50
26	1	2.0	Fine	5.13	5.0	2.4	56.4	<10%	100
27	1	8.0	Fine	5.10	5.0	2.4	97.5	90%	170
28	√	3.0	Fine	5.12	5.0	2.4	83	40%	80
29	1	1.0	Fine	5.11	5.0	2.4	30	NA	40
		1	1		1	1		1	

APPENDIX B (Continued)

### APPENDIX C

## FLOTATION RECOVERY RESULTS

RUN	10.3
Time (minutes)	Percent Flotation Recovery
0.0 3.0 6.0 9.0 13.0 15.0 22.0 33.0 38.0	0.0 25.0 64.8 84.0 93.9 96.6 99.3 99.7 99.9

	RUN N	10.4	
Time (minute	s )	P F1 Re	ercent otation covery
0.0 2.0 4.0 6.0 8.0 10.0 15.0 30.0 107.0		1	0.0 29.1 37.1 51.0 70.6 71.4 80.0 84.4 00.0

	RUN N	0.6	1		
Time (minute	s )	Percent Flotation Recovery			
0.0 2.0 5.0 8.0 13.0 28.0			0.0 59.2 82.1 90.5 97.5 98.4		

RUN N	10.8
Time (minutes)	Percent Flotation Recovery
0.0 1.0 2.0 4.0 6.0 10.0 21.0 34.0	0.0 43.5 72.7 75.6 89.2 92.1 98.2 98.2 98.2

[	RUN NO	. 12	
Time (minute	es)	P F1 R	ercent otation ecovery
0.0 2.5 4.5 12.0 41.0 63.0			0.0 2.5 11.0 34.5 71.0 76.0

	RUN	NO	•	13	
Time (minutes)				P F1 R	ercent otation ecovery
0.0 4.4 10.4 16.0 30.5 62.0 94.0					0.0 1.7 14.5 22.3 40.1 60.4 72.3

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	RUN NO	. 14	
Time (minut	es)	P F 1 R	ercent otation Recovery
0.0 3.0 5.0 9.0 18.5 60.0		¢	0.0 36.6 44.1 54.6 68.3 78.5

RUN NO	). 15
Time (minutes)	Percent Flotation Recovery
0.0 4.0 7.1 10.0 30.4 77.0	0.0 10.3 15.5 30.4 78.0 86.2

RUN NO. 16		
Time (minutes)	Percent Flotation Recovery	
0.0 3.15 5.0 10.0 23.15 31.5 75.0	0.0 30.0 36.8 59.6 75.6 84.0 90.5	

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RUN NO. 19		
Time (minutes)	Percent Flotation Recovery	
0.0 5.0 11.0 24.0 54.3 65.0	0.0 18.8 45.9 76.8 89.0 89.2	

RUN NO	). 20
Time (minutes)	Percent Flotation Recovery
0.0 2.2 5.0 11.5 20.15 55.0	0.0 47.3 68.1 81.0 87.9 92.1

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RUN NO	). 21
Time (minutes)	Percent Flotation Recovery
0.0 2.6 5.15 12.6 25.2 36.0	0.0 34.3 59.2 87.8 89.9 91.2

	RUN NC	). 22	
Time (minut	es)	P F1 R	ercent otation ecovery
0.0 4.4 8.4 15.3 42.1	5		0.0 76.6 80.5 93.2 97.7

RUN NO	). 23
Time (minutes)	Percent Flotation Recovery
0.0 3.4 9.75 16.7 60.0	0.0 32.1 59.2 79.0 87.3