IOWA STATE UNIVERSITY Digital Repository

Retrospective Theses and Dissertations

Iowa State University Capstones, Theses and Dissertations

1988

Direct filtration of Chlorella and Scenedesmus suspensions for potable water treatment

Johannes Haarhoff *Iowa State University*

Follow this and additional works at: https://lib.dr.iastate.edu/rtd Part of the <u>Civil and Environmental Engineering Commons</u>

Recommended Citation

Haarhoff, Johannes, "Direct filtration of Chlorella and Scenedesmus suspensions for potable water treatment " (1988). *Retrospective Theses and Dissertations*. 9347. https://lib.dr.iastate.edu/rtd/9347

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digrep@iastate.edu.



INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the original text directly from the copy submitted. Thus, some dissertation copies are in typewriter face, while others may be from a computer printer.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyrighted material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is available as one exposure on a standard 35 mm slide or as a $17" \times 23"$ black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. 35 mm slides or $6'' \times 9''$ black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.



300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA

-.

-

^

Order Number 8825397

Direct filtration of *Chlorella* and *Scenedesmus* suspensions for potable water treatment

Haarhoff, Johannes, Ph.D. Iowa State University, 1988



.

Direct filtration of <u>Chlorella</u> and <u>Scenedesmus</u> suspensions for potable water treatment

Ъу

Johannes Haarhoff

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Civil and Construction Engineering Major: Sanitary Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University Ames, Iowa

TABLE OF CONTENTS

	Page
NOTE ON NOMENCLATURE	xi
INTRODUCTION	1
LITERATURE REVIEW	3
Physical Characteristics of Algal Suspensions	3
Average particle diameter Specific gravity Electrical surface charge Extracellular organic matter (EOM) Bacteria	3 3 4 5 5
Algal Separation without Coagulants	6
Algal Separation with Metal Coagulants	10
Mechanisms of particle aggregation Algal flocculation and settling Algal filtration	10 11 13
Algal Separation with Synthetic Organic Polymers	15
Structure and selection of synthetic organic polymers Mechanisms of particle aggregation Algal flocculation and filtration Optimal pretreatment for direct filtration	15 17 19 21
Algal Release of EOM	24
Organic carbon cycling in natural waters The release of algal EOM The nature of algal EOM	24 25 26
EOM Effects on Algal Separation	28
Experimental evidence EOM reaction mechanisms	28 31
Chlorine Interaction with Algae	32
Chlorine chemistry Chlorine effects on algal cells Chlorination of algal suspensions Effects of prechlorination on treatment processes	32 35 36 38

.

.

,

Mathematical Modeling of Deep Bed Filtration	41
Mathematical modeling: particle removal Mathematical modeling: head loss Numerical solution of filtration equations	42 44 45
MATERIALS, METHODS AND EQUIPMENT	47
Algal Cultures	47
Reagents	50
Jar Testing	52
Sand Filtration System	52
Molecular Weight Fractionation	55
Colloid Titration	56
Other Analytical Procedures	57
CHARACTERISTICS OF ALGAL SUSPENSIONS	61
Measurements of Algal Cell Concentration	61
Measurement of Algal Cell Size	61
Effect of Prolonged Suspension on Cell Size Distribution	67
Molecular Weight Distribution of Algal EOM	71
Charge Concentration of Algal EOM	74
Summary of Findings	77
EFFECTS OF CATIONIC POLYMERS AND CHLORINE ON ALGAL SUSPENSIONS	79
Characterization of Cationic Polymers	79
Jar Testing of Algal Suspensions	83
Cationic Polymer Effects on Algal EOM	87
Chlorine Effects on Algal EOM	94
Combined Effects of Cationic Polymer and Chlorine on Algal EOM	97
Summary of Findings	100

.

.

DIRECT FILTRATION OF ALGAL SUSPENSIONS	102
Outline of Experimental Work	102
Direct Filtration without Coagulants	104
Direct Filtration with Metal Coagulants	107
Turbidity removal Head loss development rate (HDR) Turbidity breakthrough Chlorine effects	111 111 113 113
Direct Filtration with Cationic Polymers	113
Effect of polymer type Effect of polymer dosage during a single filter run Effect of polymer dosage during multiple filter runs Effect of polymer dosage on different size fractions Effect of polymer overdosage Effect of mixing Effect of prechlorination	114 114 120 123 123 126
Summary of Findings	131
CONCLUSIONS AND RECOMMENDATIONS	136
Reliability of Laboratory Cultures	136
Significance of Algal EOM	136
Options for Direct Filtration of Algae	138
Further Avenues for Research	140
ACKNOWLEDGMENTS	142
REFERENCES	143
APPENDIX A: COLLOID TITRATION PROCEDURE	151
Reagents	151
Standardize Cationic Polymer	151
Determine Charge Concentration of Unknown	151
Example	152
Remark	152

APPENDIX B:	FILTRATION DATA	153
APPENDIX C:	PARTICLE COUNTS DURING RUN 42A/B AND RUN 47A/B	177

·

LIST OF TABLES

•

Table	1.	Summary of published studies on algal filtration without the use of coagulants	8
Table	2.	Summary of published studies on algal flocculation and filtration with metal coagulants	12
Table	3.	Summary of published studies on algal flocculation and filtration with cationic polymers as primary coagulants	20
Table	4.	Composition of culture medium WC (from Guillard, 1975)	48
Table	5.	Concentration of principal cations and anions in culture medium WC (adapted from Guillard, 1975)	49
Table	6.	Concentration of principal cations and anions in typical algal suspension applied to sand filtration system	49
Table	7.	Analytical methods and instruments	59
Table	8.	Typical analysis of molecular weight fractionation results obtained after ultrafiltration	72
Table	9.	Summary of molecular weight fractionation results	73
Table	10.	Typical analysis of titration results to obtain charge concentration	75
Table	11.	Charge concentration per unit mass of NPOC for different studies	76
Table	12.	Charge concentration per unit mass of NPOC for different molecular weight fractions of the EOM from <u>Chlorella</u> <u>pyrenoidosa</u>	76
Table	13.	Characteristics of the cationic polymers used	80
Table	14.	Molecular weight fractions of a diluted suspension of MAGNIFLOC 573C	80
Table	15.	Experimental jar test conditions	84
. Table	16.	Statistical analysis of the results from jar test 1	85
Table	17.	Turbidity development in algal EOM after cationic polymer addition - effect of cationic polymer concentration	88

vi

•

•

Page

.

Table	18.	Turbidity development in algal EOM after cationic polymer addition - effect of reaction time	88
Table	19.	Chlorine demand for the EOM from suspensions of <u>Chlorella pyrenoidosa</u> with different NPOC concentrations	98
Table	20.	Turbidity development in algal EOM after addition of different concentrations of chlorine and cationic polymer	98
Table	21.	Experimental variables for the 98 filter runs	103
Table	22.	Summary of filtration results without coagulants	105
Table	23.	Summary of filtration results with ferric chloride	108
Table :	24.	Summary of filtration results with aluminum sulfate	109
Table	25.	Summary of filtration results with cationic polymer	115
Table :	26.	Average turbidity removal during filtration of <u>Scenedesmus quadricauda</u> suspensions treated with cationic polymer	124

.

.

.

LIST OF FIGURES

		Page
Figure 1.	Schematic front view of algal growth reactors and growth chamber	51
Figure 2.	Schematic arrangement of sand filtration system (only one of two parallel systems shown)	53
Figure 3.	Molecular structure of reagents used for colloid titration	58
Figure 4.	Relationship between spectrophotometric absorbance and nephelometric turbidity for <u>Chlorella pyrenoidosa</u>	62
Figure 5.	Relationship between suspended solids and nephelometric turbidity for <u>Chlorella pyrenoidosa</u>	63
Figure 6.	Relationship between calculated particle volume and nephelometric turbidity for <u>Chlorella pyrenoidosa</u>	64
Figure 7.	Relationship between calculated particle volume and nephelometric turbidity for <u>Scenedesmus quadricauda</u>	65
Figure 8.	Relationship between spectrophotometric absorbance and nephelometric turbidity for <u>Anabaena flos-aquae</u>	66
Figure 9.	Particle volume distribution of different suspensions of <u>Chlorella pyrenoidosa</u>	68
Figure 10.	Particle volume distribution of different suspensions of <u>Scenedesmus quadricauda</u>	69
Figure 11.	Change in particle volume distribution with time for a suspension of <u>Chlorella pyrenoidosa</u>	70
Figure 12.	Supernatant turbidity of a <u>Chlorella pyrenoidosa</u> suspension after 30 minutes settling, following a jar test with three different cationic polymers	81
Figure 13.	Turbidity of a <u>Chlorella pyrenoidosa</u> suspension after filtration through #2 WHATMAN filter paper, following a jar test with three different cationic polymers	82
Figure 14.	Turbidity development in algal EOM after cationic polymer addition - effect of polymer concentration	89
Figure 15.	Turbidity development in algal EOM after cationic polymer addition - effect of reaction time	91

- Figure 16. Turbidity development in algal EOM after cationic 92 polymer addition - measured turbidity for different suspensions
- Figure 17. Turbidity development in algal EOM after cationic 93 polymer addition - turbidity and polymer dosage corrected for initial turbidity and NPOC concentration
- Figure 18. Illustration of the calculation procedure for chlorine 95 demand, using a suspension of <u>Chlorella pyrenoidosa</u>
- Figure 19. Chlorine demand versus chlorine contact time for 96 Chlorella pyrenoidosa - total suspension and EOM
- Figure 20. Turbidity development in algal EOM after addition of 99 different concentrations of chlorine and cationic polymer. Chlorine contact time was 5 minutes before polymer addition
- Figure 21. Effect of pH on the filtration of <u>Scenedesmus</u> <u>quadricauda</u> with 1.8 mg Fe/L as primary coagulant. Bed depth 150 mm for 21B, 100 mm for 23B
- Figure 22. Average turbidity removal versus coagulant dosage for 112 filter runs conducted with metal coagulants. Turbidity removal expressed as the equivalent removal through a bed depth of 200 mm
- Figure 23. Comparison between two commercial polymers as primary 116 coagulants for the direct filtration of <u>Chlorella</u> <u>pyrenoidosa</u>. Bed depth 150 mm
- Figure 24. Effect of different initial cationic polymer 117 concentration, and a step change in polymer concentration after 5.5 hours. Bed depth 200 mm
- Figure 25. Turbidity removal values taken from Figure 24, 118 immediately before and after the step change. Bed depth 200 mm
- Figure 26. Average turbidity removal versus polymer concentration 119 for all filter runs with <u>Chlorella pyrenoidosa</u> suspensions treated with cationic polymer. Turbidity removal expressed as the equivalent removal through a bed depth of 200 mm
- Figure 27. Effect of polymer dosage on the direct filtration of 121 <u>Chlorella pyrenoidosa</u>. Run 47A received just enough polymer to satisfy the EOM demand. Bed depth 200 mm

- Figure 28. Removal of different particle size fractions two hours 122 into filter runs 47A and 47B
- Figure 29. Effect of rapid mixing on initial ripening period (all 125 runs shown) and on turbidity breakthrough (runs 42A and 42B). Bed depth 150 mm
- Figure 30. Effect of mixing on the removal of different particle 127 size fractions three hours into filter runs 42A and 42B
- Figure 31. Effect of prechlorination on the filtration of 129 <u>Chlorella pyrenoidosa</u>. Chlorine added to 16A during first six hours, then switched to 16B. Bed depth 250 mm
- Figure 32. Effect of prechlorination on the filtration of 130 <u>Chlorella pyrenoidosa</u> - filter runs 45A and 45B. Bed depth 250 mm
- Figure 33. Effect of chlorine concentration on the filtration of 132 <u>Chlorella pyrenoidosa</u> - filter runs 48A, 48B, 49A, 49B, 50A and 50B. Bed depth 200 mm
- Figure 34. Effect of chlorine contact time before polymer addition 133 on the filtration of <u>Chlorella pyrenoidosa</u>. Filter run 51A had 7.7 minutes of contact, filter run 51B only 0.8 minutes. Bed depth 250 mm

NOTE ON NOMENCLATURE

Two terms are used in this dissertation in connection with the organic matter encountered in water samples.

The term <u>algal EOM</u> (algal extracellular organic matter), gleaned from the most current literature, is used as a general, qualitative term to describe that part of the organic matter which remains after separation from the algal cells by centrifugation and/or filtration. It is not a rigorous, quantitative definition, for it may also include bacteria, detrital matter, organic matter introduced with the tap water used for dilution, etc.

Whenever the algal EOM concentration is expressed quantitatively, it is expressed as <u>NPOC</u> (non-purgeable organic carbon). In this case, the pore size of the filter paper used for the cell separation is clearly stated.

INTRODUCTION

The presence of algae in natural water sources poses a problem for drinking water purveyors and consumers all over the world. Algae can impart unpleasant taste, odor and appearance to drinking water which make their removal imperative. The treatment of an algal-rich water source, on the other hand, is riddled with operational problems such as high demand for treatment chemicals, algal growths and filter clogging. As the future inevitably points to the more intense use, pollution, and reuse of surface water supplies, they will without a doubt turn more eutrophic with a concomitant increase in algal concentration.

Algae, however troublesome they may be in a specific water source, will usually only pose a serious problem for a small part of the year. Algal blooms are triggered by seasonal nutrient and temperature cycles and come and go fairly quickly, often with a high quality raw water source remaining for most of the year. Such sources may be amenable to the relatively cheap process of direct filtration, were it not for the intermittent periods of algal interference. Direct filtration does not require the costly sedimentation step before filtration to remove the bulk of the solids volume; the solids volume is retained within the pores of the filter bed. Other prefiltration processes such as microscreening and filter flotation (flotation in the headspace within the filter box) have been substituted for conventional sedimentation in an effort to reduce the total treatment cost, but have not gained widespread acceptance.

This dissertation, in the broadest sense, explores ways whereby direct filtration can deal with short-lived algal blooms, using <u>chemical</u> <u>treatment only</u>. In recent years, algae and their chlorinated byproducts have been increasingly associated with the presence of halogenated organic compounds, some of which are considered carcinogenic to man, but these potential consequences to human health will not be addressed. The focus is primarily on the <u>physical</u> behavior and response of the algal suspension to different chemical dosage and pretreatment schemes.

The objectives of this study specifically are:

- To determine the filtration behavior of algal monocultures in the absence of coagulants, after dosage with metal coagulants, and after dosage with cationic polymer, respectively,
- To determine the effect of prechlorination on the above processes, if any, and
- To develop a practical, consistent way of estimating the cationic polymer feed rates required for successful filtration of algal suspensions.

A better fundamental grasp on these issues will benefit water treatment practice in two ways:

- With optimum chemical control, some water treatment plants may be able to weather the worst periods of algal blooms, thereby rendering other costly pretreatment steps unnecessary, and
- Water treatment plant operators, once they understand the mechanistic interaction between algae and different treatment chemicals, will be able to approach chemical dosing during algal blooms in a more logical, less haphazard way.

LITERATURE REVIEW

Physical Characteristics of Algal Suspensions

A suspension of planktonic algae, in the simplest terms, is a very dilute suspension of biological particles. A concentrated suspension of <u>Chlorella</u>, for example, typically represents 500 million cells/L, each about 4 μ m in diameter, which is equivalent to a solids volume of only 3 17 mm /L. This solids volume concentration falls comfortably into the region where direct filtration would be the optimal treatment process, according to a recent optimization study by Wiesner and Mazounie (1987). <u>Chlorella</u>, to the contrary, is poorly removed during direct filtration, because water treatment processes have generally been developed for the removal of <u>inorganic</u> particles such as naturally occurring silt or clay. The following paragraphs will briefly outline the similarities and differences between algal biocolloids and inorganic colloids. Model suspensions of bentonite or kaolinite clays are frequently used in water treatment research projects and many of the conclusions from such research cannot be blindly extrapolated to algal-rich suspensions.

Average particle diameter

Although there is no rigorous particle size definition of a colloidal particle, standard texts on colloid chemistry (for example Van Olphen, 1977) suggest a size range between 1 nm and 1 μ m. Some algal species, on the other hand, may get down to a minimum size of 2 μ m, but most species have an average diameter of about 10 μ m. Regardless of the exact size limits of algae and true colloids, the main point is that algal cells are considerably larger than inorganic colloidal particles; on the average, between one and two orders of magnitude.

Specific_gravity

Planktonic algae have to maintain their vertical position in a water body within fairly strict limits to stay in the zone where nutrient and

light levels are sufficient. The specific gravity of an algal cell, therefore, has to be very close to that of water. Some species of bluegreen algae have intracellular gas vesicles which are continuously regulated to keep the algae at the desired water depth, while other species carry lightweight oils or mucilaginous sheaths which are lighter than water to keep them from sinking. Different cell shapes are found amongst the larger species which greatly increase their hydrodynamic drag, such as oblong shapes or spinelike appendages. Some species are equipped with one or more flagella which are moved in a whiplike fashion to provide motility.

In contrast to these elaborate mechanisms to maintain neutral buoyancy, silicate clays such as montmorillonite and kaolinite have a specific gravity in the region of 2.6 kg/m. As a result, the mechanisms whereby algae and clay particles are transported during mixing and filtration processes, such as gravitation and momentum effects, should be substantially different.

Electrical surface charge

Most particles occurring naturally in water are negatively charged, notably clay and silt particles. Ives (1955, 1956 and 1959), in a pioneering study, determined electrophoretically that algae, in the normal pH range encountered in water treatment, are also negatively charged. He used these measurements to calculate the thickness of the electric double layer, to calculate the surface charge concentration and the zeta potential, and demonstrated the effects of ionic strength. Against this background of physicochemical principles, he postulated a simple conceptual model of electrostatic precipitation between the algal cells and the positively charged hydroxide flocculi that form upon chemical treatment with a metal coagulant. His findings also enabled him to interpret the operational results from a full-scale treatment plant.

Before the work of Ives, engineering reports on algal behavior were vague and imprecise, abounding with qualitative observations and surrogate parameters of algal concentration. The main contribution of

Ives was to remove much of the mysticism of algal behavior and to place it on a sound physical footing by dealing with cell counts, surface area, cell shapes and electric surface charge. The similarity between algal cells and other colloidal particles, from an electrical charge perspective, was clearly demonstrated. The parallels between true colloidal suspensions and algae have been valid and useful during later years to explain the fact that algae filter best at their isoelectric point (Foess and Borchardt, 1969), that flocculation can be improved by surface charge neutralization (Tenney et al., 1969), and that an increase in ionic strength leads to more efficient filtration (Folkman and Wachs, 1970).

Extracellular organic matter (EOM)

The presence of algae in a water source is always accompanied by dissolved organic carbon. When algae photosynthesize, they produce new cell material and grow, but a substantial fraction of the newly fixed organic carbon is also released as dissolved compounds into the water. A later section of this literature review will deal with the nature and release of the EOM in detail. At this point, where the nature of inorganic colloids and algae is contrasted, it bears repetition to point out that model clay suspensions are relatively free from dissolved organic carbon, whereas algal-rich suspensions could contain high concentrations of algal EOM.

Bacteria

Unlike inorganic solids, algae in nature are a vital part of a complex carbon cycle. They deplete certain inorganic nutrients, release EOM, and decompose upon death. The presence of algae in nature is always, therefore, accompanied by the presence of bacteria. The ratio of bacterial cell numbers to algal cell numbers is not constant. Oron et al. (1979) found, in samples drawn from a high-rate wastewater treatment pond in Israel, that there were 100 to 200 times more bacterial cells than algal cells, which means that the bacterial biomass amounted to 25-

35% of the total biomass. Tilton et al. (1972), in a laboratory algal culture under continuous lighting, found much less bacteria; there were 100-1000 times less bacterial cells than algal cells.

Jalali-Yazdi (1984) studied the interrelationship between algae and bacteria and came to the conclusion that "bacterial activity comprise an integral part of the algal growth and affects the surface properties and flocculation characteristics of algae." He noticed a considerable increase in bacterial biomass if cultures were left in the dark - under these conditions, bacterial biomass constituted up to 15% of the total biomass. Under conditions of continuous lighting, this percentage was as low as 1%. Because bacteria are so small relative to algae, even these small percentages could translate into a considerable contribution to the total surface area presented by the suspended particles.

Algal Separation without Coagulants

Successful sedimentation and filtration in water treatment requires the use of treatment chemicals, regardless of the nature of the suspended solids. The studies to be reviewed in this section do not suggest that algal separation without treatment chemicals could be a feasible fullscale process. They do, however, elucidate the physical response of algal cells to the processes that operate during rapid filtration through a sand bed. Other separation processes that do not employ treatment chemicals, such as microscreening, have been deliberately omitted; the emphasis is on deep bed filtration.

Algal suspensions are very dilute in terms of total particle volume. In the previous section, a typical particle volume concentration of 17 mm /L was calculated for a <u>Chlorella</u> suspension. At a typical municipal filtration rate of 8 m/h, such a suspension will apply 2,000 cm of algal volume to every square meter of filter bed in a 24 h day, which will fill only 0.5% of the pores in a 1000 mm sand bed. The head loss development rates measured in the studies about to be reviewed should be, and are very low. The main emphasis of these studies is the algal removal

efficiency during rapid sand filtration. A summary of the different studies, with their main operational variables, is shown in Table 1.

Ives (1961) used algal suspensions to verify and calibrate his proposed mathematical model for deep bed filtration behavior. The algae were radioactively labelled and their accumulation within the sand pores was directly measured by passing a scintillation counter along the side of the filter column. The removal efficiency measured for the six reported experiments ranged from about 20% to 100%. The data, however erratic, did illustrate two basic, common sense concepts. First, the removal got better as the sand size decreased. Second, the removal got better as the hydraulic loading was decreased.

Three studies on algal filtration were conducted during the 1960s at the University of Michigan. Borchardt and O'Melia (1961) measured poor removal that got even poorer as every filtration run continued, until a constant minimum removal efficiency was reached. The head loss development, small as it was, was linear with time, which indicated penetration of the algae into the sand bed. Smaller sand sizes led to better removal. They could not obtain good reproducibility between successive filtration experiments.

Davis and Borchardt (1966) continued this work with a system of four parallel filters to circumvent the lack of reproducibility between experiments. Although different algal genera were used in this study, the conclusions of the previous study were supported. A decrease in removal efficiency was demonstrated with higher hydraulic loading. If the filtration runs were continued long enough, the removal efficiency approached zero.

A further filtration study by Foess and Borchardt (1969) emphasized the effects of the surface characteristics of the algal cells and the sand grains. Under normal conditions, both silica and algae carry a negative surface charge - if either of them could become neutral or positive, the removal efficiency should be enhanced. One part of this study, therefore, dealt with conditioning the filter sand by soaking the sand in thorium or ferric iron solutions, which raised the isoelectric

Study (year)	Genus	Concentration	Media size (mm)	Media depth (m)	Hydraulic loading (m/h)
Ives (1961)	<u>Chlorella</u> <u>Scenedesmus</u>	135 mm ³ /L	0.25 to 0.71	0.61	4.9 to 14.7
Borchardt and O'Melia (1961)	<u>Anabaena</u> <u>Ankistrodesmus</u> <u>Scenedesmus</u>	0.08 to 0.26 million cells/mL	0.32 to 0.52	1.01	0.5 to 5.0
Davis and Borchardt (1966)	<u>Schizothrix</u> <u>Selenastrum</u>	0.02 to 0.18 million cells/mL	0.29 to 0.75	0.41	1.2 to 4.7
Andrews (1968)	<u>Chlorella</u> Euglena	0.2 to 2 million cells/mL	0.31 to 0.95	0.15 to 0.69	5.0 to 15.0
Foess and Borchardt (1969)	<u>Chlorella</u> <u>Scenedesmus</u>	0.01 to 0.11 million	0.71	0.62	5.0
Folkman and Wachs (1970)	<u>Chlorella</u> ·	2.9 to 7.5 million cells/mL	≃0.2	3.0	0.04 to 0.25
Naghavi and Malone (1986)	<u>Scenedesmus</u>	up to 65 mg/L as SS	0.064 to 0.355	0.003 to 0.013	9.0 max

Table	1.	Summary	of	published	studies	on	algal	filtration	without	the
		use of c	oar	gulants						

point of the sand from about pH 2 to pH 4.5 - pH 5.5. This procedure did improve algal removal, but the improvement was only marginal. The other part of the study dealt with the manipulation of the pH down to the isoelectric point of the algal cells. At pH 9, well above the isoelectric point of the algae, the removal efficiency was 60% - 70% at the start of the experiment, but then decreased, in line with the findings of earlier studies. Below pH 3, close to the isoelectric point of the algae, however, the removal efficiency was consistently above 90% and stayed at that level for the full duration of the filtration run.

Andrews (1968) performed filtration on pilot scale with different combinations of filter media and algal cultures. A mixed culture of green algae, in which <u>Chlorella</u> predominated, was poorly removed; an average of 18% of the cells were removed, but this varied from 0% to 75% from run to run. The filtration runs were terminated after only 2 to 5 hours. No reliable or consistent correlation between turbidity and cell counts was obtained.

Folkman and Wachs (1970) did a slow filtration study with dunesand in an upright concrete pipe. This study was prompted by the potential for sand aquifer recharge with wastewater pond effluent in the desert regions of Israel. Although these results are not directly relevant to this review, a few interesting phenonema were observed. First, the <u>Chlorella</u> cells divided once they entered the darkness inside the pipe and the filter media - more cells were counted within the upper sand layers than in the influent. Second, due to this division, there was a definite cell size reduction upon passage through the sand - the average cell size at the top of the bed was 4.3 μ m, compared to an average cell size of 3.6 μ m in the filtrate. Third, the removal efficiency could be increased at any point during a filtration run by increasing the electrical conductivity (ionic strength) of the suspension.

Recently, Naghavi and Malone (1986) filtered a <u>Scenedesmus</u> culture through tiny plugs (3 - 13 mm deep) of very fine sand (0.064 - 0.200 mm). Filtration runs only lasted 16 minutes and 97% - 100% of the cells were removed. All the removal took place through surface straining, with no

penetration of the algal cells into the bed. A <u>Scenedesmus</u> cell has an average diameter of about 15 μ m, which is larger than the pores one would expect between sand grains which are only 4 to 15 times larger.

The first five studies quoted showed that algae are poorly removed in the normal operating range of pH, hydraulic loading and sand size. The expected effects of hydraulic loading, sand size and low particle volume were validated. A common feature of the experimental results was the unpredictable nature of the algal removal; it improved or deteriorated from experiment to experiment without any clear reason.

Algal Separation with Metal Coagulants

Mechanisms of particle aggregation

When a salt of ferric iron or aluminum is added to water, it will dissociate to yield trivalent Fe or Al ions, which will hydrate with 3^{+} six water molecules to form the aquometal complexes Al(H 0) or 2^{+} Fe(H 0) . These complexes then pass through a series of hydrolytic reactions in which the water molecules in the hydration shell are replaced by hydroxyl ions. This gives rise to the formation of a variety of soluble species, including mononuclear species (one metal ion) and polynuclear species (several metal ions). If ferric iron or aluminum is added to water in concentrations less than the solubility limit of the metal hydroxide, hydrolysis products will form and adsorb onto the colloidal particles. When the amount of ferric iron or aluminum added is sufficient to exceed the solubility of the metal hydroxide, the hydrolysis products will form as kinetic intermediates in the formation of a metal hydroxide precipitate (Benefield et al., 1982).

The metal salts, therefore, can act as a coagulant in two ways. In most waters, enough salt is added to precipitate the metal hydroxide. This coats the colloids with a gelatinous and sticky sheath. It also provides additional targets for the original solids, thereby accelerating the flocculation of the particles into large aggregates. These targets may be necessary in coagulating waters having a low turbidity, since

excessive flocculation times may be needed to aggregate the primary solids alone. This mode of coagulation, in which a considerable amount of aluminum or iron hydroxide is formed, is termed sweep coagulation.

The second mechanism of coagulation is adsorbing positively charged metal monomers and polymers on negative colloids, thereby rendering them sticky or unstable so that aggregates are formed when contacts occur. This type of coagulation can only be used for high turbidity waters, since few additional solids are added to the water. In many cases less coagulant may be needed than for low turbidity waters, since a precipitate is not needed (O'Melia, 1978).

Amirtharajah and Mills (1982) analyzed the results of a great number of published coagulation studies, and also considered the theoretical solubility of aluminum hydroxide. They developed a concentration/pH diagram on which regions were depicted where the different coagulation mechanisms could be expected. Johnson and Amirtharajah (1983) followed this with a similar diagram for ferric iron. Although these diagrams are based on thermodynamic equilibrium (coagulation in water treatment is complete within a minute), they are nevertheless useful tools for determining approximate dosage for different mechanisms, once the pH is known. Also, in the case of aluminum, Driscoll and Letterman (<u>ca</u>. 1987) pointed out that humic and other organic substances will act as complexing ligands that may lead to high concentrations of soluble aluminum complexes, higher than predicted by theoretical solubility.

Table 2 contains a brief summary of published studies on algal removal with metal coagulants, which are discussed in the following paragraphs.

Algal flocculation and settling

Algae, through a combination of their small size and low specific gravity, do not settle easily. The cells will only settle if they are caught up in a metal hydroxide floc structure and dragged down with the metal precipitate. Ives (1959) advanced the theory of electrostatic precipitation whereby positively charged hydroxide flocculi are attracted

Study	Algae	Test type	Coagulant	Main emphasis
Ives (1956)	<u>Tribonema</u>	Microscopy	Ferric chloride	Reaction mechanism
Ives (1959)	<u>Tribonema</u> <u>Asterionella</u>	Jar test Microscopy	Ferric chloride	Reaction mechanism
Borchardt and O'Melia (1961)	<u>Scenedesmus</u> <u>Ankistrodesmus</u> Anabaena	Sand filtration	Ferric chloride	Algal removal Bed penetration Head loss
Van Vuuren and Van Duu- ren (1965)	Maturation pond, South Africa	Pilot set- tling and filtration	Alum	Algal removal Chemical dosage
Golueke and Oswald (1965)	Sewage grown	Jar test '	Alum	Chemical dosage
Davis and Borchardt (1966)	<u>Selenastrum</u> <u>Schizothrix</u>	Sand filtration	Ferric chloride	Filter run length Bed penetration Head loss
AcGarry (1970)	Sewage pond, Australia	Jar test	Alum	Chemical dosage Mixing speed
Lin et al. (1971)	Illinois river water	Jar test	Alum	Chemical dosage Algal removal
Al-Layla and Middlebrooks (1974)	<u>Selenastrum</u>	Jar test	Alum	Temperature Chemical dosage Mixing and settling
Friedman et al. (1977)	<u>Chlorella</u>	Jar test	Alum	pH Chemical dosage Algal concentration
Sastry et al. (1977)	Stabilization pond, India	Jar test	Alum	Chemical dosage Flocculation time
(lute and leis 1983)	Neckar river, Germany	Multimedia pilot filtration	Poly- aluminum chloride	Algal removal

Table 2.	Summary of	published	studies	on algal	flocculation	and
	filtration	with metal	. coagula	nts		

to the negatively charged cell surfaces to precipitate directly on the cells. This theory was deduced from several series of time photomicrographs (Ives, 1956 and 1959), showing the floc growth on the cell surfaces. Without the algal cells as nucleation sites, the precipitation would be delayed or inhibited; this was visibly shown to be true in two identical jars - one with algae and the other one without.

The most important independent variable for algal settling is the magnitude of the coagulant dosage. Al-Layla and Middlebrooks (1974) statistically screened five independent variables and found that coagulant dosage was by far the most significant. Coagulant dosage alone accounted for 70% of the variance in the experimental data; all five independent variables together improved this percentage only up to 85%. Lin et al. (1971) screened seven independent variables with a multistep regression analysis, and arrived at the same conclusion, i.e., that coagulant dosage was the most significant variable.

Coagulant dosage for most of the studies was very high. Golueke and Oswald (1965) found an optimal dosage of 70 mg/L, Van Vuuren and Van Duuren (1965) between 125 and 170 mg/L, and Sastry et al. (1977) between 120 and 240 mg/L, all expressed as alum. Golueke and Oswald (1965) worked with highly concentrated suspensions (2000 mg SS/L) and found a maximum ratio of 11 mg algae settled/mg alum added at an alum dosage of 70 mg/L. Friedman et al. (1977) worked with much lower suspensions (25-120 mg SS/L) and found the same ratio to be only 1.2 at an alum dosage of 60 mg/L.

<u>Algal filtration</u>

Only a few studies have addressed direct filtration of controlled algal suspensions with metal coagulants. Borchardt and O'Melia (1961) filtered suspensions of the genus <u>Ankistrodesmus</u> (266,000 to 351,000 cells/mL) through sand at flow rates of approximately 5 m/h. When no coagulant was added, algal removal was extremely poor and head loss buildup practically nothing, and the small fraction that was trapped, was retained in the top 50 mm of the sand bed. When ferric chloride was

added in small amounts (approximately 1 mg Fe/L), the head loss increase was slightly higher, but the algal removal was still poor. When a much larger dosage, 7.2 mg Fe/L, was added, the head loss buildup was rapid and the terminal head loss was reached within 8 hours, but algal removal improved from 10% to 50%. The vertical distribution of the algae was tracked through the 600 mm thick sand bed and three consistent observations were made. First, all the iron precipitate was retained in the top 200 mm of the bed. Second, where algae and iron precipitate were present together, the retention of the algae was enhanced. Third, the removal of algae in the bottom 400 mm of the bed was poor and the same as the removal of untreated algae. The simultaneous presence of floc and algae in the upper layers did not change the filtering characteristics of the algae once they moved out of the floc zone. The authors came to the logical conclusion that "the presence of flocculent material assists in the entrapment of algae cells, but an adequate balance between the chemical and the nonflocculent suspension appears to be vital for complete removal".

Davis and Borchardt (1966) worked with a suspension of the genus <u>Selenastrum</u> and continued to study the effects of ferric coagulant on sand filtration. Iron was introduced in three different fashions - by charging the sand with coagulant prior to filtration, by adding preformed ferric hydroxide floc to the suspension, and by adding soluble iron in the conventional way to the suspension. For a suspension of 111,000 cells/mL, the removal was practically zero in the first case, about 30% in the second case, and 45% in the third. The inferior removal with the preformed floc was ascribed to the possibility of agglomeration of the flocculi before they could attach to the algae. Subsequent tests were done with the iron added in soluble form. At small coagulant dosage of 0.8 and 1.4 mg Fe/L, the initial algal concentration had an effect; at 20,000 cells/mL the removal was 60-70%, but at ten times higher algal concentration, the removal dropped to 10-30%.

A few studies reported algal removal on larger scale filtration systems. In general, removal was most erratic and not consistent.

Johnson et al. (1977) measured removal ranging from 10% to 99%, Evins and Greaves (1979) an average of 94%, Klute and Neis (1983) removal ranging from 30% to 95%, and Halperin et al. (1986) an overall removal of about 90%. The operating conditions and raw water characteristics of these studies were each quite different and these studies cannot be analyzed comparatively.

Algal Separation with Synthetic Organic Polymers

Structure and selection of synthetic organic polymers

Synthetic organic polymers are linear or branched molecules consisting of repeating chemical units with a structure designed to provide distinctive physicochemical properties to the polymer. The polymers are also referred to as polyelectrolytes, because the chemical monomers usually have an ionic nature that imparts an electrical charge to the polymer chain. The ionic charge groups on the polymer determine whether a polymer is anionic, nonionic or cationic.

Two important characteristics of a polymer are its molecular weight and its charge concentration. High molecular weight is synonymous with longer or larger molecular filaments which have a better chance of bridging the gap between particles. The charge concentration is usually expressed as the number of charge equivalents per unit mass of the polymer, typically in μ eq/mg. A high charge concentration is synonymous with high charge neutralization ability.

The positive charge on the cationic polymers used in water treatment is due to the presence of amine groups. The nitrogen atom can be bonded into the polymer structure in different ways, leading to the following sequence of monomeric structures (Morrison and Boyd, 1973):

RNH ----> R NH ----> R N ----> R N X 2 2 3 4 (primary) (secondary) (tertiary) (quaternary)

The first three structures are more basic than water and they will establish a positive charge at lower pH, e.g., the primary amines:

$$\frac{RNH}{2} + H_{3} + H_{2} +$$

At higher pH, the first three amines will lose their positive charge, e.g., the secondary amines:

$$R_{2}NH^{+}$$
 + OH^{-} ----> $R_{2}NH$ + $H_{0}O^{-}$

Below pH 5.5, all the polyamines will carry an ionic charge. At pH 8, the monomeric tertiary amines will lose their charge, but within a polymeric structure, the positive charge will persist up to a maximum of pH 10 (Mangravite, 1983).

The quaternary amines behave differently than the other amines. They will not give up their positive charge in the presence of hydroxide ions and, therefore, are very little impaired at high pH.

Chlorine will react with unquaternized amine sites to reduce the charge of the polymer, thereby reducing the efficiency of the polymer. The quaternary polyamines, on the other hand, are very seldom affected by chlorine, and if they are, the effects are minimal. Pressman (1967) demonstrated this insensitivity to chlorine 20 years ago and Mangravite (1983) has found this to be generally true.

Cationic polymer has been proved in a number of studies to be a feasible primary coagulant for direct filtration. Yeh and Ghosh (1981), for example, showed that good particle removal can be achieved by a number of commercial cationic polymers. They found that the low to medium molecular weight cationic polymers (10 to 100 kiloDalton) were most suitable for direct filtration with low head loss buildup. High molecular weight (HMW) cationic polymers (above 1,000 kiloDalton) also removed particles well, but led to high head loss buildup.

Cationic polymer will also remove part of the dissolved contaminants during direct filtration. Amy and Chadik (1983) evaluated four different cationic polymers of different molecular weight for the removal of DOC (dissolved organic carbon) and THMFP (trihalomethane formation potential) from humic acid solutions, without finding significant differences between polymers. The THMFP was reduced by 25% to 60%, with the removal of DOC slightly less. The polymers themselves added only a very small DOC fraction to the water; 0.18, 0.19, 0.32 and 0.15 mg TOC per mg of polymer added to the suspension. Edzwald et al. (1987) measured a 40% removal of DOC in two natural streams after direct filtration with cationic polymer only.

Mechanisms of particle aggregation

The mechanisms of polymer-induced aggregation have been studied for many years by scientists from a great variety of disciplines. There is consensus that three primary mechanisms are at work during the interaction of polymers with colloidal systems. Edzwald and Lawler (1983) recently provided a lucid summary of the reaction mechanisms.

Charge_neutralization This mechanism requires that the charge groups on the polymer are attracted to the oppositely charged colloidal surface. The polymer then attaches itself electrostatically on the colloidal surface, covering part of the surface and reducing the net electrical charge on the particle. If this process continues, the net charge on the particle will be reduced to zero. At this point, the colloidal stability disappears and the particles will collide and stick to each other. If too much polymer is attached to the particles, the net charge on the particles will be reversed and the suspension will be restabilized. The electrostatic patch theory, a further refinement of the same basic concept, suggests that, if a cationic polymer is added to a suspension of negatively charged particles, the adsorbed polymer forms positive patches on the colloidal surface. These positive patches will attach to negative patches on other particles, even if the net charge on the particles has not yet been reduced to zero. The patch theory is also used to explain why anionic polymers will attach to negatively charged particles. In this case, the polymer will stick to positive patches on a

predominantly negatively charged particle. The bond between the colloid surface and the charge group on the polymer is not necessarily only due to electrostatic attraction. Stronger bonds, such as covalent or hydrogen bonding, may also cause adsorption to the colloid surface even after net charge neutralization is complete. This continued adsorption will eventually lead to restabilization.

Interparticle bridging This mechanism operates when the opposite ends of a polymeric filament attach to two different particles. As the process continues, more and more particles will be tied together until clusters of particles are formed. Interparticle bridging will only occur if the polymer has sufficient size (molecular weight) to overcome the interparticle distance, and if there are enough other particles to bridge with. If the polymer is too small, bridging will not occur. If there is not enough contact opportunity with other particles, the extended end of the filament will eventually wrap itself around one particle only.

<u>Charge neutralization/precipitation</u> This mechanism is essentially charge neutralization, except that the cationic polymer reacts with oppositely charged anionic polymer such as humic or fulvic acids. Microparticles are precipitated as a result of the mutual charge neutralization, and they will eventually be agglomerated to form a fine, but measurable precipitate. The charge neutralization/precipitation mechanism explains how cationic polymer can precipitate some soluble compounds from solution, while the two mechanisms before explain the interaction between cationic polymer and particulate matter.

In a real suspension, more than one of these mechanisms may be at work. In a recent study by Edzwald et al. (1987), to name only one example, partial removal of DOC (charge neutralization/precipitation) took place at the same time when turbidity was reduced (charge neutralization only). Nonionic and anionic polymers are generally available with higher molecular weights than cationic polymers. The cationic polymers, therefore, operate mostly by charge neutralization and charge neutralization/precipitation.

The mechanisms discussed are generally true for all polymer systems, and not only for synthetic polymers. Harris and Mitchell (1973) reviewed the role of polymers, synthetic and natural, in processes where microbial aggregation predominates. They demonstrated how diverse processes such as the bioflocculation of bacteria in an activated sludge waste treatment system, the formation of dental plaque, and the fermentation of yeast, all depend on particle aggregation induced by natural polymers.

Algal flocculation and filtration

Algal cells, as stated before, are relatively large and carry a negative surface charge. Interparticle bridging by cationic polymers is unlikely because of the large cell size; charge neutralization is a more likely mechanism. Quite a few studies have confirmed that anionic and nonionic polymers are indeed totally ineffective as the primary coagulant in algal suspension, even at high dosage, e.g., Cohen et al. (1958), Tenney et al. (1969), McGarry (1970), Tilton et al. (1972) and Sastry et al. (1977).

Cationic polymers have been demonstrated to have the ability to flocculate algal cells. Table 3 contains a brief summary of these studies. The unsuccessful experiment by Friedman (1977) is poorly documented and cannot be rationally explained with the available information. Volkova et al. (1982), found that their polymers lost almost all their flocculating effect if the cultures were allowed to age to the point where the algal cells were partly decomposed. In general, the attempts were successful, although the optimum polymer dosages were quite different in the different studies.

Two studies tested polymers with a range of molecular weights to find the polymer that would allow paper filtration of a fixed sample volume in the shortest possible time. Tilton et al. (1972) found this optimum at 21 kiloDalton (the upper end of their polymer range) and Volkova et al. (1982) at 60 kiloDalton (the intermediate weight of the three polymers they evaluated). For charge neutralization, the polymer charge density should be more important than the molecular weight, but

Study	Genus	Conc.	Polymer	Dosage	Remarks
Cohen et al. (1958)	<u>Chlorella</u>	8 million cells/mL	synthetic cationic	0-200 mg/L	above 120 mg/L >99% removal after settling
Golueke and Oswa (1965)	? 1d	?	PURIFLOC synthetic cationic	3-10 mg/L	95% removal at 3 mg/L after 1h settling
Golueke and Oswa (1965)	? ld	?	SONDELLITE synthetic cationic	2.5-4 mg/L	90% removal at 4 mg/L after 4h settling
Tenney et al. (1969)	mixed green algae	100-350 mg/L as SS	polyamine 5000 kiloDalton	0-1000 mg/L	linear relation be- tween optimum dosage and SS
Tilton et al. (1972)	<u>Chlorella</u>	50-3000 mg/L as SS	polyamine 0.8-21 kiloDalton	10 to 1000 mg/L	optimum dosage de- pends on polymer MW and SS
Friedman et al. (1977)	<u>Chlorella</u>	?	PURIFLOC synthetic cationic	?	no effective flocculation
Volkova et al. (1982)	<u>Microcystis</u> / <u>Aphanizomenon</u> mixture	2000-25000 mg/L as SS	polyamine 30-80 kiloDalton	1-10 mg/L	measured filtration rate through filter paper

١

Table 3.	Summary of	published	studies on	algal	floccu	lation	and
	filtration	with catio	onic polyme:	rs as	primary	coagul	.ant

.

.
the charge densities were not reported.

Flocculation behavior was not sensitive to pH in the range normally encountered in water treatment. Golueke and Oswald (1965) found no changes between pH 4 and pH 10, and Tilton et al. (1972) found no changes between pH 4 and pH 8. At extreme pH values, sudden changes were observed; Golueke and Oswald (1965) found that the flocculation abruptly ceased above pH 10.4, and Tenney et al. (1969) found maximum flocculation in the range pH 2 to pH 4, in the vicinity of the algal isoelectric point.

The optimum polymer dosage for the different studies varied considerably. Tenney et al. (1969) did establish a linear relationship between optimum dosage and algal concentration, at about 1 mg of polymer for every 80 mg of dry algal mass. Tilton et al. (1972), however, found the optimum polymer dosage to be much higher; 1 mg of polymer for every 5 - 10 mg of dry algal mass. When they compared their results with other studies on crystalline silica suspensions, they found that algae required about 200 times more polymer for effective flocculation than a silica suspension of equal surface area.

Optimal pretreatment for direct filtration

Direct filtration is characterized by the absence of any preceding solid/liquid separation processes such as sedimentation or flotation. The solid/liquid separation occurs upon passage through the granular filter media, and all the solids captured during a filter cycle have to be retained within the pores of the media bed. The capacity of a filter bed is, therefore, set by the <u>volume</u> of solids it can accumulate. If the solids are trapped in a loose, voluminous and flocculent structure, the filter capacity will be reached quickly; if the solids are deposited as a dense, compact aggregate, the bed will retain much more solids before it reaches its capacity.

The main process variables in the pretreatment system are the rapid mixing time and intensity at and immediately after the point of coagulant addition, and the slow mixing time and intensity for flocculation

following rapid mixing. No published studies on these parameters could be traced that focused specifically on algal separation with cationic polymers. A few studies did address the flocculation and filtration of other suspensions with cationic polymers, from which a number of general conclusions can be drawn.

Adin and Rebhun (1974) demonstrated the effectiveness of cationic polymers as primary coagulants in direct filtration, even at very high filtration rates (20 m/h) where other coagulants such as alum failed to produce filtrate of acceptable quality. They worked with a clay suspension and did not allow for any special mixing of the polymer other than the hydraulic mixing within the feed pipe. It was further demonstrated that the optimum dosage for regular jar tests was the same as the optimum dosage for direct filtration, and that slight over- or underdosage had less effect on direct filtration than on jar test performance.

There is convincing experimental evidence that vigorous rapid mixing improves the performance of cationic polymers. Morrow and Rausch (1974) found that cationic polymers, at a rapid mixing velocity gradient of 250 /s, were not as effective as alum. When higher mixing intensities were provided, polymer performance was excellent and just as good as alum. They consistently found, at three different pilot plant locations, that a minimum rapid mixing velocity gradient G of 400 /s was required for cationic polymers and that coagulation was complete within 2 minutes. No slow mixing period between rapid mixing and filtration was provided.

Stump and Novak (1977) tested a wide range of cationic polymers (molecular weight between 0.6 and 5,000 kiloDalton) with a kaolinite suspension, doing both settling and filtration tests. For the high molecular weight (HMW) polymers, settling was improved as the rapid mixing velocity gradient was increased from 100 /s to 750 /s, but for low molecular weight (LMW) polymers, practically no difference was detected over the same range of rapid mixing intensity. During filtration, increased rapid mixing decreased the HDR four times for HMW polymers, but very little for LMW polymers. There was almost no difference between a

rapid mix period of 30 seconds and 240 seconds, for both HMW and LMW polymers. Slow mixing affected the different polymers differently, but generally reduced the head loss development rate. The optimum slow mix time was between 10 and 20 minutes.

Yeh and Ghosh (1981) found cationic polymers with molecular weight between 10 and 100 kiloDalton most suitable for the direct filtration of a clay suspension. At higher molecular weight, excellent filtrate quality could still be achieved, but at the expense of excessively high head loss. Best filter performance was achieved at rapid mixing velocity gradients between 300 /s and 650 /s, with a rapid mixing time ranging from 3 to 8 minutes. They did not find it necessary to provide a period. of slow mixing. Their conclusions were echoed in a later set of practical design guidelines for polymer feed systems by Amirtharajah and Kawamura (1983).

Edzwald et al. (1987) conducted a filtration experiment with highly colored river water, where most of the solids load originated from the charge neutralization/precipitation of humic organic macromolecules. Two identical filters were used, with the exception that one filter was provided with a flocculation tank which provided a mixing intensity of G- 22 /s for a period of 9.2 min. Filtrate turbidity was about the same, but the flocculation caused much less head loss, and led to deeper floc penetration into the filter bed. It was speculated that the primary particles (that formed upon charge neutralization/precipitation) were very small and were deposited very quickly in the top of the bed by Brownian motion. Flocculation before filtration caused the particles to grow to the point where sedimentation was the most important transport mechanism; this led to deeper floc penetration.

The quoted studies generally agree that a period of intense rapid mixing greatly improves filtration performance, but these studies dealt with clay suspensions or suspensions with high DOC concentration. No study specifically addressed algal filtration. Clay particles have to grow from a primary particle size of less than 1 μ m to an average floc size of 20 μ m for effective filtration (Yeh and Ghosh, 1981), whereas a

<u>Chlorella</u> suspension, for example, starts of with a primary particle size of 4 μ m or more. it may be that less vigorous, or shorter rapid mixing will be adequate for algal suspensions.

Algal Release of EOM

Organic carbon cycling in natural waters

Algae are distinguished from other forms of plankton by their ability to photosynthesize, i.e., turning light energy and inorganic carbon into organic carbon compounds. They are, therefore, the primary producers upon which the entire aquatic food chain is based.

The continuous production of organic carbon leads to an organic carbon cycle with many different pathways. Organic carbon exists either in particulate form (POC), or in dissolved form (DOC). There is a continuous interchange between POC and DOC; living organisms ingest and excrete organic carbon, changing the character of the organic carbon with each metabolic cycle. Our understanding of these cycles in nature is confounded by the refractive (non-biodegradable) nature of some detrital particulates, the alternative aerobic or anaerobic metabolic pathways (which result in different end products), and the fact that all these processes are superimposed on the diurnal and seasonal cycles of temperature, light and water movement.

Algae do not convert all the photosynthate into new cell matter. Even during the active growth phase, a part of the photosynthate is released into the surrounding water as extracellular organic carbon (EOM). As algal populations age and senescent cells become more plentiful, the total EOM release rate increases. The EOM release rate, according to a summary by Lüsse et al. (1985), can be as low as 5% of the TOC synthesized for healthy cultures, or as high as 95% of the TOC for stressed cultures.

Algal EOM is a complex mixture of many different compounds and a complete analysis is out of the question. A fractionation of the EOM by

molecular weight is a relatively simple measure which is useful to characterize the EOM mixture. The significance of the molecular weight of synthetic organic polymers is well established in water treatment, and similar classification of algal EOM may provide a conceptual bridge to understand EOM effects on water treatment processes.

When the relative fractions of LMW and HMW compounds are examined in further paragraphs, the selective nature of bacterial nutrient uptake must be kept in mind. Simple, small organic molecules are a preferred bacterial food source, while large macromolecules are least likely to be metabolized. Furthermore, the bacterial utilization of algal EOM is very rapid. A water sample will, therefore, show a higher fraction of HMW EOM than the mixture originally released by the algae. Lüsse et al. (1985), for example, quoted a case where glucose was identified in the EOM of a bacteria-free culture of <u>Scenedesmus</u>, but where it could not be detected in the presence of bacteria.

The release of algal EOM

The release rate of algal EOM is to a large extent dependent on the age of the algal culture. Lüsse et al. (1985) tracked a number of non-axenic (i.e., not free from bacteria) large scale algal monocultures with time and found a consistent increase in the DOC of the centrifugate as the cultures passed from the logarithmic growth phase to the stationary growth phase. For <u>Chlorella</u>, the DOC increased from 2 to 15 mg/L, and for <u>Scenedesmus</u> from 5 to 15 mg/L.

The release of EOM by algae is not easily discernible, due to the nature of the algal cell wall. The composition of a typical cell wall, as described by Mackie and Preston (1974), is a composite construction of two distinctly different components. The structural integrity of the wall is due to a matted layer of microfibrils of cellulose, which are embedded in a mucilaginous, non-crystalline matrix of polysaccharides. The mucilage may be partially sloughed off or dispersed, in which case it becomes part of the EOM. It is difficult to determine at which point a compound is a part of the cell wall and at which point it becomes part of the EOM. Lüsse et al. (1985) pointed out that planktonic algae may have polysaccharidic microfilaments on their cell surfaces, which are vulnerable to the way the sample is handled. If the cells are separated from solution by membrane filtration, these filaments are sheared off and appear in the filtrate as EOM. If cell separation is done centrifugally, the filaments will remain part of the cell wall and will be measured as part of the biomass.

According to Hellebust (1974), algae release EOM through three major pathways. First, simple substances, such as sugars and amino acids, are simply released by diffusion through the cell wall. The process is driven by the concentration gradient across the cell wall and the release rate of individual compounds may be different due to the differential membrane permeability for different cell metabolites. Second, larger molecules, such as polysaccharides and proteins, are probably excreted by a more complex process. It is likely that some intracellular vesicles, which contain the macromolecules to be released, will fuse with the cell wall and eventually discharge the macromolecules as EOM. It was not stated how the compounds migrate through the cell wall. Third, the direct loss of the cell contents to the surrounding water will occur as the result of cell lysis. Cell lysis is prevalent during the stationary or declining growth phases, but EOM may also be released during reproduction when mature cells break open to release juvenile cells.

The nature of algal EOM

Wetzel (1983) categorized algal EOM into two main categories. The first category includes the <u>intermediate</u> products of algal metabolism, which are normally LMW compounds. The intermediate products of photosynthesis are mainly glycolic acid and polysaccharides (these compounds are ideal bacterial substrate); the intermediate products of respiration include organic acids, organic phosphates, and amino acids. The second main category of algal EOM consists of the <u>end</u> products of algal metabolism, which are mostly HMW compounds. The end products include carbohydrates, volatile compounds, peptides, and enzymes.

Hellebust (1974) and Bernhardt et al. (1986) provided limited information on the relative abundance of these compounds. The carbohydrate group, according to both studies, dominates the composition of the EOM - the sugars and alcohols make up more than half of the carbon. Hellebust added that the very simple LMW sugars and alcohols are present in small amounts, implying that most of the carbohydrates must have relatively complex structures. Bernhardt et al. reported that glycolic acid is the next most abundant group, comprising between 12% and 34% of the EOM. Hellebust also found that glycolic acid is the most abundant organic acid, but found it to be less than 10% of the total EOM. The nitrogenous compounds (amino acids and peptides) are very common in algal suspensions, but in smaller amounts (Bernhardt et al. found a maximum of 18%). Hellebust added that the percentage can be much higher in the EOM of blue-green algae, because they have the ability to fix their own organic nitrogen. Lipids are the last major constituent of algal EOM; both researchers agree that the percentage is around 10% of the total EOM. The other compounds, such as phenols, organic phosphates, volatile compounds, enzymes, vitamins and toxins, appear only in minute quantities. They are, however, not less significant; much of the nuisance value associated with algae is due to the tastes and odors produced by the volatile compounds, and the health hazards posed by the toxins produced by some of the blue-green algae.

Lüsse et al. (1985), Hoyer et al. (1985), and Bernhardt et al. (1985a) published complementary accounts of a study in Germany which was aimed at the characterization of EOM in non-axenic large-scale algal monocultures and its effects on flocculation and filtration. Centrifugate was collected at different growth phases and prefiltered through a 0.1 μ m membrane. The filtrate was then separated into HMW and LMW fractions, with the cutoff at about 2 kiloDalton. The MW distribution of the EOM from <u>Chlorella</u> and <u>Scenedesmus</u> was approximately the same. The largest size fraction dominated in both these genera. As the cultures aged, there was a gradual decline in the LMW fraction and a gradual increase in the HMW fraction. This trend was not always observed

for the other genera studied. A consistent trend was a gradual increase in the nitrogen:carbon ratio in the EOM as the cultures progressed from logarithmic growth to stationary growth; for <u>Chlorella</u> the ratio increased from 0.05 to 0.08, and for <u>Scenedesmus</u> from 0.07 to 0.11. The EOM was screened for the main monomeric components and the sugars dominated the EOM composition in all cases; for <u>Chlorella</u> and <u>Scenedesmus</u>, the average percentage of sugars was 15%. Their main conclusions on the nature of the EOM were threefold. First, the main functional groups in the mixture of compounds in EOM are the carboxyl and hydroxyl groups. Second, there are two major classes of compounds; neutral and acidic polysaccharides, and non-saccharidic acidic compounds similar to humic and fulvic acids. Third, the algal EOM is similar to an anionic polymer, i.e., it carries a net negative charge concentration.

EOM Effects on Algal Separation

Experimental evidence

Tenney et al. (1969) demonstrated how the algal growth phase influences the required polymer dosage for optimum flocculation. In their case, a mixture of green algae treated with a HMW polyamine, the required polymer dosage for a freshly inoculated batch culture was 1.7 mg/L. As the culture developed through the log growth phase, the required polymer dosage steadily decreased until it reached a minimum of 0.6 mg/L during the declining growth phase. At the end of the declining growth phase the required dosage shot up sharply to 1.5 mg/L and remained at that level during endogenous respiration. EOM was not specifically measured, but the increase of EOM with culture age is well documented and it is highly likely that the measured flocculation behavior was caused by the algal EOM.

Volkova et al. (1982), during their filtration and flotation tests on a mixed culture of <u>Aphanizomenon</u> and <u>Microcystis</u>, found that polymer treatment, which was normally quite effective, had practically no effect

if the culture aged to the point where "partly decomposed" algae were present.

Avnimelech et al. (1982) studied the mutual flocculation of algae and clay without any coagulants. Clay particles had a high affinity to cluster on the algal surface and this phenomenon was credited to the EOM which is present in high concentration at the algal cell surface. They went on to speculate that algal/clay flocculation in natural systems may be a population control mechanism whereby older algal cells are preferentially flocculated and sedimented because of their high EOM release rate.

Narkis and Rebhun (1983) reported on a study that was conducted in Israel over a period of years. In the first phase, flocculation tests were performed with mixtures of clay and humic acid. Humic acid, as shown earlier in this review, is similar to algal EOM in the sense that it is an anionic polymer of natural origin. The presence of humic acid added significantly to the dosage of cationic polymer for optimum flocculation. With clay alone, flocculation was observed at low polymer dosage. With humic acid alone, a colloidal precipitate was formed upon addition of the cationic polymer which was observed as turbidity. A stoichiometric relationship existed between optimum polymer dosage and humic acid concentration. After this experimental phase, they concluded;

"In the case of mineral clay suspension dispersed in humate or fulvate solution, the presence of soluble organic matter in the solution controls the behavior of this system. There is competition in the reaction with the flocculant between the soluble organic matter and the mineral clay particles in suspension. The cationic flocculant reacts preferentially with the organic matter. Only after complete reaction with the free humate or fulvate in solution does flocculation of clay mineral suspension begin."

In the second phase of their work, secondary effluent from the Haifa sewage treatment works was used. The secondary effluent was rich in organic material (mainly bacteriological EOM) with the chemical oxygen demand (COD) equal to 240 mg/L. The results corresponded closely with their earlier findings using clay and humic acid. The secondary effluent

required a very high dosage of 40 mg/L of cationic polymer. The effluent was then separated by paper filtration into a clear filtrate and the suspended solids. The clear filtrate, upon polymer addition, became turbid due to charge neutralization/precipitation and eventually flocculated at an optimum dosage of 40 mg/L. If the suspended solids, which were filtered out, were resuspended in organic-free tap water, it only required 2 mg/L of polymer for optimum flocculation. This work clearly showed that the polymer demand of an organic-rich water is practically independent of solids concentration, and almost entirely dependent on the organic content. The effects of the cationic polymer were insensitive to pH in the range pH 5 to pH 9. Non-ionic polymers alone had no flocculation effect.

Bernhardt et al. (1985a) conducted a very comprehensive sequence of flocculation/filtration experiments as part of a large German research project, on which seven papers have been published up to the present. Algal EOM was extracted and concentrated from different cultures at different points in their growth cycle, and added in controlled amounts to a quartz particle suspension. The suspension was then coagulated with ferric iron, flocculated and then filtered through small sand filters. Small differences were noted amongst the EOM mixtures from different species, but a few general trends were observed. First, algal EOM behaved like an anionic flocculation aid at low concentration (<1 mg C/L), and improved flocculation and filtration, as measured by a higher filtration coefficient and longer filter run time. Chlorella was the exception, where the improvement was not as prominent as the other species. Second, at higher levels of algal EOM (>1 mg C/1), algal EOM caused a disturbance of the flocculation and filtration process. Turbidity is insufficiently retained, floc breaks through the filter prematurely and coagulant appears in the filtrate. Third, the HMW fraction (> 2 kiloDalton) of the algal EOM exerted greater influence than the LMW fraction. Fourth, EOM from the late stationary phase exerted a greater influence than the EOM from the logarithmic growth phase. Fifth,

the EOM disturbance could be compensated for by increasing the ferric coagulant dosage.

In two follow-up papers, Bernhardt et al. (1985b) and Schell and Bernhardt (1986) dealt with the electrical charge concentration of the The algal EOM, being predominantly anionic polymers, carried algal EOM. a negative electrical charge which could be measured by titration with a cationic polymer of known charge density. With this technique they found that the EOM from blue-green algae had a charge concentration three times as high as the EOM from green algae, regardless of growth phase. The charge concentration is expressed as mg/L of cationic polymer per mg C/L of EOM. It was also demonstrated that the effects of algal EOM on flocculation and filtration could be mimicked by using commercially available products with similar structure as the main constituents of algal EOM. Alginic acid (a HMW carboxylic acid) and WISPROFLOC (a naturally-derived starch-based flocculation aid) were found to have similar effects on flocculation and filtration as the algal EOM. Nonionic polymers of low to medium molecular weight had practically no effect; neither did monomeric sugars and sugar alcohols.

EOM reaction mechanisms

Bernhardt et al. (1985b and 1986) presented a mechanistic explanation for the effects of algal EOM on ferric coagulant during flocculation and filtration. The explanation has three main parts. First, the algal EOM, although it consists mainly of anionic polymer, has the ability to attach to negatively charged particles. It was demonstrated that negatively charged quartz particles did increase their charge by as much as 50% (measured electrophoretically) when algal EOM was added to the solution. The attachment was presumed to be due to hydrogen and covalent bonding according to the electrostatic patch theory. Second, at low EOM concentration, the EOM polymers are attached to the quartz particles. As the particles are destabilized by the polynuclear hydroxo complexes, the EOM acts as a flocculation aid by bridging the distance between adjacent particles. Third, at high EOM

concentration, some of the EOM will be in solution and will react very quickly with the positively charged hydroxo complexes and iron hydroxides that form upon addition of the ferric salt. In this way, the further agglomeration of the hydroxo complexes is inhibited, as well as the electrostatic attraction to the quartz particles. The EOM/iron complexes so formed are colloidal in nature, break through the filter and increase the turbidity and residual iron content of the filtrate.

Chlorine Interaction with Algae

Prechlorination, during the past fifty years, has been touted as an efficient way to alleviate the operational problems associated with algae in water treatment. More recently, prechlorination of surface water has been curbed due to the discovery of halogenated organic compounds of which some are carcinogenic to man. Much emphasis is presently being placed on alternative disinfectants. This review nevertheless focuses on prechlorination for three reasons. First, its effects on algal filtration have not been quantitatively assessed for controlled algal suspensions. Second, the mechanisms whereby chlorine acts on algal suspensions are still poorly understood. Third, if chlorine does indeed offer a powerful chemical method of algal control during direct filtration, it could still be used without harm, if followed by proper post-treatment processes such as air stripping or carbon adsorption.

Chlorine chemistry

Chlorine is commonly added to water in elemental gaseous form or as a liquid hypochlorite solution:

4

These hydrolysis reactions proceed very rapidly and are complete within seconds, with practically all the chlorine or bleach converted to hypochlorous acid. Although both the elemental and hypochlorite forms produce hypochlorous acid, they tend to drive the pH in opposite directions, because reaction (1) produces protons, and reaction (2) consumes protons.

The hypochlorous acid rapidly dissociates and establishes an equilibrium with hypochlorite:

HOC1 ---->
$$H^{+}$$
 + OC1 (3)

Hypochlorous acid and hypochlorite are measured and reported together as free chlorine. Morris (1966a) determined the ionization constant of reaction (3) between 5 and 35 degrees Celsius as:

$$pK_{a} = -10.0686 + 0.0253*T + 3000/T$$
(4)

with T measured in degrees Kelvin. Above pH 9, practically all the chlorine will be in the hypochlorite form, and below pH 6 practically all the chlorine will be hypochlorous acid. Hypochlorous acid, on the basis of mass applied, is a more efficient disinfectant than the hypochlorite ion. Morris (1966b) presented data which showed that the hypochlorite concentration (expressed as chlorine) required for a 99% kill of enteric bacteria, viruses, bacterial cysts and bacterial spores, was about 100 times higher than the required hypochlorous acid concentration (expressed as chlorine). The kill was measured after 10 minutes at 5 degrees Celsius.

The presence of ammonia triggers a chain of reactions between the chlorine, ammonia and intermediate products. A common, simplified reaction scheme is given by Benefield et al. (1982). Ammonia will first react with hypochlorous acid to form monochloramine:

$$\frac{NH}{3} + HOC1 \qquad \cdots > NH_2C1 + H_2O \qquad (5)$$

Once the monochloramine is formed, it will react with more hypochlorous acid to be converted to dichloramine:

$$\frac{\text{NH}_{2}\text{Cl} + \text{HOCl}}{2} + \frac{\text{H}_{0}}{2}$$
(6)

The availability of more hypochlorous acid will react with the dichloramine to form either nitrogen trichloride or nitrogen gas:

If enough hypochlorous acid is added, the monochloramine will all be eventually converted to dichloramine, while the dichloramine will be consumed through reactions (7) and (8). Once all the mono- and dichloramines have disappeared, additionally added chlorine will remain as free chlorine. The addition of chlorine in excess of that required for the removal of the mono- and dichloramines, is known as breakpoint chlorination, with the breakpoint at the point of minimum chloramine concentration.

Reactions (1) through (3) are practically instantaneous, but reactions (5) through (8) are relatively slow and may need tens of minutes before equilibrium (Cleasby, 1985). The chloramines have less disinfecting ability than free chlorine, but persist longer in water than free chlorine.

The presence of organic nitrogen, rather than the chemically simpler ammonia nitrogen, complicates the outcome of chlorination considerably. White (1968) stated two main differences between the chlorination of organic nitrogen and ammonia. First, with organic nitrogen, there is not as sharp a decrease in chloramines before the breakpoint. Second, the reaction kinetics associated with organic nitrogen are markedly slower. Reactions with ammonia are practically complete after an hour, but reactions with organic nitrogen may need days for completion. Taras (1953) did extensive testing on a range of individual nitrogenous compounds which may be present in natural water. A total of 31 compounds were chlorinated, ranging from simple amino acids to complex polypeptides and proteins. Chlorine dosage for each compound was such that a free chlorine residual of at least 0.5 mg/L was measured after 24 hours. Although the compounds behaved quite differently, certain general trends were evident. The simpler amino acids showed a total nitrogen reduction of more than 50% after 24 hours, while the polypeptides and proteins showed a total nitrogen reduction of less than 20%, or even below 10%, after 24 hours. Under comparable conditions, ammonia lost more than 90% of its nitrogen.

Chlorine effects on algal cells

The effects of chlorine on <u>bacterial</u> cells were first investigated in the 1940s. Scientists, prior to that, were perplexed by two aspects of chlorine behavior; its bactericidal efficiency at low concentration, and the failure of other strong oxidants to kill bacteria with the same efficiency.

Green and Stumpf (1946), through painstaking experimentation, provided the first answer by showing that chlorine did not destroy the bacteria by complete oxidation, but by the selective destruction of the intracellular enzyme triophosphate dehydrogenase. (Triophosphate dehydrogenase is a key enzyme for metabolizing glucose.) Other oxidants, however, could destroy this enzyme equally well if it was isolated outside living cells. Chlorine, therefore, had to have a superior ability to penetrate the bacterial cell wall. Fair et al. (1948), then demonstrated that hypochlorous acid is the most effective bactericide of the different chlorine species, and attributed the penetrating ability of chlorine to the electroneutrality of the hypochlorous molecule and its small molecular size.

The action of chlorine on <u>algal</u> cells has not been clearly defined. Griffin (1947) speculated that the algicidal properties of chlorine may be partly due to the fact that free ammonia, which is an important algal

ς.

food source, is oxidized in the presence of chlorine. Algae would, therefore, eventually be starved to death. This theory must be seriously questioned, because such a starvation effect would only be operational in the absence of nitrates (an alternative nitrogen source). Even if such an unlikely event would occur, starvation would be of no consequence in the short time frame offered by conventional treatment.

Ives (1956) studied the electrophoretic characteristics of a number of algal genera, and how they were affected by a number of algicides. Although chlorine was not used, he did use ozone (a strong bxidant) and iodine (a halogen). The negative surface charge of the algal cells was marginally increased in both cases, but not enough to change their physical behavior.

The concept of cell lysis upon chlorination is mentioned in many studies dealing with algal chlorination. It does offer a plausible reason for the release of EOM upon chlorination, which will be discussed shortly. Only two studies specifically reported on the physical condition of the cells after chlorination, with conflicting results. Kott (1971), using light microscopy, unequivocally denied any observable change in algal cell numbers or condition during the first two hours following chlorination, whether the chlorine is present in free or Sukenik et al. (1987) recently published scanning combined form. electronmicrographs of Scenedesmus cells before and after treatment with chlorine, ozone and chlorine dioxide. In all three cases, the cells were visibly damaged. Chlorine caused a shrivelling of the outer sheath (the reticulate layer) and in some cases leakage of the intracellular contents through the cell wall could be observed. (Chlorine dioxide, incidentally, showed a similar, but more severe effect, whereas ozone did not shrivel the reticulate layer, but gave it a perforated and fibrous appearance.)

Chlorination of algal suspensions

Echelberger et al. (1971) performed a series of chlorination experiments on algal cells from a laboratory culture of mixed green

algae. They worked only with the cells, and not with the EOM. The cells were centrifuged from the culture and resuspended in organic-free water. A number of key points were established. First, the suspension showed a typical breakpoint curve like that obtained in the presence of ammonia, which emphasized the importance of the reaction between chlorine and the nitrogenous groups on the algal cell wall. Second, there was a linear relationship between the chorine dose to obtain a given free chlorine residual after a given time, and the algal concentration, measured as suspended solids. Third, the free chlorine residual steadily decreased with time, even after 3 hours had elapsed. This slow rate of decrease suggests that the nitrogenous groups on the algal cell wall are complex macromolecules which are not readily susceptible to oxidation. Fourth, it was demonstrated that the filtrate of a suspension with a free chlorine residual, had a higher chemical oxygen demand than an unchlorinated control; the chlorine, therefore, induced a release of additional EOM. Fifth, they demonstrated that the EOM released upon chlorination caused significant flocculation and settling when compared to an unchlorinated control.

Kott (1971) measured the residual chlorine levels in a variety of sewage effluent samples. All samples were spiked with 3 million cells/mL of <u>Chlorella</u>. He found that the residual chlorine after five minutes of contact was only slightly higher than after 6 hours. At a chlorine dosage of 14 mg/L, for example, the average residual chlorine was 5.0 after 5 minutes, and 4.0 mg/L after 6 hours. Not enough detail is given to allow a thorough comparison, but this finding seems to contradict the results of Echelberger et al. (1971) which indicated a slow, gradual reaction between chlorine and organic nitrogen. Kott's second finding was that the algal numbers in laboratory cultures, as well as pond effluents, stayed unchanged for 2 hours after chlorination; regardless of the chlorine dosage and whether the chlorine is in free or combined form. After 2 hours, the number of healthy cells started to decline.

Hom (1972) collected sewage pond effluent which contained 2.6 million cells/mL of <u>Chlorella</u>, and chlorinated a number of subsamples.

After the required contact time, which was the main experimental variable, the samples were dechlorinated and analyzed for BOD. He found that the BOD increased as the chlorine contact time increased, up to a maximum BOD after 20 minutes of chlorine contact time. Thereafter, it decreased again and stabilized after about 60 minutes at a level which is higher than the original BOD before chlorination. For example; a chlorine dosage of 32 mg/L increased the initial BOD of 20 mg/L to 100 mg/L after 20 minutes, after which the BOD decreased again to about 55 mg/L. Hom speculated that the chlorine somehow elicited a rapid release of easily oxidizable organics, and that the organics were oxidized soon after release. This is an important finding, for it shows a short-lived transient effect which will probably be missed in full-scale experimentation.

Wight et al. (1978) experimented with a series of sewage lagoons in Illinois in which <u>Chlorella</u> was present at about 2.6 million cells/mL. Despite their own earlier laboratory experiments, in which they clearly showed an increase in soluble chemical oxygen demand when the chlorine dosage and/or contact time was increased, they could not demonstrate these trends at a statistically significant level in their field experiments. When they re-analyzed only those data points which showed a free chlorine residual, they did, however, demonstrate these trends. The trends were most obvious when the free chlorine residual was above 1.8 mg/L. Their conclusion was that an EOM increase is probably due to the action of free residual chlorine only.

Sukenik et al. (1987) also demonstrated an increase of DOC after chlorination. After 10 minutes of chlorine contact time, the DOC concentration increased by 5%, 20% and 15% for chlorine dosages of 2, 10 and 20 mg/L respectively.

Effects of prechlorination on treatment processes

Sukenik et al. (1987) measured the effects of chlorination on the alum dosage required for the flocculation of <u>Scenedesmus</u>. At a chlorine dosage of 2 mg/L, the required alum dosage was the same as for the

unchlorinated sample, but at a higher chlorine dosage more alum was required to obtain the same degree of flocculation. To remove 50% of the cells by settling after 30 minutes, 55 mg/L of alum was required if 20 mg/L of chlorine was added, while 45 mg/L of alum was required in the absence of chlorine.

There are a few reports in the literature on the effects of prechlorination on the performance of <u>slow</u> sand filters. There are fundamental differences in the principal removal mechanisms between slow and rapid sand filters; at the same time, the two processes induce similar physical interaction between sand grains and suspended particles, and do share a lot of common ground. The following two reports on slow sand filtration should give some qualitative indication of probable chlorine effects in rapid sand filtration.

Jacobsen and Wellington (1949) reported a series of experiments with one slow sand filter being treated with chlorine while another was monitored as an untreated control. Chlorination started at 2.0 mg/L and was gradually increased until it reached 6.0 mg/L at the end of the run. The filtrate production of the chlorinated filter before terminal head loss was 72% higher than for the untreated control. Microscopic analysis of sand samples showed a great diversity of organisms and slimy deposits within the grain pores for the control filter, and a much cleaner sample with only one motile species for the chlorinated filter. There were no noticeable effects on the taste, odor and appearance of the water, but the chlorine led to a definite improvement in bacteriological quality. During the discussion of this paper, two participants shared their own experience of prechlorinating slow sand filters; both found increased filtrate production due to chlorination, in the one case it was more than doubled.

Ludwig (1961) measured the effect of prechlorination on two experimental slow sand filters. A number of beneficial effects were attributed to prechlorination; longer filter run length, lower effluent turbidity (an average of 2.04 NTU vs. an average of 2.41 NTU), less penetration of organic solids into the bed (10 to 20 mm deep vs. 50 to

60 mm), and no ammonia in the filtrate. This study concluded that prechlorination, coupled with slow sand filtration, is an excellent treatment method for small water supply systems.

A few early incidents of chlorination prior to <u>rapid</u> sand filtration had been reported, and they were also positive. Whitener (1928) described an experience where chlorination of the raw water supply had no measurable results on subsequent treatment, but when chlorine was added just prior to filtration (the settled water had only 5 units of turbidity), the results were dramatic. The final water appearance changed within hours from "cloudy green" to "sparkling clear", the average filter run length increased from 25 to 80 hours, and even filter cracks of 50 to 70 mm eventually disappeared.

Raab (1931) reported a severe odor problem in the Minneapolis water supply due to an <u>Aphanizomenon</u> bloom in the Mississippi River. The combined application of chlorine and ammonia to the raw water caused no improvement, with chlorine dosage up to 2.0 mg/L and the chlorine: ammonia ratio between 2:1 and 5:1. The ammonia dosage was then stopped, and the situation improved immediately. At an eventual chlorine dosage of 2.2 mg/L, the free chlorine residual going to the filters was about 0.2 mg/L, and the average filter run length improved from 8 to 28 hours.

Streeter and Wright (1931), during their full-scale experimentation, did not measure any improvement in filter run length upon chlorination, but still advocated prechlorination of the raw water due to the much improved performance of the filters in terms of bacterial removal.

Janssens et al. (1985), during pilot-scale filtration of water from the river Meuse in Belgium, clearly demonstrated the beneficial effect of chlorine on filtrate quality. A metal salt was used as primary coagulant, supplemented by a polymeric filtration aid. When prechlorination was stopped for 3 hours in the middle of a filter run, the filtrate turbidity shot up from 0.20 NTU to 0.38 NTU, and dropped back to 0.17 NTU after resumption of prechlorination. (Ozone, incidentally, improved turbidity removal in the same fashion.)

Chlorine has some indirect beneficial effects on treatment processes which also warrant brief attention. Ibrahim et al. (1982) documented the problems posed by algal growths in the warm climate of Lebanon during spring and summer. Algal growths were sloughed off the sides of tanks and canals, and eventually reached the filter beds, where they rapidly blocked the passage of water. They found that a total chlorine residual of 0.7 to 0.8 mg/L within the treatment units prevented all algal growths. The reduction of total residual chlorine with time was experimentally measured on a mixed suspension of green algae (about 0.1 million cells/mL); a total chlorine residual of 1.2 mg/l immediately after dosing decreased to about 1.0 mg/L after 30 minutes, and eventually to about 0.25 mg/L after 24 hours. The minimum lethal residual was measured for 13 isolated species (also at about 0.1 million cells/mL); in all cases, the total chlorine residual required for total disappearance in 10 days, was less than 1.8 mg/L. For <u>Chlorella</u> and <u>Scenedesmus</u>, the critical residual was 1.4 to 1.5 mg/L.

Mathematical Modeling of Deep Bed Filtration

The final part of this review will briefly address the mathematical modeling of deep bed filtration. Filtration theory serves two main purposes. First, it offers a mechanistic understanding of the processes at work within the pores of a sand bed. Second, it can be used to reduce head loss and particle removal data to more fundamental parameters which are better suited for quantitative comparison.

An efficient deep bed filter exhibits two macroscopic properties. First, it traps a significant fraction of the suspended particles within the filter pores as the suspension flows through the filter bed. Second, it causes a slow, gradual increase in head loss as the interstitial pores are clogged by the trapped particles.

These two properties are equally important. Excellent particle removal is impractical if the bed must be backwashed at short intervals;

conversely, slow clogging means little if particle removal is poor. The observation of both head loss development and particle removal is, therefore, an essential part of deep bed filter evaluation. Both head loss development and particle removal are, however, only consequences of the same process; the clogging of the interstitial pores.

The aim of mathematical modeling is to relate head loss development and particle removal to the specific deposit, i.e., the fraction of the total bed volume occupied by the trapped particulates. A host of mathematical models, reflecting fundamentally different approaches, have been proposed during the past 25 years, and there is no common consensus yet as to which ones are more realistic.

Mathematical modeling: particle removal

Two fundamental, as yet unchallenged, assumptions are common to all modeling efforts. The first, conservation of particle volume, leads to the simplified equation:

 $-\frac{\delta C}{\delta L} = \frac{1}{v} \cdot \frac{\delta \sigma}{\delta t}$ (1) with v = hydraulic loading, or approach velocity t = time $\sigma =$ specific deposit C = particle volume concentration L = bed depth, in the direction of flow.

The specific deposit σ , as defined here, does not take any bulking of the deposited particles into account. In reality, the particles will bulk as they are trapped in the bed. The <u>volume occupied</u> in the filter bed by the deposited particles is obtained by multiplying the specific deposit σ by the bulking factor β .

The second assumption postulates first-order kinetics of deposition as the suspension flows through the bed:

$$-\frac{\delta C}{\delta L} = \lambda C$$
(2)
with λ - filtration coefficient.

As filtration proceeds, the filtration coefficient is changed due to the specific deposit. At this point, there is considerable disagreement as to the nature of the $\lambda = f(\sigma)$ function, and many relationships have been proposed. Ives (1985) proposed the following relationship:

$$\lambda = \lambda_0 \cdot \left[1 + \frac{B\beta\sigma}{\epsilon_0}\right] \cdot \left[1 - \frac{\beta\sigma}{\epsilon_0}\right] \cdot \left[1 - \frac{\sigma}{\sigma_1}\right]$$
(3)

with x,y,z = exponents

 σ - the ultimate specific deposit, at which point no more u particles are deposited

 ϵ = initial clean bed porosity

- β = bulking factor of the incoming particles upon deposition in the bed
- λ_{-} = initial filter coefficient

 \tilde{B} = ripening coefficient.

The ultimate specific deposit is also defined as the volume that would have been occupied if the removed particles did not bulk at all. The product of the bulking factor and the ultimate specific deposit is, therefore, theoretically limited by the clean bed porosity. In practice, this product will be less than the clean bed porosity.

The Ives model is the most general and flexible available and will accommodate a number of other models with appropriate choice of the exponents x, y and z. It is mathematically consistent and satisfies all the boundary conditions imposed by the physical nature of a deep bed filter. The model is derived from plausible assumptions and the model parameters, exponents excluded, have physical meaning. The first bracketed factor in the above equation accounts for an increase in removal efficiency during the initial stages of a filtration cycle (the "ripening" phenomenon). The second bracketed factor accounts for a decrease in removal efficiency as the media surface area is reduced by the filling of the media pores with specific deposit. The third bracketed factor decreases the filtration efficiency as the interstitial deposit approaches the ultimate deposit.

Mathematical modeling: head loss

The equation for flow through porous media is expressed by the Carman-Kozeny expression (Sakthivadivel et al., 1972):

$$\frac{H}{L} - K. \frac{v\nu S^2}{g} \cdot \left(\frac{L'}{L}\right)^2 \cdot \frac{(1-\epsilon_0)^2}{\epsilon_0^3}$$
(4)

with v = hydraulic loading, or approach velocity

- S specific surface area of the media, i.e., the media surface area divided by the volume of the media grains
- ν kinematic viscosity
- g = gravitational acceleration
- H = head loss
- L = media bed depth
- L' = length of flow path through the pores
- K Karman shape factor

This equation follows from the general Carman equation when appropriate substitions are made for the hydraulic radius of granular media, and for the fact that the sinuous flow path through the media pores is longer than the linear depth of the media bed. As the media bed begins to clog, the specific area, flow path length, bed porosity and head loss all change with time. If the Carman-Kozeny equation (4) is set up for the initial conditions (time = 0), and again after a random time step (time = t), the following head loss ratio is obtained:

$$\frac{H_{t}}{H_{o}} = \left[\frac{K_{t}}{K_{o}}\right] \cdot \left[\frac{S_{t}}{S_{o}}\right]^{2} \cdot \left[\frac{L'}{L'_{o}}\right]^{2} \cdot \left[\frac{1-\epsilon}{1-\epsilon_{o}}\right]^{2} \cdot \left[\frac{\epsilon}{\epsilon_{o}}\right]^{3}$$
(5)

With
$$\epsilon = \epsilon - \beta \sigma$$
, equation (5) becomes:
t o

$$\frac{H_{t}}{H_{o}} = \left[\frac{K_{t}}{K_{o}}\right] \cdot \left[\frac{S_{t}}{S_{o}}\right]^{2} \cdot \left[\frac{L'}{L'_{o}}\right]^{2} \cdot \left[\frac{1-\epsilon_{o}}{1-\epsilon_{o}}\right]^{2} \cdot \left[\frac{\epsilon_{o}}{\epsilon_{o}}\right]^{3}$$
(6)

Equation (6) is a fundamentally correct, but impractical expression, because most of the variables are not measurable. A number of greatly simplified, semi-empirical equations have, therefore, been proposed for practical use. The most prominent of these expressions have been reviewed by Sakthivadivel et al. (1972). An empirical expression by Deb (1969), for example, has been successfully used for modeling purposes:

$$\frac{H_{t}}{H_{o}} = [1 + 3.2(1 - 10^{-13.3\sigma})] \cdot [\frac{\epsilon}{\epsilon_{o}} - \frac{\sigma}{\beta\sigma}]$$
(7)

In equation (7), the first four bracketed factors in equation (6) have been replaced by an empirical function of the specific deposit.

Numerical solution of filtration equations

If the partial derivative of concentration over time is eliminated from equation (1) and equation (2), and equation (3) substituted for the filtration coefficient, the following is obtained, with x - y - z - 1:

$$\frac{\delta\sigma}{\delta t} = v.C.\lambda_{o} \cdot \left[1 + \frac{B\beta\sigma}{\epsilon_{o}}\right] \cdot \left[1 - \frac{\beta\sigma}{\epsilon_{o}}\right] \cdot \left[1 - \frac{\sigma}{\sigma_{u}}\right]$$
(8)

This is a classical initial value problem of the form $\sigma' = f(\sigma)$. It can be numerically solved in any of a number of ways. A standard Runge-Kutta textbook method, for example, described by Scheid (1968), leads to:

$$\sigma_{t+1} = \sigma_{t} + (k_{1} + 2k_{2} + 2k_{3} + k_{4}) / 6$$
(9)
with $k = \delta t \cdot f(\sigma)$
 $k = \delta t \cdot f(\sigma + k_{1}/2)$
 $k_{2} = \delta t \cdot f(\sigma + k_{1}/2)$
 $k_{3} = \delta t \cdot f(\sigma + k_{2}/2)$
 $k_{4} = \delta t \cdot f(\sigma + k_{3})$

With the specific deposit and incoming volume concentration known at the beginning of a time step, the specific deposit at the end of the time step can be calculated with equation (9) provided that v, C , B, λ , β and σ are constant for a specific filtration cycle.

A boundary condition exists at the top of the bed, where the incoming particle volume concentration remains constant. Another set of initial values are obtained at time zero when the filter coefficient has not yet been altered by the specific deposit. The reduction in particle volume concentration for the first slug of suspension passing through the bed, is readily calculated.

For calculation purposes, the media bed is treated as a series of discrete layers; likewise, the filtration cycle is divided into a number of discrete time steps. The mathematical solution proceeds from the top of the media bed to the bottom, and from time zero to the end of the cycle. The calculation sequence was first explicitly formulated by Ives (1960), and later more elaborately by Adin (1978).

MATERIALS, METHODS AND EQUIPMENT

Algal Cultures

Algal monocultures were obtained from the Culture Collection of Algae at the University of Texas at Austin. Three genera were eventually selected because they could be consistently cultured at reasonably high concentrations. The genera were <u>Chlorella pyrenoidosa</u> (UTEX 1230), <u>Scenedesmus quadricauda</u> (UTEX 76) and <u>Anabaena flos-aquae</u> (UTEX 1444).

One culture medium was used throughout the project for all the algal genera, i.e., the "WC" medium described by Guillard (1975). The nutrient composition is shown in Table 4, and the ionic concentrations in Table 5. Suspension was drawn from the growth reactors at regular intervals, and the reactors were immediately filled back up with fresh culture medium. A maximum quantity of 20 L was drawn from the 50 L growth reactors at the time. The average dilution rate was maintained at approximately 0.1 /d throughout the study; the reactor volume was, therefore, effectively replaced about every ten days.

The large rectangular reactors (which were used for practically the entire project), were constructed from 5.5 mm Plexiglass sheets with a total capacity of 50 L each. The reactors were 460 mm long by 300 mm wide by 450 mm high. Fresh nutrient was fed on the surface and suspension was drawn from a side outlet just above the reactor floor. Each reactor was capped with a wooden cover onto which an electrical mixer was mounted. The mixer powered a three-bladed paddle at about 150 to 200 rpm to keep the cultures well mixed and suspended.

The reactors were housed in a continuously lighted growth chamber. Light was supplied with twelve fluorescent 30 Watt tubes mounted vertically on the sides and back of the chamber. Six WARM WHITE tubes were alternated with six COOL WHITE tubes to supply a broader frequency spectrum. The measured light intensity on the sides and back of the reactors was 150 μ E/m .s (microEinstein per square meter per second).

Reagent	Concentration
CaCl ₂ .6H ₂ 0	36.8 mg/L
MgS0 ₄ .7H ₂ 0	37.0 mg/L
NaHCO3	12.6 mg/L
к ₂ нро ₄	8.71 mg/L
NaNO3	85.0 mg/L
H ₃ BO ₃	6.0 mg/L
THAM ^a	250 mg/L
HCl	147 mL/L
Biotin	0.5 µg/L
Vitamin B12	0.5 µg/L
Thiamine HCl	100 µg/L
CuSO ₄ .5H ₂ 0	0.098 [.] µg/L
ZnS0 ₄ .7H ₂ 0	0.22 µg/L
CoCl ₂ .6H ₂ O	0.10 µg/L
MnCl ₂ .4H ₂ O	1.8 µg/L
Na ₂ MoO ₄ .2H ₂ O	0.063 µg/L
FeCl ₃ .6H ₂ 0	3.15 mg/L
Na ₂ EDTA ^b	4.36 mg/L

Table 4. Composition of culture medium WC (from Guillard, 1975)

^aTris (hydroxymethyl) aminomethane.

^bEthylenediamine tetraacetic acid.

Cation/anion	Molar concentration		
Na	0.00135 mol/L		
K	0.00010 mol/L		
Са	0.00025 mol/L		
Mg	0.00015 mol/L		
NO	0.00100 mol/L		
C1 ³	0.00050 mol/L		
CO,	0.00015 mol/L		
so ₄ ³	0.00015 mol/L		
Ionic strength = 0.0029 mol/L			

Table 5.	Concentrati	on of principal.	. cations	and anions	in culture
	medium WC	(adapted from G	Guillard,	1975)	

Table 6. Concentration of principal cations and anions in typical algal suspension applied to sand filtration system

Cation/anion	Mass concentration	Molar concentration
K Na Mg Ca	2.34 mg/L 16.9 mg/L 6.69 mg/L 45.3 mg/L	0.00006 mol/L 0.00073 mol/L 0.00028 mol/L 0.00113 mol/L
$\frac{HCO_3}{SO_4}$ NO ₃ + Cl ^a	33.2 mg/L 76.7 mg/L	0.00054 mol/L 0.00080 mol/L 0.00086 mol/L
Ionic strength -	0.0055 mol/L	

 $^{\rm A}{\rm NO}_{3}$ and Cl not analyzed. Molar concentration estimated from electrical charge balance.

The front of the reactors received only the reflected light from the inside of the front cover - the minimum light intensity on the front of the reactors was 50 μ E/m .s.

Cooling was supplied by a simple household three-speed box fan mounted horizontally on top of the growth chamber which forced ambient air from the top through the chamber. It was set at the slowest speed and ran continuously. The temperature within the large reactors stabilized at about 26 degrees Celsius. Figure 1 shows a schematic layout of the growth reactors, lighting and ventilation.

The algal suspension used for filtration experiments, after being drawn from a reactor, was diluted with tap water in a large 100 L feed tank and continuously stirred until, and for the duration of the filter runs at about 150 to 200 rpm.

Reagents

Deionized water was used for making up the algal culture medium and for dissolving and diluting all reagents and chemicals. It starts out as steam condensate from the university heating system and is piped to the laboratory, where it is run through a cationic exchange bed, an anionic exchange bed and a bed of activated carbon, consecutively.

Ames tap water was used for the dilution of the algal suspension. The typical analysis for the principal ions in the tap water/algal culture mixture is shown in Table 6.

Chlorine was obtained from commercial CHLOROX bleach. The active ingredient, sodium hypochlorite, was determined and found to be equivalent to 47,500 mg/L as chlorine, slightly lower than the stated value on the label. Fresh dilutions with concentrations of 1000 mg/L or 2000 mg/L were prepared every day or two.

Aluminum sulfate stock solution (0.5 M) was prepared from reagent grade granular aluminum sulfate. At regular intervals, the stock solution was diluted down to a working solution of 1000 mg Al/L.



(front lid, reactor supports and light tubes on back wall not shown)



Ferric chloride stock solution (1.0 M) was prepared from reagent grade ferric chloride lumps and acidified with 10 mL hydrochloric acid per liter. At regular intervals, the stock solution was diluted down to a working solution of 1000 mg Fe/L.

Three commercial cationic polymers were used during different phases of the research. CATFLOC T was obtained from the Calgon Corporation Pittsburgh, Pennsylvania), and MAGNIFLOC 572C and 573C from the American Cyanamid Company (Indianapolis, Indiana). Fresh stock solutions were made every day or two with concentrations ranging from 1000 mg/L to 4550 mg/L and stored in the dark. During the early phase of the research, stock solutions of the cationic polymers were kept for up to a few weeks at a time, but extended storage was abolished after some aging effects were suspected.

Jar Testing

Jar tests were performed in 1 L glass beakers with a PHIPPS AND BIRD six-place stirring apparatus, equipped with a light table, from the Phipps and Bird Company (Richmond, Virginia).

Chemicals were injected with plastic syringes through stainless steel needles. The needle tips were held close to the top of the mixing paddles in the middle of the beakers and the syringe contents was rapidly discharged.

Samples were drawn from the beakers with a large-bore steel needle and a plastic syringe. The samples were slowly drawn, and the tip of the needle was held about one-third from the top of the liquid surface.

The mixing and settling routines were different for different jar tests and are described later with the jar test results.

Sand Filtration System

Figure 2 shows a schematic arrangement of the filtration apparatus. Only one of two parallel filtration trains is shown.



Figure 2. Schematic arrangement of sand filtration system (only one of two parallel systems shown)

The raw water suspension was prepared in a plastic tank, 440 mm in diameter and 700 mm high, with a working capacity of about 100 L. This tank was common to both filtration trains. Two parallel streams of suspension were withdrawn with a MASTERFLEX peristaltic pump from the Cole-Parmer Instrument Company (Chicago, Illinois), equipped with two #18 pumping heads. The pumping rate was maintained at approximately 45 to 50 mL/min/filter. Pumping rates were constant for any single filter run, but variations in flow rate between runs were due to an insensitive speed controller which could not be set at exactly the same position from run to run.

Chemical feed solutions were kept in 1000 ml and 500 mL measuring cylinders, and pumped directly from there with another MASTERFLEX pump equipped with four #14 pumping heads. Feed solution concentrations were calculated for each run to enable a constant dosing rate of about 1.1 mL/min for each of the dosing streams. Feed solutions were prepared from undiluted CHLOROX and from 1000 mg/L working solutions of Fe, A1 and polymer.

Raw water flow and chemical feed rates were determined volumetrically. Total flow rates were measured with a spot measurement during the run at the discharge point, and chemical feed rates were calculated from the volume of chemical pumped during the entire filter run.

Filter sand was supplied by the Northern Gravel Company (Muscatine, Iowa). A subsample of the shipment was separated by mechanical sieving. The sand fraction remaining between the 0.701 mm and 0.833 mm sieves was used in this project. The geometric mean sand grain diameter was 0.771 mm. The filter tube diameter was 27 mm, or about 35 times the mean grain diameter. The sand was supported on a stainless steel screen. Bed depths of 100 mm to 250 mm were used.

The filter head loss was measured as the difference in water level between two tubes - one coming from the upstream end of the filter, and the other from the downstream end of the filter. Samples could be collected at three points during the filtration process - directly from

the raw water tank (prior to chemical addition), at the hydraulic break directly before the filters (but after chemical addition and contact), and at the discharge point after filtration.

After every filter run, the filter tubes were disconnected and the filter sand emptied into a beaker. The sand was vigorously stirred with a glass rod and rinsed until clean, and then oven-dried for at least 12 hours at 103 degrees Celsius. After drying, the right amount of sand was weighed, put back into the tubes and tapped until the exact required bed depth was reached. In this way, the clean bed porosity could be maintained at 0.40.

The retention time in the different parts of the filtration train could be varied by changing the glass tubes which acted as the primary and secondary contact chambers.

Molecular Weight Fractionation

Samples of algal EOM, cationic polymer and tap water were separated into different molecular weight fractions by ultrafiltration. Ultrafiltration, in general terms, is a process whereby a water sample is pressurized against a membrane with closely controlled pore size. A part of the sample is pushed through the membrane (filtrate), while a part is recycled back into the sample container (retentate). The membrane will only allow macromolecules of a certain size or smaller to pass through. With a series of membranes, a sample can be fractionated into fractions of different molecular size, analogous to the sieving of a soil sample through a stack of mechanical screens. The polyethersulfone ultrafiltration membranes are characterized by their nominal molecular weight limit (NMWL), which is the molecular weight of a globular protein that is 90% retained on a particular membrane. Membranes with NMWL's ranging from 3 to 100 kiloDalton were used.

The ultrafiltration apparatus, purchased from the Filtron Technology Corporation (Clinton, Massachusetts), consisted of a stainless steel

MINISETTE cell into which the different membrane cassettes could be loaded. An external positive displacement pump forced the sample through the cell at 100-200 mL/min at a pressure of 65-105 kPa. The retentate flow rate was maintained at at least 75 mL/min.

All samples were prefiltered through GF/C glassfiber filters (nominal rating 1.2 μ m) before ultrafiltration. Duben (1987) provided a detailed description of the actual separation procedure. The total recovery of non-purgeable organic carbon (NPOC) typically ranged from 85% to 95% of the NPOC before fractionation.

Colloid Titration

When two oppositely charged polymer solutions are mixed together, the polymers will react to form a colloidal precipitate. This reaction is the result of the charge neutralization/precipitation mechanism discussed in the literature review. A polymer in solution can, therefore, be precipitated by titration with an oppositely charged polymer. With a titrant of known charge concentration and an indicator to signal the change of polymer charge from positive to negative, or vice versa, such a titration can be used for the quantitative determination of the charge concentration of the polymers in an unknown sample.

Kawamura and Tanaka (1966), and Kawamura et al. (1967) described the successful application of colloid titration to determine the alum dosage for optimum coagulation and flocculation. It was shown that the isoelectric point, as determined by colloid titration, corresponded very closely to the point of zero electrophoretic mobility. More recently, Schell and Bernhardt (1986) applied a slightly modified procedure to determine the charge concentration of algal biopolymer and also demonstrated that the charge concentrations measured by colloid titration and electrophoretic mobility were practically the same. The procedure of Schell and Bernhardt (1986) was adopted for this study.
A solution of potassium polyvinylsulfate (PPVS) in doubly distilled water was used as the standard anionic polymer. Schell and Bernhardt (1986) listed the charge concentration of a 324 mg/L PPVS solution as 2 meq/L. The commercial polymers (MAGNIFLOC 572C, 573C and CATFLOC T) were used as cationic reagents. They were standardized, after appropriate dilution, by direct titration with PPVS. Toluidine blue (TB) was used as colorimetric indicator, which changed from blue to purple when the isoelectric point was reached.

PPVS derives its negative charge from a sulfate ion on the monomer, whereas the cationic polymers (CP) derive their positive charge from a quaternary amine group on the monomer. Toluidine blue, a monomeric compound, also derives its charge from an amine group. The structures of the reagents are shown in Figure 3. The equilibrium constant for the PPVS-CP reaction is significantly greater than the equilibrium constant for the PPVS-TB reaction. The PPVS-CP reaction will, therefore, be practically complete before the PPVS-TB reaction begins.

Algal biopolymers are anionic. The titration of an algal sample starts with the addition of enough CP to a known volume of algal EOM to leave an excess of CP after reaction with the algal biopolymers. After five minutes, the excess cationic polymer is backtitrated with PPVS to the TB endpoint. After subtraction of the PPVS required to reach the TB endpoint in a doubly distilled blank, the charge concentration of the original sample is readily calculated. Appendix A provides a detailed description of the procedure used.

Other Analytical Procedures

Table 7 contains a listing of the other most important analytical procedures used, with a description of the procedure and/or instrument used.



toluidine blue



potassium polyvinylsulfate



polyquaternary amine

Figure 3. Molecular structure of reagents used for colloid titration

Parameter measured	Method/Instrument					
Alkalinity	SM ^a 403					
Calcium	SM 303A					
Magnesium	SM 303A					
Potassium	SM 303A					
Sodium	SM 303A					
Sulfate	SM 426D					
Suspended solids	SM 209C					
Iurbidity	SM 214A					
-	HACH ratio turbidimeter					
	GELEX solid standards					
pH	FISHER ACCUMET model 610					
	BECKMAN EXPANDOMATIC IV					
Free Cl,	SM 408G					
NPOC ²	BECKMAN 915A SM 505A					
	DOHRMAN DC 180 SM 505B					
Particle counts	HIAC-ROYCO model PC-320					
	with 60 μ m sensor					
Light intensity	LI-COR model LI-185B					
licroscopy	OLYMPUS BH-2 with					
	phase contrast optics					

Table 7. Analytical methods and instruments

^aStandard Methods for the Examination of Water and Wastewater (1985).

The spectrophotometric absorbance of the algal suspensions was measured at a wavelength of 680 nm. This was the wavelength of maximum absorbance for suspensions of <u>Chlorella</u>.

The electronic particle counts were used to calculate a theoretical particle volume. All particles were assumed to be single spheres.

Algal EOM was separated from the cells by glassfiber filters and vacuum filtration. When small volumes were separated, the suspension was filtered directly through GF/C WHATMAN filters. When larger volumes of EOM were required, the suspension was first filtered through a G6 WHATMAN glassfiber filter on a 110 mm BUCHNER funnel to remove the bulk of the algal cells, and then through GF/C WHATMAN filters.

CHARACTERISTICS OF ALGAL SUSPENSIONS

Measurements of Algal Cell Concentration

During the course of the study, four different measures were used to quantify the algal concentration; turbidity, suspended solids, spectrophotometric absorbance and electronic particle counting. In many cases, more than one measure were used on a single sample. A compilation of these alternative analyses on identical samples allows comparison between the different techniques. Figures 4 through 8 reflect these comparisons. Turbidity, the most widely used routine parameter in the water treatment industry, was used throughout as the independent variable.

Figures 4 through 8 all reflect an obvious correlation between the different measurements, and in all cases the trend is linear. As would be expected, all linear regression lines passed very close to the origin. The correlation coefficients were practically unchanged whether the lines were forced through the origin or not. For simplicity, the lines through the origin are reported on the graphs, which turn the relationships into simple ratios.

There are significant differences between the regression lines for different algal genera. The ratio between absorbance and turbidity is 0.0066 for <u>Anabaena</u>, but 0.0115 for <u>Chlorella</u>. Likewise, the ratio between particle volume and turbidity is 5.84 for <u>Scenedesmus</u>, but only 4.01 for <u>Chlorella</u>. While any of the used measurements are adequate for monitoring monocultures, they will be inadequate for monitoring mixed cultures, because they are affected by both cell concentration and species composition.

Measurement of Algal Cell Size

Electronic particle counts were taken throughout the project of <u>Chlorella</u> and <u>Scenedesmus</u> suspensions. The results from a number of randomly selected counts are presented as cumulative particle size



Figure 4. Relationship between spectrophotometric absorbance and nephelometric turbidity for <u>Chlorella pyrenoidosa</u>



Figure 5. Relationship between suspended solids and nephelometric turbidity for <u>Chlorella pyrenoidosa</u>

Š



Figure 6. Relationship between calculated particle volume and nephelometric turbidity for <u>Chlorella pyrenoidosa</u>



Figure 7. Relationship between calculated particle volume and nephelometric turbidity for <u>Scenedesmus quadricauda</u>



Figure 8. Relationship between spectrophotometric absorbance and nephelometric turbidity for <u>Anabaena flos-aquae</u>

distributions in Figures 9 and 10. No particle counts were attempted for the <u>Anabaena</u> suspensions, due to the filamentous nature of the cells. (The electronic particle counter measures the amount of light blocked by a particle. The particle size is then expressed as the diameter of an area-equivalent disc. Particles have to be approximate spheres for sensible results.)

The results show that the particle size distribution for the different genera remains fairly constant, even though the presented counts reflect a number of suspensions of different age and of different concentration. The particle size distribution of the algal cells in each genus is, therefore, considered to be constant throughout the project.

The volume-average particle diameter, d , can be read directly from 50 the figures. These average diameters compare very well with average cells depicted by Palmer (1977). For <u>Chlorella pyrenoidosa</u>, the measured d ranged from 3.7 μ m to 4.6 μ m, while Palmer showed typical diameters 50 between 3.8 μ m and 4.8 μ m. Palmer showed a typical <u>Scenedesmus</u> <u>quadricauda</u> cell to be 14 by 20 μ m, while the measured d for the same 50 species ranged between 16 μ m and 19 μ m.

Effect of Prolonged Suspension on Cell Size Distribution

Working suspensions were normally prepared the day before an experiment, or the same suspension was used on two consecutive days for different experiments. The working suspension was continuously stirred in an environment which was dark or dimly lit most of the time. It was, therefore, important to track the cell size distribution under these conditions. Figure 11 shows the results of such a test for <u>Chlorella</u>.

There was practically no difference in the particle size distribution during the first 7 hours, and very little after 25 hours. The d diameter remained constant at about 4.2 μ m. After 200 hours, 50 however, there was a drastic change in the particle size distribution. There were fewer small cells, while the larger cells increased in number.



Figure 9. Particle volume distribution of different suspensions of Chlorella pyrenoidosa



Figure 10. Particle volume distribution of different suspensions of <u>Scenedesmus quadricauda</u>



Figure 11. Change in particle volume distribution with time for a suspension of <u>Chlorella pyrenoidosa</u>

The fact that the cumulative distribution did not level off at the top end of the particle size range, indicated that there were many particles larger than the counting channels selected for this experiment. Under prolonged mixing in the dark, some cells apparently start to clump together to form agglomerated particles.

Working suspensions were always discarded after two days (three days under exceptional circumstances) and particle counts taken anywhere in this time period can be considered to be representative of the suspension.

Molecular Weight Distribution of Algal EOM

A few samples were drawn directly from the growth reactors, filtered through glassfiber filters to remove the algal cells and then separated by ultrafiltration into different molecular weight fractions. The detailed results of a typical analysis are shown in Table 8 to demonstrate the calculation sequence. The final results of a number of samples are shown in Table 9.

The first nine samples in Table 9 were collected and analyzed by Duben (1987) with the same equipment used for this project. Three different surface water impoundments in Iowa (Spirit Lake, Montezuma and Creston) were sampled during the early, mid- and late summer of 1987, which covered the period when algal problems are normally encountered. The samples were filtered through glassfiber filters prior to analysis. These samples did not form part of this study, but the results are presented to indicate which levels of NPOC are found in natural systems, and how the molecular weight fractions are distributed. The next three samples were taken from the growth reactors at different times during the study. The tap water sample was taken from the Ames municipal supply and was analyzed because the algal cultures were diluted with tap water prior to filtration. The results in the bottom four lines were taken from Bernhardt et al. (1985b). The "early" and "late" indicate that the

		molecular weight fraction									
		whole ^a	<3K ^b	3-10К	10-50K	50-100K	>100K				
(1)	sample left after ultrafiltration (mL)	3255	1815	510	400	488	433				
(2)	NPOC in subsample (mg/L)	6.19	2.74	3.78	4.32	5.02	15.86				
(3)	NPOC in subsample (mg) (1) x (2) / 1000	20.1	4.97	1.93	1.73	2.45	6.07				
(4)	NPOC in original sample (mg/L) (3) x 1000 / 3255	6.19	1.53	0.59	0.53	0.75	1.86				
(5)	<pre>% of NPOC before ultrafiltration (4) x 100 / 6.19</pre>	100.0	24.7	9.6	8.6	12.2	34.2				
	NPOC re	covery af	fter ultr	afiltratio	on = 89	.3%					

Table 8.	Typical	analysis	of	molecular	weight	fractionation	results
	obtained	i after u	ltra	afiltration	n		

^aSample <u>Chlorella</u>/2.

.

^bKiloDalton.

sample	a	Irac	tion of N	POC	N 1007	NPOG	NPOG		
	<3K	3-10K	10-50K	50-100K	>100K	recovery	whole		
	2	8	£	÷	\$	8	mg/L		
st./1 ^b	34 3	10 4	10.7	13 1	21 6	90.1	7 34		
SL/2 ^b	29 0	9 5	8 6	11 1	26.4	84.6	7.34		
SL/3 ^b	22.0	9.0	8.6	10 5	20.4	83 9	7.67		
M7/1 ^b	36 6	12 0	11 6	13 7	16 2	90 1	4 30		
M7/2 ^b	34 5	12.0	13 1	12 8	15 5	80.2	4.50		
MZ/3 ^b	42 3	14 4	12 2	12.0	3 9	92.8	5 29		
$\frac{112}{CR}$	34 6	10.2	10.8	13 7	20 4	89 7	6 21		
$CR/2^{b}$	35 1	12.8	11 7	15 1	16 5	91 2	5 55		
CR/3 ^b	43.2	13.3	13.5	20).1	90.1	5.53		
<u>Chlorella/1</u>	30.1	9.0	9.3	39	9.5	87.9	7.49		
<u>Chlorella/2</u>	24.7	9.6	8.6	12.2	34.2	89.3	6.19		
<u>Chlorella</u> /3	14.5	6.3	8.0	8.6	35.6	73.0	8.35		
tap water	57.0	13.8	12.5	15	j.3	98.6	1.28		
<u>Chlorella</u> C	76			7.4			94		
- early - late	55			4 45			24 81		
Scenedesmus									
- early	86		1	4			8.1		
- late	55	******		45			17.5		
2000			_				27,5		

Table 9. Summary of molecular weight fractionation results

^aKiloDalton.

^bSampled and analyzed by Duben (1987).

^cFrom Bernhardt et al. (1985b).

samples were collected when their laboratory cultures were at the early and late stationary growth phases. The actual cut-off point during their molecular weight fractionation was at 2 kiloDalton.

The tap water shows a molecular weight distribution distinctly different from the other samples. The low molecular weight fraction is higher, while the high molecular weight fractions are lower. (Ames municipal tap water is pumped from an alluvial aquifer and treated by lime softening.) The EOM obtained from the growth reactors is fairly similar in molecular weight distribution to the samples from the natural impoundments, even though the experimental cultures were under continuous lighting and at higher temperature (about 25 to 28 degrees Celsius in the laboratory versus 19 to 28 degrees Celsius in the natural impoundments). The results of Bernhardt et al. (1985b) show a much smaller high molecular weight fraction than the results of this study. Their method of EOM separation was different (centrifugation followed by 0.1 μ m membrane filtration) and the samples were then concentrated by evaporation up to levels of NPOC > 200 mg C/L before ultrafiltration. These procedural differences may account for the observed differences.

The overall level of NPOC in the natural impoundments is surprisingly high. Bernhardt et al. (1985a) found noticeable effects on flocculation and filtration if the NPOC (from algal EOM) went beyond 1 mg C/L, and considerable interference if the NPOC reached levels of 4 to 5 mg C/L.

Charge Concentration of Algal EOM

Table 10 shows a typical set of calculations to determine the charge concentration of the different molecular weight fractions, and to calculate the charge concentration/NPOC ratio. Table 11 shows the charge concentration of a number of samples from this and other published studies.

		<3K ^b	Mo] 30-10K	lecular w 10-50K	eight fra 50-100K	ction ^a >100K	whole
Aliquot volume	(mL)	100	100	100	100	100	100
Replicate titrat	ions	4	3	3	3		3
Cationic polymer added (573C ^C)	(mg) (µeq)	0.250 0.990	0.250 0.990	0.250 0.990	0.250 0.990	0.250 0.990	0.250 0.990
Anionic polymer added (PPVS ^d)	(mg) (µeq)	0.152 0.938	0.156 0.963	0.154 0.950	0.115 0.710	_ ^e	0.055 0.346
Charge in aliquot (573C - PPVS)	: (μeq) (μeq/L)	0.052 0.52	0.027 0.27	0.040 0.40	0.280 2.80	_e	0.644 6.44
Subsample volume Original sample	(mL) (mL)	1815 3255	510 3255	400 3255	488 3255	_e	3255 3255
Charge in origina sample	al (µeq/L)	0.29	0.04	0.05	0.42	5.64 ^f	6.44
NPOC in original sample (Table 8)	(mg/L)	1.53	0.59	0.53	0.75	1.86	6.19
Charge/NPOC	(meq/g)	0.19	0.07	0.09	0.56	3.03	1.04

Table 10.	Typical	analysis	of	titration	results	to	obtain	charge
	concent	ration						

^aSample <u>Chlorella</u>/2.

^bKiloDalton.

 C Magnifloc 573C (1 mg - 6.17 μ eq).

^dPotassium polyvinyl
sulfate (1 mg = 3.96 μeq).

^eTitration abandoned because of difficult endpoint.

^fCalculated assuming conservation of charge.

Source	Sample	Ċ	Charge/NPOC µeq/mg C
This study	<u>Chlorella</u> /2 <u>Chlorella</u> /3		1.04 0.86
Bernhardt et al. (1985b)	<u>Chlorella</u> <u>Scenedesmus</u> <u>Pseudanabaena</u> <u>Dictyosphaerium</u>	 late stationary early stationary late stationary early stationary late stationary early stationary early stationary late stationary 	1.09 0.62 1.55 3.10 2.57 3.41 2.88
Edzwald et al. (1987)	Fulvic acid Colored Norwegia New England stre) n lake) am }	4 to 5

Table 11.	Charge	concentration	per	unit	mass	of	NPOC	for	different
	studies	3							

Table 12. Charge concentration per unit mass of NPOC for different molecular weight fractions of the EOM from <u>Chlorella</u> <u>pyrenoidosa</u>

Sample	<3K ^a	3-10K	10-50K	50-100K	>100K	Whole
Chlorella/1	0.33	0.28	0.22		-1	-
Chlorella/2	0.19	0.07	0.09	0.56	3.03 ^D	1.04
<u>Chlorella</u> /3	0.60	0.34	0.21	0.69	1.89 ⁰	0.86

All values in microequivalents per milligram of NPOC

^aKiloDalton.

^bCalculated assuming conservation of charge during ultrafiltration.

The charge concentration of the cultures used in this study corresponds well with the values reported by Bernhardt et al. (1985b) for their cultures of green algae. Their values for blue-green algae, however, are roughly twice as high as the values for green algae. Edzwald et al. (1987) reported on waters with high levels of color (humic and fulvic acids) where algal EOM probably contributed less to the organic content. These waters have a charge concentration/NPOC ratio higher than any of the algal EOM values.

The total charge concentration/NPOC ratios of three <u>Chlorella</u> cultures are broken down by molecular weight in Table 12. The largest molecular weight fraction (>100K) also trapped the very small particles (approximately < 1.2 μ m) that made it through the filter used for the EOM separation. These fractions were visibly turbid (the ultrafiltration process concentrated this fraction about ten times) and did not respond to the colloid titration endpoint like the other fractions. The blue color slowly faded to grey instead of changing to purple - no endpoint could be detected reproducibly. In the "whole" sample, the concentration of microparticles was 10 times lower and did not interfere with the endpoint. The charge concentration/NPOC ratio was calculated on the assumption that the total charge remained unchanged during ultrafiltration.

Table 12 shows that the high molecular weight fraction (including some very small particles) contributes significantly more to the total charge concentration than the lower molecular weight fractions.

Summary of Findings

In this chapter, the objective was to characterize the laboratory monocultures (which were cultured under continuous lighting with artificial nutrients) and to determine how well they correspond to suspensions used in other research projects. The findings and conclusions were:

- Algal cell concentrations were measured gravimetrically, nephelometrically and spectrophotometrically. Each of these measurements was compared to the total cell volume, which was calculated from electronic particle counts. For individual species, all these comparisons yielded linear relationships through the origin. The relationships were markedly different for different species.
- The algal cell sizes stayed constant throughout the research project, and were the same as average sizes reported elsewhere for the same species.
- The cell size distribution of the algal cultures stayed constant for about two days after being diluted with tap water and kept in relative dark. Thereafter, the cells started to clump together.
- The molecular weight distribution of the algal EOM corresponded closely with results obtained (with the same procedure) on samples from algae-rich Iowa impoundments in summer.
- The negative charge concentration of the algal EOM corresponded closely with reports from another study with green algae. The charge concentration is not as high as the charge concentration from the EOM from blue-green algae, or from humic and fulvic acids in colored waters.
- The laboratory cultures, for every measured parameter, showed great similarity with other values from the literature. Therefore, it is concluded that the laboratory cultures can be used with confidence to model the behavior of the same species in natural impoundments.

EFFECTS OF CATIONIC POLYMERS AND CHLORINE ON ALGAL SUSPENSIONS

Characterization of Cationic Polymers

The most pertinent information on the three commercial cationic polymers used in this study is listed in Table 13. The values from other published studies show good agreement with the measured values.

The charge density upon dilution in water is markedly different between CATFLOC and MAGNIFLOC. The charge densities of 50 mg/L solutions, stored for 8 days in the dark at 20 degrees Celsius, remained practically constant. Provided that stock solutions of polymer are made up weekly (which they practically always were), polymer aging effects should not effect experimental results.

MAGNIFLOC 573C was separated into three different molecular weight fractions by ultrafiltration. These results are shown in Table 14. The charge concentration before ultrafiltration was 4.0 μ eq/mg of polymer in a 16.7 mg/L polymer solution. The charge concentration found in the >100K fraction after ultrafiltration accounts for 3.8 μ eq/mg in the original solution, which shows that electrical charge on the polymers is almost completely conserved during ultrafiltration.

A series of jar tests with a predominantly <u>Chlorella</u> suspension (with slight <u>Anabaena</u> contamination) was performed to compare the relative efficacy of the three polymers. The polymer dosage was based on the product as received. The suspended solids (SS) of the suspension was 17.6 mg/L. The suspensions were mixed at 150 rpm for 1 minute after polymer addition, flocculated at 50 rpm for 10 minutes, and settled for 30 minutes. A supernatant sample was drawn after settling and analyzed for turbidity (results in Figure 12). Another sample was drawn immediately after flocculation, filtered through WHATMAN #2 filter paper (approximate pore size 8 μ m) and analyzed for turbidity (Figure 13).

Figure 12 clearly shows how inappropriate conventional jar testing is for dealing with polymers and algal suspensions. The algal cells are

	CATFLOC T	MAGNIFLOC 572C	MAGNIFLOC 573C
Manufacturer Type Molecular weight Form	Calgon DADMAC ^a high viscous liquid	Cyanamid PQA ^b medium viscous liquid	Cyanamid PQA high viscous liquid
Charge concentration after dilution (μ eq/mg)	1		
immediately after	1.6	4.2	3.9
after 1 day	1.6	4.2	3.9
after 3 days	1.4	4.2	4.0
after 8 days	1.4	4.1	4.0
average	1.5	4.2	4.0
Edzwald et al. (1987) - pH 7	4.1	4.2
NPOC (mg NPOC/mg polyn	er)		0.21

Table 13. Characteristics of the cationic polymers used

^aPoly(diallyldimethyl ammonium chloride).

^bPolyquaternary amine.

Table 14.	Molecular	weight	fractions	of	а	diluted	suspension	of
	MAGNIFLOC	573C						

	Recovery after ultrafiltration	Mol <10K ^a	ecular weight. 10-100K	fraction >100K
% of NPOC	102%	15	3	84
<pre>% of charge concentration</pre>	95%	0	0	95

^aKiloDalton.



Figure 12. Supernatant turbidity of a <u>Chlorella pyrenoidosa</u> suspension after 30 minutes settling, following a jar test with three different cationic polymers



Figure 13. Turbidity of a <u>Chlorella pyrenoidosa</u> suspension after filtration through #2 WHATMAN filter paper, following a jar test with three different cationic polymers

too close to neutral buoyancy to settle, even if they are agglomerated into small floc particles. Unlike the metal coagulants which form a heavy, voluminous floc, the polymers also do not have any settling tendency by themselves. Jar tests have a similar drawback when using polymers on colored water with low turbidity. In such a case, Edzwald et al. (1987) noted that "...dosages are not selected based on good clarification...", but "...the presence of pin point floc in the beakers at the end of the jar test is desirable...". Following this reasoning, the paper filtration results in Figure 13 should give a measurable indication of the presence of pin point floc. Figure 13 does not show a sharp optimum for any of the polymers, but a marked improvement in turbidity is clearly discernible around 5 mg polymer/L. The turbidity after paper filtration was, therefore, adopted as the most appropriate response in further jar tests which will be presented in the next section.

Jar Testing of Algal Suspensions

Five series of jar tests were performed to measure the effects of a number of operational variables on algal suspensions. Table 15 summarizes the most important experimental conditions for every series.

The results of jar test 1 are analyzed in Table 16. All three polymers were used at different levels of pH (6.5 and 9.0) and chlorine dosage (0 and 10 mg/L). MAGNIFLOC 573C and CATFLOC T achieved about the same removal, with the performance of MAGNIFLOC 572C markedly poorer. In general, prechlorination improved the turbidity, and the polymers performed better at higher pH. The individual polymers, however, do not all follow the same pattern. CATFLOC T shows a highly significant improvement at high pH and is indifferent to prechlorination. The MAGNIFLOC coagulants, on the other hand, are much more affected by prechlorination than by higher pH.

	Test 1	Test 2	Test 3	Test 4	Test 5
Genus	<u>Chlorella</u>	<u>Chlorella</u>	Anabaena	<u>Chlorella</u>	<u>Chlorella</u>
SS (mg/L)	17.6	11.7	6.3	16.4	17.4
Temperature	23 ⁰ c	24 ⁰ c	27 ⁰ C	26 ⁰ C	-
рН	9.0	8.2	7.8	7.4	
NPOC	8.1	10.9	9.0	13.3	-
Polymer	all	573C	CFT	573C	573C
Dosage (mg/I	2) 5.0	0.5	6.0	15.0	3.0
Effects stud	lied:				
	polymer pH prechlor.	prechlor. contact t pH	genus pH prechlor.	prechlor. contact t mixing t	prechlor. G mixing t
Experimental design:	•				
	2x2x2 factorial 3 repl.	2x2x2 factorial 3 repl.	2x2 factorial 3 repl.	2x2x2 factorial 3 repl.	2x3x4 factorial no repl.

Table 15. Experimental jar test conditions

.

		Average turbidity a	fter paper filtration
		no chlorine	10 mg/L chlorine
······ , ·····	CFT	0.92 NTU	0.99 NTU
pH = 6.5	572C	1.71 NTU	1.34 NTU
-	573C	1.21 NTU	0.73 NTU
	CFT	0.73 NTU	0.80 NTU
рН = 9.0	572C	1.56 NTU	1.17 NTU
•	573C	0.88 NTU	0.68 NTU
Average for	all CFT measure	ments :	0 86 NTU
Average for	all 572C measures	ments :	1 45 NTU
Average for	all 573C measure	ments :	0.88 NTU
Average for	all unchlorinate	ed measurements :	1.17 NTU
Average for	all prechlorinate	ed measurements :	0.95 NTU
Average for	all measurements	at pH 6.5 :	1.15 NTU
Average for	all measurements	at pH 9.0 :	0.97 NTU
F-statistic:	s for main effects	s and interaction:	
	chlorine	DH	interaction

Table 16. Statistical analysis of the results from jar test 1

.

chlorinepHinteractionCFT2.924.5 **0.0572C13.4 **2.40.0573C25.3 **8.3 *4.2

**Significant at $\alpha = 0.01$.

*Significant at $\alpha = 0.05$.

In jar test 2, the effects of pH (6.5 and 9.0), prechlorination (0 and 10 mg/L) and chlorine contact time (1 and 10 minutes) were tested, but this time at a very low polymer dosage. Treatment effects were only observed at $\alpha > 0.20$, which is much less significant than the same effects measured in jar test 1. At low polymer dosage, therefore, the effects on the algal cells are markedly less than at higher polymer dosage.

Jar test 3 was done with an <u>Anabaena</u> suspension with low SS, but high NPOC. The effects of pH (7.4 and 8.5) and chlorine dosage (0 and 10 mg/L) were tested. The supernatant turbidity after settling did not show any meaningful response, just as was found previously for <u>Chlorella</u>. However, in the case of <u>Anabaena</u>, the paper filtration results also did not show any significant response to the different treatment levels. The F-statistics for both pH and chlorine effects were practically zero. This lack of response can be explained by the filamentous form of the <u>Anabaena</u> cells. The majority of these filaments will be filtered out on the filter paper anyway, whether they are first flocculated or not. After paper filtration, almost all the cells will be retained on the filter paper. This is evidenced by the average turbidity after paper filtration of only 0.40 NTU. (The average turbidity for CATFLOC T and <u>Chlorella</u> at a comparable dosage in jar test 1 was 0.86 NTU.)

In jar test 4, different levels of polymer mixing time (10 seconds and 3 minutes), chlorine dosage (2 and 10 mg/L), and chlorine contact time (1 minute and 15 minutes) were compared. Highly significant ($\alpha <$ 0.01) prechlorination and chlorine contact time effects were measured when the polymer mixing time was kept at 10 seconds only. When the polymer mixing time was increased to 3 minutes, these same effects could not be observed ($\alpha >> 0.25$).

Jar test 5 compared four different polymer mixing intensities (velocity gradient G = 50, 100, 200 and 400 /s) and three polymer mixing periods (t = 30 seconds, 2 minutes and 5 minutes), with and without prechlorination at 10 mg/L with a chlorine contact time of 10 minutes. The effects of prechlorination and polymer mixing time were not

significant ($\alpha > 0.25$). An increase in G did decrease the turbidity at a significance level of $\alpha = 0.12$.

Cationic Polymer Effects on Algal EOM

Two tests were conducted to shed more light on the charge neutralization/precipitation reaction between the anionic polymers in the algal EOM and the commercial cationic polymers. Algal EOM was separated from an undiluted culture in the usual manner, and additionally filtered through a 0.45 μ m membrane to obtain a very clear sample of EOM. The NPOC of the filtered sample was 20.7 mg/L and the turbidity 0.71 NTU.

The first test had two objectives. First, could the formation of the polymer/polymer precipitate be measured nephelometrically? Second, is the precipitate filterable? A number of EOM samples were treated at different levels of 573C and mixed for 20 minutes. The turbidity was then measured, the sample filtered through a 0.45 μ m membrane, and the turbidity measured again. The results of this test are reflected in Table 17 and Figure 14.

As the polymer dosage is increased up to about 10 mg/L, there is a sharp increase in turbidity. Thereafter, the turbidity slowly drops off. The neutralization/precipitation reaction seems to be complete around a dosage of 10 mg/L, and all additional polymer goes towards flocculating the colloidal precipitate into larger particles. As the particles grow and become fewer, the suspension scatters less light, which explains the drop in turbidity.

From a polymer dosage of 10 mg/L upward, the precipitated particles are larger than 0.45 μ m, because the turbidity after membrane filtration is slightly less than the original turbidity. At a dosage of 5 mg/L, before the point of net charge neutralization, a sizable fraction of the colloidal particles must be smaller than 0.45 μ m, as evidenced by the jump in turbidity after membrane filtration.

573C dosage (mg/L)	0	5	10	15	20	25	30
Turbidity after 20 minutes (NTU)	0.71	3.7	5.9	5.5	4.7	4.0	3,5
Turbidity after filtration (NTU)	0.62	1.38	0.43	0.51	0.51	0.42	0.49

Table 17.Turbidity development in algal EOM after cationic polymeraddition - effect of cationic polymer concentration

Table 18. Turbidity development in algal EOM after cationic polymer addition - effect of reaction time

573C dosage (mg/L)	0	10	10	10	10	10
Mixing time (minutes)	20	1	3	10	20	40
Turbidity (NTU)	0.71	5.4	5.6	6.0	6.2	6.2



Figure 14. Turbidity development in algal EOM after cationic polymer addition - effect of polymer concentration

The maximum turbidity in Figure 14 should correspond to the point of net charge neutralization. The dosage at maximum turbidity is about 10 mg 573C/L, which is equivalent to an added charge of 10 x 4.0 = 40 μ eq/L. At the NPOC of 20.7 mg/L, the charge/NPOC ratio is then 40/20.7 = 1.9 μ eq/mg NPOC, which is within the range of experimentally measured values for algal EOM (refer back to Table 11).

The second test measured the kinetics of the polymer/polymer reaction. A polymer dosage of 10 mg 573C/L was added to filtered EOM and continuously mixed. Samples were drawn after 1, 3, 10, 20 and 40 minutes and immediately analyzed for turbidity. The results are reflected in Table 18 and Figure 15.

It is clear from Figure 15 that the neutralization/precipitation reaction is substantially complete after 1 minute. A standard reaction time of 5 minutes was subsequently adopted for all other tests that involved polymer/polymer reactions. A comparison between Tables 17 and 18 shows good reproducibility between experiments - in Table 17 the turbidity was 5.9 NTU after 20 minutes at a dosage of 10 mg 573C/L, and in Table 18 the turbidity was 6.2 NTU under identical conditions.

The development of turbidity upon polymer addition was used as a crude method for determining the polymer dosage required for the filtration experiments. Algal EOM was separated from the suspension to be filtered, and treated with different polymer dosages. The polymer dosage required for charge neutralization was taken at the point where the turbidity started to level off. The results of six such tests, done for six different suspensions, are shown in Figure 16.

The results in Figure 16 show wide scatter, because of different EOM turbidity after separation, and because of different charge concentration. The numbers were, therefore, standardized by subtracting the EOM turbidity before polymer addition (to get the turbidity <u>increase</u> after polymer addition), and then by dividing both the polymer dosage and the turbidity increase by the NPOC of the EOM. The standardized results are shown in Figure 17.



Figure 15. Turbidity development in algal EOM after cationic polymer addition - effect of reaction time



Figure 16. Turbidity development in algal EOM after cationic polymer addition - measured turbidity for different suspensions


Figure 17. Turbidity development in algal EOM after cationic polymer addition - turbidity and polymer dosage corrected for initial turbidity and NPOC concentration

Figure 17 conveys two important points. First, the general trend of the curves, which are now much more in agreement, seems to level off somewhere between 0.5 and 0.7 mg 573C/mg NPOC. This range is equivalent to 2.0 to 2.8 μ eq/mg NPOC. Second, the closeness of the curves suggests that the NPOC is a good surrogate parameter for the charge concentration of the anionic polymers in the EOM.

The development of a colloidal precipitate upon polymer addition has been documented for other types of suspensions. Narkis and Rebhun (1983) demonstrated this for solutions of humic acid, fulvic acid and a suspension of secondary wastewater effluent. Schell and Bernhardt (1986) reported the same phenomenon for the reaction of oppositely charged polymeric reagent-grade chemicals, and for a solution of alginic acid.

Chlorine Effects on Algal EOM

It is well established that organic nitrogen, such as is present in algal suspensions, exerts a chlorine demand. A procedure was used whereby the chlorine demand could be estimated by only measuring the free chlorine residual. Chlorine was added to a number of aliquots from the same sample, at different concentrations, and the free chlorine residual was measured after the required contact time. The linear regression line through the non-zero residuals was extrapolated back to the X-axis to obtain an intercept representative of the chlorine demand. The procedure is demonstrated in Figure 18 with typical data.

Using the procedure just described, a chlorine demand test was done on a <u>Chorella</u> suspension with SS - 26 mg/L at pH 8.8. The chlorine demand was determined after 5, 10, 20 and 30 minutes. Another series of similar tests was run on the EOM portion only of the same culture. The NPOC of the EOM was 5.6 mg/L. The results of these tests are presented in Figure 19.

Figure 19 shows a number of important points. First, it is obvious that the EOM, in this case, exerts a much greater chlorine demand than



Figure 18. Illustration of the calculation procedure for chlorine demand, using a suspension of <u>Chlorella pyrenoidosa</u>



Figure 19. Chlorine demand versus chlorine contact time for <u>Chlorella</u> <u>pyrenoidosa</u> - total suspension and EOM

the cells. After 30 minutes, for example, the EOM exerts 77% of the total chlorine demand. After 30 minutes, the chlorine demand of the EOM is 4.1 mg/mg NPOC, and the chlorine demand of the cells is 0.26 mg/mg SS. Second, after 30 minutes the demand is still rising. Third, a substantial fraction of the 30-minute demand is satisfied after 10 minutes.

Echelberger et al. (1971) determined the chlorine demand of algal cells by centrifuging the cells from a culture and resuspending them in tap water. They measured a chlorine demand of 45.5 mg/L at a chlorine dosage of 50 mg/L for a suspension with 300 mg SS/L. This amounts to a chlorine demand of 0.15 mg/mg SS, lower than the 0.26 mg/mg SS (after subtraction of the EOM demand) measured in this study. Their study is misleading in the sense that it deliberately ignores the EOM contribution to the chlorine demand, but carries the broad title of "Disinfection of Algal Laden Waters".

Attempts were made to relate the chlorine demand of the EOM to the NFOC. These results, shown in Table 19, show wide scatter in the chlorine demand - between 3.3 and 9.7 mg/mg NPOC after 10 minutes of contact time. These tests were not repeated with longer chlorine contact times, which might have brought the measured values closer together.

Combined Effects of Cationic Polymer and Chlorine on Algal EOM

An experiment was designed to determine the effects of chlorine on the turbidity development caused by the addition of cationic polymer to algal EOM. Chlorine was added to samples of EOM and mixed for 10 minutes. Polymer was then added and the sample mixed for another 5 minutes before the turbidity was measured. The EOM had a NPOC concentration of 3.47 mg/L, pH of 8.4, temperature of 24.5 degrees Celsius and chlorine demand of 29 mg/L after 10 minutes. The measured turbidity results are shown in Table 20. The same data are represented in Figure 20.

mg/L	Demand/NPOC mg/mg
90 -	9.7
18.5	3.3
18.2	3.4
17.0	5.0
22.0	8.3
29.0	8.4
	mg/L 90 18.5 18.2 17.0 22.0 29.0

Table 19.	Chlorine demand for the EOM i	from suspensions of <u>Chlorella</u>
	pyrenoidosa with different NI	POC concentrations

Table 20. Turbidity development in algal EOM after addition of different combinations of chlorine and cationic polymer

Polymer dosage (mg 573C/L)		Chl	orine dosag (mg/L)	e	
	0	6	12	18	24
		T	urbidity (N	IU)	
0.00	1.51	1.38	1.39	1.91	2.00
0.33	1.55	1.37	1.35	2.00	2.20
0.67	1.41	1.51	1.31	1.89	2.20
1.00	1.71	1.68	1.54	2.00	2.20
1.33	1.80	1.71	1.66	2.20	2.50
1.67	2.00	1.68	1.94	2.40	2.80
2.00	2.10	1.97	2.00	2.50	3.00
2.50	2.20	2.00	2.20	2.70	3.10

.



Figure 20. Turbidity development in algal EOM after addition of different concentrations of chlorine and cationic polymer. Chlorine contact time was 5 minutes before polymer addition

The turbidity, generally, increased with increased polymer dosage, regardless of the chlorine dosage. Chlorine, on its own and in combination with polymer, also increased the turbidity, but only after a chlorine dosage of about 10 mg/L was reached. The three-dimensional presentation in Figure 20 clearly shows a plateau between a chlorine dosage of 0 and 10 mg/L, with the turbidity sharply increasing after 10 mg/L.

Summary of Findings

- Three commercial cationic polymers were characterized in a number of ways. The MAGNIFLOC polymers imparted a higher charge concentration upon dilution than the CATFLOC T polymer.
- Supernatant turbidity was shown to be an inadequate jar testing response for algal suspensions treated with cationic polymer. The turbidity after paper filtration through WHATMAN #2 filter paper, immediately after flocculation, was found to be more suitable, and was subsequently used for all jar tests. This paper filtration technique, however, was shown to be inadequate for filamentous algae.
- During the jar test experiments, prechlorination, at a fixed polymer dosage of 5 mg/L, was shown to improve the performance of MAGNIFLOC coagulants, but not of CATFLOC T. This improvement was evident at high polymer dosage (5 mg/L), but not at low polymer dosage (0.5 mg/L). It was also evident at a very short rapid mixing time of 10 seconds, but not at a longer rapid mixing time of 3 minutes. Longer chlorine contact time was only beneficial for turbidity removal at a rapid mixing time of 10 seconds, and not at 3 minutes.

- The rapid mixing velocity gradient had a slight effect on the polymer performance during jar testing. As the velocity gradient was increased from 50 /s to 400 /s, the turbidity removal improved.
- The algal EOM reacted with cationic polymer to form measurable turbidity, in complete accordance with the charge neutralization/ precipitation mechanism. The reaction was essentially complete after 1 minute. The turbidity development was verified in a number of suspensions, each with different background turbidity and with different levels of NPOC.
- The algal EOM caused a considerably higher chlorine demand than the algal cells themselves; about 75% of the total demand was exerted by the EOM. Most of the measured demand was exerted after 10 minutes, but the demand was still rising after 30 minutes, at which time the tests were abandoned.
- Chlorine, alone or in combination with cationic polymer, caused an increase in EOM turbidity. At low chlorine concentration, there was little effect on turbidity, but after a certain threshold, the turbidity sharply increased.

DIRECT FILTRATION OF ALGAL SUSPENSIONS

Outline of Experimental Work

The design and operation of the experimental sand filtration system were guided by two objectives. First, the algal cultures had to be well controlled to ensure suspensions of only one, known algal species. The size of the filtration apparatus was, therefore, determined by the maximum quantity of suspension that could be produced for every filtration experiment. Second, it was desirable to amplify the treatment effects above those that normally would be measured in practice. In this way, the system would be more responsive to changes in operational variables. Algal cultures of high concentration were used, which required high concentrations of treatment chemicals. Likewise, very short filters were used to detect the early onset of turbidity breakthrough. The reader should remember throughout that actual treatment situations would very probably require lower dosage of chemicals (because of lower algal concentration) and would achieve substantially better removal (because of filters that are four to five times deeper).

A total of 51 filtration experiments was done. In 47 of these, two filters were operated in parallel, while only one filter was operated in the remaining 4 experiments. The filter runs are designated as 1A (the first filter in the first experiment), 17B (the second filter in the seventeenth experiment), etc. Thus, 98 designated filter runs were completed.

The 98 filter runs were performed with four types of coagulation no coagulation at all, with aluminum sulfate, with ferric chloride and with cationic polymer. Table 21 shows the main experimental variables for these 98 runs.

The detailed results of all filter runs are presented in Appendix B. Nephelometic turbidity was used throughout as the measure of algal

Experimental Condition	Number	of	Filte		Runs
No coagulant Aluminum sulfate Ferric chloride Cationic polymer					17 17 22 42
		t	otal	-	98
Prechlorination No prechlorination		t	otal	-	56 42 98
<u>Chlorella</u> <u>Scenedesmus</u>		t	otal		78 20 98
Bed depth 100 mm Bed depth 150 mm Bed depth 200 mm Bed depth 250 mm		t	otal		10 34 14 40 98

Table 21. Experimental variables for the 98 filter runs

.

•

concentration in the raw water and in the filtrate. The parameter C/C, therefore, is the ratio between the turbidity after and before passage through the sand bed.

The actual C/C measured reflects the removal by sand beds ranging from 100 mm to 250 mm in depth. Besides the measured C/C values, the expected removal through a 200 mm sand bed has also been calculated on the basis of first-order removal. The calculated C/C values allow direct comparison between filter runs, and are listed in the following tables.

The hydraulic filter loading (shown in Appendix B) was approximately constant throughout the entire project at 5 m/h.

Direct Filtration without Coagulants

A summary of the filtration results in the absence of coagulants is shown in Table 22.

In one experiment (filter runs 10A and 10B), the pH was lowered by the addition of sulfuric acid down to the vicinity of the reported isoelectric point of the algal cells. The subsequent removal for the unchlorinated suspension (run 10B) was 76.6% - by far the highest achieved during this part of the research. Prechlorination, under similar conditions (run 10A), lowered the removal to 31.2%. The results of run 10A and 10B, although useful for illustrating the effect of net surface charge, are not indicative of anything that would be encountered during a real treatment situation. They are, therefore, excluded from the statistical comparisons that follow, and from the computed averages at the bottom of Table 22.

A number of observations follow from Table 22. First, the algal removal, in all cases, is poor and not nearly acceptable for drinking water treatment standards. The use of coagulants is imperative.

Second, the most obvious trend in the data is the difference in the removal of the different algal genera. The average removal for <u>Chlorella</u>

Run	Genus	pН	Part. Vol.	Prechl.	Depth	Ave. C/Co	λ	C/Co for
			mm ³ /L	mg/L	mm	a	/m	200 mm
- <u></u>	Sce	0 1	32	5/1 8	150	0 805	1 45	0 748
8R	<u>30e</u> . Sce	9.1 8 1	32	0	150	0.505	3 52	0.740
9A	Chl	81	4.0	õ	150	0.320	1 99	0.475
9R	$\frac{O(11)}{Chl}$	9.1	3.9	6.1	150	0.936	0.44	0.916
1.0A	Sce.	3.3	42	68.0	150	0.755	1.87	0.688
10B	Sce.	3.1	40	0	150	0.336	7.27	0.234
11A	$\frac{1}{Chl}$	6.5	5.1	0	150	0.841	1.15	0.795
11B	Ch1.	5.9	5.2	63.8	150	0.930	0.48	0,908
12A	Sce.	8.8	33	66.4	250	0,600	2.04	0.665
12B	Sce.	6.2	36	69.1	250	0.492	2.84	0.567
13A	Sce.	n/a	28	0	250	0.513	2.67	0.586
29A	Chl.	7.3	33	0	250	0.878	0.52	0.901
29B	\overline{Chl} .	7.4	32	3.0	250	0.917	0.35	0.932
32A	Chl.	7.5	13	4.1	250	0.838	0.71	0.868
32B	<u>Chl</u> .	7.4	15	0	250	0.851	0.65	0.878
35B	<u>Chl</u> .	7.7	13	0	250	0.750	1.15	0.795
38A	<u>Chl</u> .	n/a	25	0	250	0.892	0.46	0.912
Aver	age rem	oval i	for a bed dept	ch of 200	mm (excl	uding runs	10A and	1 10B):
	Chlore	<u>11a</u> ,	without chlo	orine : 1	17.5%	(6 runs)		
	Uniore	LLA,	with chiorir		ッ.48 とこ 00	(4 runs)		
	Scened	esmus,	without chic	orine : 4	+J,98	(2 runs)		
	<u>эсепеа</u>	<u>esmus</u> ,	with chiorir	ie : :	04.08	(5 runs)		

Table 22. Summary of filtration results without coagulants

·

L

^aComputed from a portion of the run where the removal was stable.

was 14.0%, whereas it was 38.8% for <u>Scenedesmus</u>. A statistical comparison (Student t-test) between these means shows them to be different at $\alpha < 0.01$. This difference can be explained by the previously reported difference in the volume-average diameter between <u>Chlorella</u> (d₅₀ = 3.9 μ m) and <u>Scenedesmus</u> (d₅₀ = 17 μ m).

Third, the algal concentration appears to have a small effect. For the <u>Chlorella</u> runs without prechlorination, the average removal was 27% when the particle volume concentration (PVC) was under 10 mm /L, 16% when the PVC was between 10 and 20 mm /L, and 9% when the PVC was above 20 $_{3}^{3}$ mm /L.

Fourth, prechlorination caused poorer removal. If a paired comparison is made for the six experiments where prechlorination was the only difference between the two filters (8, 9, 10, 11, 29 and 32), the prechlorination effect is significant at $\alpha = 0.033$. Prechlorination lowered the average removal by 18.1%. The cause of this adverse effect is not clear. The direct action of the chlorine on the cells was not apparent from the results of either microscopic analysis or of electronic particle counting. The addition of chlorine to algal EOM was earlier shown to increase the turbidity of the the EOM (refer back Figure 20). This colloidal precipitate may have been carried through the filter to cause a relative increase in the filtrate turbidity.

Fifth, the chlorine concentration had little effect. Dosage was varied between extreme ranges, without any obvious effect.

Sixth, the form of the chlorine (hypochlorous vs. hypochlorite) appears to have a small effect. Run 12A and 12B was designed to test this effect by adjusting the pH to achieve all hypochlorous acid (12B) or hypochlorite (12A). Chlorine in the hypochlorous form led to better removal than chlorine in the hypochlorite form (43.3% vs. 33.5%). Chlorine was added at high dosage to ensure a free chlorine residual after reaction with the algal EOM.

Seventh, the phenomenon of filter ripening (improved removal shortly after the start of a filter run) was never observed. In some cases, a gradual decrease in removal was observed as the filter run progressed.

Direct Filtration with Metal Coagulants

Metal coagulants act in one of two different ways. At low pH (< pH 6), the metal remains in polymeric form and destabilizes the particles by charge neutralization. At somewhat higher pH (> pH7), the metal precipitates and captures the particles in a metal hydroxide floc. Algal laden water is normally at high pH due to the net uptake of carbon dioxide during photosynthesis, and precipitation of the metal hydroxide into flocs is normally anticipated. The metal precipitate would add to the solids load imposed on the sand bed, leading to more rapid clogging. In the evaluation of this section of the experimental results, the head loss development is of importance. Good algal removal is necessary for successful treatment, but the head loss development rate (HDR) should also be within reason for the process to be economically feasible.

The results of the filter runs with ferric chloride are summarized in Table 23, and the results with aluminum sulfate in Table 24.

Before any general conclusions are made about the filter runs with metal coagulants, two filtration experiments will be discussed. These experiments demonstrated unusual effects.

Filter experiment 23 (<u>Scenedesmus</u> treated with ferric chloride) was performed after deliberately lowering the pH to pH 3.7. At this low pH, the solubility of iron is high enough to leave all the iron in dissolved, polymeric form. The filtration results clearly demonstrate that this indeed happened - the removal was excellent, but with a very low HDR. The HDR for filter experiment 21 (same genus, iron dosage and removal range, but at higher pH) was five times higher. During experiment 21 the iron precipitated as floc, but remained in solution during experiment 23. Figure 21 shows a comparison between 21B and 23B.

Filter experiment 26 was the only example during the entire research project where surface straining was the primary removal mechanism rather than deep bed filtration. It cannot, therefore, be considered with the other runs to draw generalizations about deep bed filtration behavior. It is pointed out as a caution, and does not imply a significant finding.

Run	Genus	рН	Turb. NTU	Depth mm	Cl ₂ mg/L	Fe mg/L	Aver HDR mm/h	age ^a C/C _o	λ /m	C	:/C for 280 mm
1A	<u>Chl</u> .	7.5	3.7	250	0	2.2	130	0.265	5.3		0.346
1B	<u>Chl</u> .	7.6	3.7	250	0	1.8	60	0.595	2.1		0.660
2A	<u>Chl</u> .	n/a	3.0	150	0	2.0	258	0.052	19.7		0.019
2B	<u>Chl</u> .	n/a	3.3	150	0	2.6	278	0.026	24.3		0.008
3A	<u>Chl</u> .	6.5	2.5	150	0	2.5	217	0.025	24.6		0.007
3B	<u>Chl</u> .	6.7	2.3	150	0	2.2	196	0.064	18.3		0.026
4A	<u>Chl</u> .	n/a	2.0	150	5.4	1.8	139	0.073	17.4		0.031
4B	<u>Chl</u> .	n/a	2.1	150	0	1.8	145	0.095	15.7		0.043
5A	<u>Chl</u> .	n/a	4.0	150	10.8	2.1	97	0.252	9.2		0.159
5B	Chl.	n/a	3.9	150	0	2.2	18	0.362	6.8		0.258
6A	Chl.	7.3	2.9	150	12.5	2.4	27	0.543	4.1		0.443
6B	Ch1.	7.2	2.8	150	0	2.5	44	0.576	3.7		0.479
7A	Chl.	n/a	2.5	150	0	2.6		not co	nstant	-	rising
7B	Chl.	n/a	2.4	150	9.7	2.7		not co	nstant	-	rising
20A	Chl.	n/a	6.7	150	29,9	2.1	53	0.376	6.5		0.271
20B	Chl.	n/a	6.5	150	0	2.2		not co	nstant	-	rising
21A	Sce.	7.4	3.1	150	0	1.7	173	0.054	19.5		0.020
21B	Sce.	7.1	3.2	150	34.8	1.8	180	0.040	21.5		0.014
22A	Chl.	6.8	3.8	250	30.0	2.1		not co	nstant	-	rising
22B	Ch1.	6.8	3.9	250	30.5	2.2	256	0.173	7.0		0.246
23A	Sce.	3.7	2.0	100	32.2	1.7	33	0.090	24.1		0.008
23B	<u>Sce</u> .	3.7	2.3	100	32,8	1.8	36	0.064	27.5		0.004

Table 23. Summary of filtration results with ferric chloride

^aComputed from a portion of the run where the removal was stable.

Run	Genus	pH	Turb.	Depth	C1_	A1	Ave	rage ^a	λ	C/Co for
		-		-	2		HDR	C/Co		200 mm
			NTU	mm	mg/L	mg/L	mm/h		/m	
24A	<u>Chl</u> .	7.1	6.1	100	32.4	3.4	3	0.785	2.4	0.616
24B	<u>Chl</u> .	7.5	5.7	100	0	3.5	7	0.683	3.8	0.466
25A	<u>Chl</u> .	5.3	7.1	100	19.5	1.0	47	0.642	4.4	0.412
25B	<u>Chl</u> .	5.5	7.4	100	0	1.1	71	0.657	4.2	0.432
26A	<u>Sce</u> .	4.7	5.7	100	18.1	1.4	15	0.477	7.4	0.228
26B	<u>Sce</u> .	4.8	5.3	100	0	1.5	27	0.241	14.2	0.058
27A	<u>Chl</u> .	7.8	4.0	250	19.2	1.0	42	0.409	3.6	0.489
27B	<u>Chl</u> .	7.7	4.0	250	19.7	1.1	27	0.386	3.8	0.467
28A	<u>Chl</u> .	7.4	6.7	250	9.9	1.1	110	0.255	5.5	0.335
28B	<u>Ch1</u> .	7.3	6.7	250	10.0	1.1	60	0.310	4.7	0.392
31A	Chl.	6.6	5.2	250	2.7	1.7	121	0.012	17.7	0.029
31B	Chl.	6.5	5.2	250	0	1.7	125	0.018	16.1	0.040
34A	<u>Ch1</u> .	6.9	3.6	250	19.3	1.9	147	0.015	16.8	0.035
34B	Chl.	6.7	3.1	250	0	1.9	251	0.034	13.5	0.067
37A	Chl.	n/a	7.4	250	0	2.4	125	0.015	16.8	0.035
40A	Chl.	6.0	9.5	250	3.2	3.3	140	0.016	16.5	0.037
40B	<u>Ch1</u> .	6.1	8.5	250	0	3.1	291	0.023	15.1	0.048

Table 24. Summary of filtration results with aluminum sulfate

^aComputed from a portion of the run where removal was stable.

.



Figure 21. Effect of pH on the filtration of <u>Scenedesmus quadricauda</u> with 1.8 mg Fe/L as primary coagulant. Bed depth 150 mm for 21B, 100 mm for 23B

The following general conclusions follow from the analysis of the remainder of the filtration results of this section.

Turbidity removal

Tables 23 and 24 show a remarkable pattern for turbidity removal. During roughly half the runs, the turbidity removal was excellent (>95% for iron and > 93% for aluminum). During the other runs, the removal was markedly poorer.

The turbidity removal does not correlate with any of the other measured operational parameters. The relationship between turbidity removal and coagulant dosage (found to be significant during jar tests in other studies) is shown as a scatter plot in Figure 22. The lack of a significant trend is visibly obvious. The average Fe dosage for the runs that removed more than 95% of the turbidity was 2.0 mg/L, while the average for the other runs was 2.2 mg/L. For aluminum, these dosages were 2.3 and 1.7 mg/L respectively. Correlations between turbidity removal and pH, raw water turbidity, hydraulic loading and bed depth were sought, but without success.

Head loss development rate (HDR)

The filter runs that showed turbidity removal higher than 93%, also showed a considerably higher HDR than those with turbidity removal lower than 93%. In the case of aluminum, the average HDR was 171 mm/h when C/C > 93%, but only 48 mm/h when C/C < 93%. For iron, the corresponding HDRs were 198 mm/h and 86 mm/h.

Full-scale water treatment plants are normally designed for a maximum head loss across the filters of 2 to 3 m. Filter runs of at least 24 hours duration are expected in practice, otherwise the water and energy losses associated with backwashing become exorbitant. The highest tolerable HDR in practice, therefore, lies approximately between 80 and 120 mm. The average HDRs measured in this study (171 mm for Al and 198 mm for Fe) are considerably higher. The sole use of metal coagulants for the direct filtration of algal suspensions, even if it did lead to



Figure 22. Average turbidity removal versus coagulant dosage for filter runs conducted with metal coagulants. Turbidity removal expressed as the equivalent removal through a bed depth of 200 mm

consistent turbidity removal, would not be an economically attractive option.

Turbidity breakthrough

A number of filter runs experienced turbidity breakthrough (a sharp increase in filtrate turbidity after a period of relatively constant turbidity removal) before the end of the filter run. During the seven runs with <u>Chlorella</u> when the turbidity removal with aluminum was higher than 93%, breakthrough was observed six times (31A/B, 34A, 37A and 40A/B). During the six runs with <u>Chlorella</u> when the same turbidity removal was achieved with iron, breakthrough was never observed. The presence, or onset of breakthrough was not related to turbidity loading, hydraulic loading or pH.

Chlorine effects

In most cases, prechlorination affected neither the turbidity removal, nor the HDR. In a few cases, definite chlorine effects were observed, but no general trends were obvious. During 25A/B, 34A/B and 40A/B, prechlorination caused a lower HDR, but it did not affect the turbidity removal. During 5A/B, the effect of prechlorination was the opposite - it caused a higher HDR.

When turbidity breakthrough occurred, prechlorination did cause earlier breakthrough. During 34A (prechlorinated at 19.3 mg/L), breakthrough occurred after 6 h, while 34B (no chlorine) experienced no breakthrough during the 10 h filter run. During 40A/B, prechlorination at 3.2 mg/L shortened the period before breakthrough from 4 h to 2 h.

Direct Filtration with Cationic Polymers

A total of 42 filter runs was performed with cationic polymer as the primary, and only coagulant. During the first 21 runs, CATFLOC T was

used, and MAGNIFLOC 573C during the last 21 runs. The most important variables are summarized in Table 25.

Effect of polymer type

Filter runs 41A and 41B were run in parallel out of the same feed tank, at approximately the same polymer dosage. Run 41A was made with 1.7 mg CFT/L and run 41B with 1.6 mg 573C/L. Figure 23 shows the comparative results. The HDR was practically identical, but there was a considerable difference in turbidity removal. The calculated average removal for a 200 mm deep bed was 22.6% in the case of CATFLOC T, but it was 39.7% (almost double) for MAGNIFLOC 573C.

This difference is explained by the higher charge concentration of 573C relative to CFT, which was reported in Table 13.

Effect of polymer dosage during a single filter run

During runs 46A and 46B, the two filters were treated with different dosages of 573C. Halfway through the runs, the dosages were changed. An immediate effect on turbidity removal was observed. Figure 24 shows the turbidity removal with time. The turbidity removal, measured immediately before and after the dosage change, is plotted against 573C dosage in Figure 25. It shows clearly that, for a specific filter run, the polymer dosage has a direct, almost linear effect on turbidity removal.

Effect of polymer dosage during multiple filter runs

In Figure 26, the average turbidity removal is compared to the polymer dosage for the filtration experiments with <u>Chlorella</u>. The polymer dosage is expressed as μ eq/L (to account for the difference in charge concentration between the two cationic polymers used) and then divided by the turbidity of the algal suspension (to account for the difference in particle volume amongst different suspensions).

A similar plot for inorganic suspensions, such as clay, should show maximum turbidity removal at the optimum dosage, with poorer removal to the left (not enough polymer for destabilization) and to the right

Run	Genus	рН	Turb.	Depth	C1 ₂	Polymer	λ	C/Co	NPOC
			NTU	mm	mg/L	mg/L	/m	200mm	mg/L
13B	<u>Sce</u> .	n/a	4.9	250		32.2 CFI	8.8	0.171	
14A	<u>Ch1</u> .	7.0	2.3	100		10.5 CFT	2.8	0.567	
14B	<u>Chl</u> .	7.0	2.3	100	40.4	10.8 CFT	8.0	0,202	
15A	Sce.	6.2	3.9	250	75.1	9.9 CFT	11.1	0.110	
15B	Sce.	6.2	3.9	250		10.1 CFT	9.1	0.164	
16A	<u>Chl</u> .	6.6	2.6	250	var.	5.3 CFT	6.6	0.268	
16B	<u>Chl</u> .	6.6	2.6	250	var.	5.4 CFT	3.9	0.454	
17A	Sce.	n/a	3.1	250		5.4 CFT	9.8	0.142	
17B	<u>Sce</u> .	n/a	3.1	250	20.5	5.5 CFT	10.5	0.122	
18A	<u>Ch1</u> .	6.3	8.4	150	29.5	5.2 CFT	2.4	0.622	
18B	<u>Chl</u> .	6.3	8.4	150	30.0	5.4 CFT	2.6	0.593	
19A	Sce.	8.1	3.4	150	20.3	5.3 CFT	18.2	0.026	
19B	Sce.	8.1	3.4	150	21.1	5.6 CFT	18.4	0.025	
30A	Chl.	7.2	6.7	250	5.8	5.0 CFT	11.8	0.094	
30B	<u>Chl</u> .	7.2	6.7	250		5.2 CFT	11.0	0.111	
33A	<u>Chl</u> .	7.8	4.6	250	3.3	3.4 CFT	12.8	0.078	
33B	<u>Ch1</u> .	7.8	4.6	250		3.4 CFT	13.0	0.075	
36A	<u>Chl</u> .	n/a	5.1	250		0.6 CFT	3.0	0.548	
39A	<u>Chl</u> .	n/a	8.8	250	4.3	2.3 CFT	0.4	0.929	
39B	<u>Chl</u> .	n/a	8.8	250		2.2 CFT	0.5	0,900	
41A	<u>Chl</u> .	7.8	3.3	150	10.9	1.7 CFT	1.6	0.718	
41B	<u>Chl</u> .	7.8	3.3	150	9.8	1.6 573C	3.5	0.495	
42A	<u>Chl</u> .	8.0	7.9	150	var.	4.0 573C	13.9	0.063	
42B	<u>Chl</u> .	8.0	7.9	150	var.	3.7 573C	12.7	0.078	
43A	<u>Chl</u> .	7.3	6.7	150		3.3 573C	6.5	0.273	
43B	<u>Chl</u> .	7.3	6.7	150		3.0 573C	6.2	0.291	
44A	<u>Chl</u> .	7.9	6.8	150	12.6	4.1 573C	8.8	0.171	8.7
44B	<u>Chl</u> .	7.9	6.8	150	13.1	3.8 573C	6.8	0.256	8.7
45A	<u>Chl</u> .	7.7	12.9	200	var.	3.4 573C	1.9	0.689	5.4
45B	<u>Chl</u> .	7.7	12.9	200	var.	4.3 573C	3.6	0.485	5.4
46A	<u>Chl</u> .	8.1	15.2	200		var. 573C	2.9	0.558	3.5
46B	<u>Chl</u> .	8.1	15.2	200		var. 573C	4.2	0.432	3.5
47A	<u>Chl</u> .	7.8	14.1	200	21.2	2.3 573C	2.0	0.677	3.4
47B	<u>Chl</u> .	7.8	14.1	200	22.4	4.6 573C	5.2	0.355	3.4
48A	<u>Chl</u> .	7.5	10.2	200	19.0	1.6 573C		var.	3.0
48B	<u>Chl</u> .	7.5	10.2	200	9.2	1.5 573C		var.	3.0
49A	<u>Chl</u> .	7.0	8.9	200	24.2	2.2 573C	1.8	0.697	2.6
49B	<u>Chl</u> .	7.0	8.9	200	11.0	2.0 573C	2.8	0.566	2.6
50A	<u>Chl</u> .	6.7	9.6	200	21.5	4.3 573C		var.	3.5
50B	<u>Chl</u> .	6.7	9.6	200	11.0	4.6 573C		var.	3,5
51A	<u>Chl</u> .	7.8	9.5	200	22.5	5.0 573C		var.	5,8
51B	<u>Chl</u> .	7.8	9.5	200	22.6	4.8 573C		var.	5,8

Table 25. Summary of filtration results with cationic polymer



Figure 23. Comparison between two commercial polymers as primary coagulants for the direct filtration of <u>Chlorella</u> <u>pyrenoidosa</u>. Bed depth 150 mm



Figure 24. Effect of different initial cationic polymer concentration, and a step change in polymer concentration after 5.5 hours. Bed depth 200 mm



Figure 25. Turbidity removal values taken from Figure 24, immediately before and after the step change. Bed depth 200 mm



Figure 26. Average turbidity removal versus polymer concentration for all filter runs with <u>Chlorella pyrenoidosa</u> suspensions treated with cationic polymer. Turbidity removal expressed as the equivalent removal through a bed depth of 200 mm

(restabilization due to excess polymer). Such a trend is not evident from Figure 26. At the dosage where the highest removal (> 90%) was obtained, turbidity removal as low as 50% was also measured. This result demonstrates the fact that the polymer demand is not only caused by the turbidity from the algal cells, but also by another, unmeasured constituent - most probably the algal EOM.

Effect of polymer dosage on different size fractions

During run 47A, the polymer dosage was adjusted to 2.3 mg 573C/L, which was just enough to satisfy the EOM demand for polymer as measured turbidimetrically. For run 47B, which was done in parallel with 47A, the polymer dosage was doubled to 4.6 mg 573C/L. The filtration results are shown in Figure 27. The results speak for themselves. During 47A, the removal was poor, with a very low HDR. During 46B, the removal was roughly doubled, with a concomitant increase in HDR.

After a filter run time of 2 hours, samples were drawn from the feed tank and the two filtrate lines, and analyzed with the electronic particle counter. In this way, the particle removal could be calculated for every size fraction. Figure 28 shows the calculated removal for every size fraction.

In the case where polymer was added in excess of that demanded by the EOM (47B), the smaller size fractions were removed more efficiently than the larger size fractions. During 47A, the removal trend was reversed. A likely explanation, which was not experimentally verified, is that the polymer apparently did nothing to flocculate the algal cells during 47A, but only reacted with the algal EOM. The larger cells were, therefore, preferentially removed simply because they were bigger. During 47B, some polymer was left after satisfying the EOM demand, and the smaller cells were then flocculated to larger sizes, where a fraction of them was removed. In other words, during 47A only filtration was operative, whereas filtration <u>and</u> flocculation were operative during 47B. The actual cell counts are given in Appendix C.



Figure 27. Effect of polymer dosage on the direct filtration of <u>Chlorella pyrenoidosa</u>. Run 47A received just enough polymer to satisfy the EOM demand. Bed depth 200 mm



Figure 28. Removal of different particle size fractions two hours into filter runs 47A and 47B

Effect of polymer overdosage

Table 26 summarizes the turbidity removal during the filtration of <u>Scenedesmus</u> suspensions.

Two observations follow from Table 26. First, the addition of cationic polymer doubled the percentage of turbidity removal, as evidenced by the parallel filter runs 13A and 13B. Second, the well documented phenomenon of charge reversal/restabilization upon overdosage of cationic polymer was not observed. The turbidity removal reported in Table 26 stayed in the same range, regardless of the fact that the cationic polymer dosage was varied from a low of 5.3 mg/L to a very high 32.2 mg/L.

Effect of mixing

For all the filter runs except 42A, 43A and 44A, the cationic polymer was injected into the algal suspension in a glass tube with a constriction immediately below the injection point to ensure complete and immediate blending. Thereafter, no agitation or stirring was provided. During 42A, 43A and 44A, the polymer was dosed as the suspension flowed into an Erlenmeyer flask which was agitated by a magnetic stirrer. The Erlenmeyer flask provided a mean hydraulic residence time of 17 to 20 minutes. This mixing period caused four effects.

First, the HDR was higher in the absence of mixing. During 43B (unmixed), the HDR was 23 mm/h, but during 43A (mixed) it dropped to 13 mm/h. During the first half of 42B (unmixed), before chlorine was added, the HDR was 31 mm/h, but during the same period, 42A (mixed) showed a HDR of only 21 mm/h. Second, filter ripening was evident during the first 3 to 4 hours of the run when mixing was absent. With mixing, the initial quality was better, but no initial ripening was observed, as is evident in Figure 29. Third, mixing delayed turbidity breakthrough during 42A/B, also shown in Figure 29. Fourth, there was a distinct difference in the removal of the different size fractions. The fraction of particles remaining in different size fractions were calculated from the electronic particle counts, which are included in Appendix C. Figure

Run	Turbidity NTU	CFT dosage mg/L	Removal ^a %
 13A	4.9	nil	41
13B	4.9	32.2	83
15A	3.9	9.9	89
15B	3.9	10.1	84
17A	3,1	5.4	86
17B	3.1	5.5	88
19A	3.4	5.3	97
19B	3.4	5.6	98

.

Table	26.	Average turbidity remove	al during	filtration	of
		<u>Scenedesmus_quadricauda</u>	suspensio	ons treated	with
		cationic polymer			

•

•

^aRemoval calculated for a 200 mm sand bed.



Figure 29. Effect of rapid mixing on initial ripening period (all runs shown) and on turbidity breakthrough (runs 42A and 42B). Bed depth 150 mm

30 shows the percentages for samples drawn from 42A and 42B after 3 hours, when turbidity removal was almost the same.

Figure 30 contains information which appears erroneous at first. It shows, for 42B, a larger number of large particles leaving in the filtrate than were present in the feed suspension. These extra particles could only have come from the flocculation of smaller particles. It is hypothesized that free cationic polymer was left after reaction with the EOM, but that it did not flocculate the algal cells before filtration, due to a lack of contact opportunities. When the suspension started to flow through the filter bed, the greatly increased contact opportunities allowed the cationic polymer to flocculate the smaller particles into fewer larger particles. The flocculation took place as the suspension flowed through the sand, and the larger particles were only formed deep in the bed. Before they could be effectively filtered, they reached the bottom end of the sand bed. If the sand bed were deeper, they probably would have been captured. During 42A, when mixing was introduced, the free cationic polymer had plenty of contact opportunities to flocculate the smaller cells into larger particles before the suspension reached the sand. In this case, the full sand depth was available for the removal of the larger particles. This hypothesis also holds for the previously reported results of jar test 5. (In that case, an increase in mixing intensity led to decreased turbidity in a paper-filtered sample.)

The difference in HDR can be explained by a difference in the density of the floc agglomerates that are formed in the two cases. During rapid mixing, a denser floc might be formed which will take up less space within the filter pores - hence a lower HDR. During contact flocculation, a looser, more voluminous floc may be deposited which will cause a higher HDR. This hypothesis is only speculative and no attempt was made to verify it experimentally.

Effect of prechlorination

During a few filtration experiments, prechlorination was introduced partway through the experiment. Filter run 16A started out with



Figure 30. Effect of mixing on the removal of different particle size fractions three hours into filter runs 42A and 42B

prechlorination, with no prechlorination to 16B. After almost 6 hours of filtration, the prechlorination was switched from 16A to 16B, leaving 16A without prechlorination. The corresponding changes in turbidity removal are shown in Figure 31.

During filter run 45A, just enough polymer was added to satisfy the EOM demand (measured nephelometrically), while 45B received 1.5 mg 573C/L more than 45A. Both filters started off without prechlorination. After 4 hours, just enough chlorine was added to both filters to satisfy the 10 minute chlorine demand of the EOM (which was separately determined as 18.2 mg/L). After another 3 hours, the chlorine dosage was cut in half for both filters. The filtration results are shown in Figure 32.

Figures 31 and 32 provide intriguing clues regarding the effects of prechlorination. First, prechlorination led to a sharp improvement in removal efficiency during filter runs 16B and 45B. The improvement upon chlorination was evident with both CATFLOC T and MAGNIFLOC 573C. (During jar test 1 described in the previous chapter, only 573C appeared to benefit from the addition of chlorine.) Second, the prechlorination only had an effect if polymer was added in excess of that demanded by the algal EOM. Filter run 45A, which had just enough polymer added to meet the EOM demand, was practically unchanged by prechlorination. Third, it is recalled from the first part of this chapter that chlorine alone, in the absence of any coagulants, led to a <u>reduction</u> in removal efficiency. Fourth, there appears to be a difference between the effects of high and low chlorine dosages. Figure 32, however, provides only one or two data points to support such a conclusion. The next paragraph deals with other experiments to pursue this question.

<u>High versus low chlorine dosage</u> Experiments 48 to 50 were designed to measure the difference in effects between high and low chlorine dosage. For every experiment, the polymer dosage between the two filters was approximately equal. During 48 and 49, the polymer dosage was at or below the EOM polymer demand, and during 50 it was in excess of the EOM polymer demand. The high chlorine dosage was approximately equal to the 10 minute EOM chlorine demand, which meant


Figure 31. Effect of prechlorination on the filtration of <u>Chlorella</u> <u>pyrenoidosa</u>. Chlorine added to 16A during first six hours, then switched to 16B. Bed depth 250 mm



Figure 32. Effect of prechlorination on the filtration of <u>Chlorella</u> <u>pyrenoidosa</u> - filter runs 45A and 45B. Bed depth 250 mm

that the suspension was exposed to the action of free chlorine for most or all of the chlorine contact time. The low chlorine dosage was half the high dosage, which meant that the suspension was exposed to combined chlorine for most of the chlorine contact time. The turbidity removal results are shown in Figure 33. These figures show consistent patterns. First, the high chlorine demand caused an extended filter ripening period. During 48A and 49A, the turbidity removal only levelled off after 4 hours. During 50A, it took even longer, but the exponential head loss increase indicates the presence of surface straining. Second, the lower chlorine dosage did not cause any ripening, but caused much better initial removal efficiency. After a few hours, however, the relative removal efficiency for high and low chlorine dosages reversed. Third, the high chlorine dosage caused a slightly higher HDR. Except in the case of run 50A (where straining probably had taken place), all the HDRs are sufficiently low not to be of any concern in full-scale operation.

Chlorine contact time The final experiment of the project (runs 51A and 51B), made a comparison between relatively short (0.8 minutes) and long (7.7 minutes) chlorine contact time before polymer addition. The results are shown in Figure 34. The longer contact time (51A) showed an exaggerated ripening period, which again could be due to a surface straining phenomenon if the relatively high HDR is considered. The shorter contact time showed the same ripening trend, but to a lesser degree. The reaction of chlorine with the algal suspension appears to be a slow reaction which is not as far advanced after 0.8 minutes as it is after 7.7 minutes. This is in agreement with the kinetic data for the reaction of chlorine with EOM, presented in the previous chapter.

Summary of Findings

• Without coagulants, algal removal by filtration was very poor. Lowering the pH down to the vicinity of the isoelectric point of the algal cells improved the removal dramatically. <u>Scenedesmus</u>, a

131



Figure 33. Effect of chlorine concentration on the filtration of <u>Chlorella pyrenoidosa</u> - filter runs 48A, 48B, 49A, 49B, 50A and 50B. Bed depth 200 mm



Figure 34. Effect of chlorine contact time before polymer addition on the filtration of <u>Chlorella pyrenoidosa</u>. Filter run 51A had 7.7 minutes of contact, filter run 51B only 0.8 minutes. Bed depth 250 mm

species with substantially larger cells, was better removed than <u>Chlorella</u>.

- Prechlorination, in the absence of coagulants, caused the algal removal to be even poorer.
- Metal coagulants generally caused good removal, but failed in a number of cases to do so. The decreased removal had no correlation with the coagulant or the algal concentration.
- In the cases where removal with the metal coagulants was good, the HDR was very high too high to be acceptable for continuous full-scale direct filtration.
- Prechlorination had only small effects on the removal efficiency and HDR of metal coagulants. Most notably, prechlorination caused earlier turbidity breakthrough.
- Turbidity removal with cationic polymer, for individual filter runs, was dependent on the cationic polymer charge concentration, and on the polymer concentration itself. Turbidity removal was not always reproducible from filter run to filter run.
- If just enough cationic polymer was added the satisfy the EOM demand for cationic polymer, removal was poor with a low HDR. At double that concentration, the removal was vastly improved and the HDR increased, but not excessively so. At lower cationic polymer concentration, the smaller particles were removed less efficiently than the larger particles, while the pattern was reversed at the high cationic polymer concentration.
- A rapid mixing period immediately after polymer addition had beneficial effects. The HDR was lowered and initial turbidity

removal was better, but without a period of filter ripening. Mixing also delayed turbidity breakthrough and caused about constant removal of all particle sizes. In the absence of mixing, smaller particles were removed well, but more large particles were found in the filtrate than were present in the feed suspension.

- Prechlorination, under certain conditions, markedly improved the turbidity removal by cationic polymers. If the cationic polymer was added in excess of the EOM demand for cationic polymer, the improvement was substantial. If less cationic polymer was added than the EOM demand for cationic polymer, no change in removal efficiency was observed.
- The concentration of chlorine affected the turbidity removal pattern. If enough chlorine was added to satisfy the chlorine demand of the EOM after 10 minutes, an extended filter ripening period was observed. If only half the chlorine concentration was added, no ripening was observed, but the initial removal efficiency was better.
- The chlorine contact time, prior to polymer addition, has to be fairly long to allow the reaction between the chlorine and the algal suspension. The chlorine effects were not nearly as evident after a contact time of 0.8 minutes as after a contact time of 7.7 minutes.

CONCLUSIONS AND RECOMMENDATIONS

Reliability of Laboratory Cultures

For this research project, laboratory cultures were used which were maintained with artificial nutrients and kept under continuous lighting. Such cultures normally have much lower bacterial biomass than natural suspensions and may influence the flocculation behavior of the algae (Jalali-Yazdi, 1984). Results have been presented to demonstrate that the laboratory-grown cultures used in this study were very similar to their counterparts in nature. The <u>Chlorella</u> and <u>Scenedesmus</u> laboratory cultures were characterized in four important ways; cell size, nonpurgeable organic carbon (NPOC) in the algal extracellular organic matter (EOM), molecular weight distribution of the NPOC in the algal EOM, and the charge concentration of the algal EOM. The results compared favorably to the results from other studies which dealt with very large cultures or with natural systems. If there were any significant differences between the laboratory monocultures and natural suspensions, they were not evident from the measured parameters.

Significance of Algal EOM

Algal growth results in a two-component system. The one part is the particulate cell fraction, while the other part consists of the suspending medium which contains the algal byproducts, collective called the algal EOM. Both of these fractions affect the behavior of the suspension during potable water treatment processes. It was experimentally shown that the soluble fraction exerted a significant demand for cationic polymer and chlorine, and Bernhardt et al. (1985b) have demonstrated the direct influence of the algal EOM on the demand for metal coagulants. The soluble fraction is, therefore, an important component to consider during the treatment of algal suspensions, in addition to the particulate fraction.

Cationic polymer reacted with the algal EOM in complete accordance with the charge neutralization/precipitation mechanism. The reaction between the EOM and cationic polymer is rapid and is almost complete after 1 minute. According to the literature, the complete reaction between cationic polymer and particles is considerably slower. Yeh and Ghosh (1981), for example, have shown that a rapid mixing time of 6 to 11 minutes is required for the complete reaction between a clay suspension and cationic polymer. During the competition between the algal cells and the algal EOM for the cationic polymer, the EOM will probably react first, until completion, before the reaction with the algal cells begin. The principle is the same as in a humic acid/clay suspension, which was so elegantly demonstrated by Narkis and Rebhun (1983). Their conclusion bears repetition:

"The cationic flocculant reacts preferentially with the organic matter. Only after complete reaction with the free humate or fulvate in solution does flocculation of clay mineral suspension begin."

The parallels between humic/fulvic acid and algal EOM invite an observation which is not directly within the focus of this research. During this project, no NPOC reduction was measured in the algal EOM after treatment with cationic polymer. Edzwald et al. (1987) measured a 40% DOC reduction in stream water (high in humic and fulvic acids) after treatment with cationic polymer. The explanation for this observed difference lies in the charge concentration difference between the suspensions. Algal EOM does not have such a high charge concentration as humic/fulvic acid. Furthermore, a large percentage of the NPOC in algal EOM has low molecular weight and is not polymeric in nature, while most of humic and fulvic acid is in the medium to high molecular weight bracket. If cationic polymer reacts only with the polymeric part of anionic suspensions, which the charge neutralization/precipitation

137

mechanism suggests, it will precipitate a much larger part of the NPOC from a humic/fulvic acid suspension than it would from algal EOM.

The electrical charge on the polymers within the algal EOM determines the demand for cationic polymer. The electrical charge on the algal polymers and the cationic polymer can be measured individually by colloid titration, and the EOM demand for cationic polymer calculated based on stoichiometric charge neutralization. The EOM demand for cationic polymer can also be measured by a much simpler turbidimetric method. The algal cells are separated from the suspension, and the remaining filtrate is then treated with different concentrations of cationic polymer. The resulting turbidity will increase with increasing cationic polymer dosage, up to a point where the turbidity will level off. This point corresponds to complete charge neutralization between the cationic polymer and the algal polymers. The turbidimetric method is simple, direct, requires no charge concentration standards, and can be carried out at a treatment plant with equipment that is available and with which operators are familiar.

Options for Direct Filtration of Algae

It is a clearly established fact that algal suspensions definitely require the addition of coagulants for reasonable removal. Without coagulants, the removal is very poor and not at all acceptable for water treatment practice.

The practical choice of a primary coagulant for direct filtration is currently restricted to either a metal coagulant, or a cationic polymer. Two very common metal coagulants, aluminum sulfate and ferric chloride, were investigated and achieved about the same results. The removal was mostly very good, with some exceptions where the removal was sharply lower. Although not demonstrated directly, it is highly probable that the poor removal was caused by interference from the algal EOM. Bernhardt et al. (1985b) showed how algal polymers complexed with the metal ions to keep the metal ions from precipitation, and how increased metal coagulant dosage will eventually overcome the interference. The most important disadvantage of metal coagulants, however, at the relatively high pH of algal suspensions, is that they precipitate to form additional particles. These metal hydroxide flocs add to the particle volume loaded onto the filter, causing head loss development rates which are unacceptable for prolonged and continuous operation. For <u>conventional</u> treatment, in contrast to <u>direct filtration</u> which this dissertation focuses on, this disadvantage would largely disappear. Conventional treatment is preceded by another solid/liquid separation step such as sedimentation, which removes the bulk of the solids before filtration.

Cationic polymer, at the concentrations used in this study, did not remove the algal cells very consistently. The removal was not very good for the shallow laboratory filters used, but would be acceptable if first-order removal continued throughout the much deeper filters used in practice. (A 60% removal through a 200 mm laboratory sand bed would then be equivalent to a removal of 94% through a similar sand bed of 1000 mm.) The head loss development, however, in contrast to the metal coagulants, was quite low. The cationic polymer dosage can be substantially increased for better removal without causing an unacceptable head loss development rate. It may be that higher polymer dosage will be prohibitively expensive - the cost aspect was not analyzed.

The next options to be considered would be combinations of metal coagulants and polymers. Such combinations were not pursued experimentally, but they would be the next logical step. Metal coagulants (which are cheaper than polymers on a mass basis), might prove useful to complex all the algal polymers first, followed by cationic polymer to flocculate the algal cells without creating a voluminous floc. (Such a strategy might not be feasible at very high pH, which is sometimes associated with algal growth.) Another alternative might be to add metal coagulants up to the point of the incipient formation of

139

hydroxide flocculi, and then add non-ionic or anionic polymer as a flocculation aid.

The introduction of a period of fairly vigorous mixing immediately after cationic polymer addition had beneficial effects. It lowered the head loss development rate, eliminated the initial period of filter ripening, and delayed the onset of turbidity breakthrough. The experimental mixing apparatus was crude and no quantitative measure of velocity gradient could be calculated. The experimental data do, however, indicate that mixing intensity and mixing time are important variables that should receive careful consideration in further research or pilot plant studies.

The role of chlorine remains enigmatic. Its effect on algal EOM alone is to increase the turbidity, whether used in conjunction with cationic polymer or not. Its effect on algal cells is to shrivel the cell membranes (Sukenik et al., 1987). When applied to a suspension with both cells and EOM, it causes poorer removal when no coagulants are used. If just enough cationic polymer is added to satisfy the EOM demand, chlorine has very little effect. If excess cationic polymer is added, the removal is significantly improved by prechlorination. Prechlorination, under the right conditions, will improve algal removal in accordance with the literature reviewed earlier, but a mechanistic explanation of its action on the different parts of the suspension remains to be proposed and verified.

Further Avenues for Research

While this study has identified and clarified a number of the operational variables involved in the treatment and filtration of algae, it has also brought several new issues into focus:

• It is necessary to verify the findings of this study on a larger scale. In this study, concentrated laboratory monocultures and high

140

concentrations of treatment chemicals were deliberately used on very small and shallow sand filters. In this way, well controlled suspensions were guaranteed and treatment effects were considerably amplified. The next logical step would be the operation of a larger depth experimental filter fed from a larger laboratory culture or from a natural impoundment.

- The selection of coagulants should be broadened to include combinations of metal coagulants and cationic polymers.
- The effects of polymer mixing intensity and time should be investigated in a quantitative manner to allow meaningful scale-up to full-scale treatment situations.
- The action of chlorine on algal suspensions should be approached in a systematic way to explain the observed effects during direct filtration. Chlorine effects on the algal cells should be investigated separately from the chlorine effects on the algal EOM, for the hypochlorous, hypochlorite, and combined forms respectively. Once these separate reactions are individually understood, it may provide the basis for a mechanistic explanation of the simultaneous reaction between the chlorine and the algal cells, and the chlorine and the algal EOM.

ACKNOWLEDGMENTS

The Engineering Research Institute at Iowa State University, the South African Foundation for Research Development, and GF&J Inc. provided financial support to make this program of study a reality.

My major professor, Dr. John L. Cleasby, assisted by committee members Drs. G. J. Atchison, E. R. Baumann, W. G. Crumpton and C. S. Oulman, guided me through the research program in a friendly, fair and supportive way.

My fellow students provided the intellectual prodding, stimulus and camaraderie which added so much fun to an otherwise lonely endeavor.

Tertia, Johann and Rudi offered boundless love, strength and understanding throughout.

REFERENCES

- Adin, Avner. "Solution of Granular Bed Filtration Equations". Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers, 104 (1978): 471-484.
- Adin, Avner, and Menahem Rebhun. "High-Rate Contact Flocculation -Filtration with Cationic Polyelectrolytes." <u>Journal of the American</u> <u>Water Works Association</u>, 66 (1974): 109-117.
- Al-Layla, M. Anis, and E. Joe Middlebrooks. "Algae Removal by Chemical Coagulation." <u>Water and Sewage Works</u>, 121 (1974): 76-80.
- Amirtharajah, Appiah, and K. M. Mills. "Rapid-Mix Design for Mechanisms of Alum Coagulation." <u>Journal of the American Water Works</u> <u>Association</u>, 74 (1982): 210-216.
- Amirtharajah, Appiah, and Susumu Kawamura. "System Design for Polymer Use." <u>Use of Organic Polyelectrolytes in Water Treatment</u>. Proceedings of an American Water Works Association Seminar, Las Vegas, Nevada, June 5-9, 1983.
- Amy, Gary L., and Paul A. Chadik. "Cationic Polyelectrolytes as Primary Coagulants for Removing Trihalomethane Precursors." <u>Journal of the</u> <u>American Water Works Association</u>, 75 (1983): 527-531.
- Andrews, R. H. G. "Gravity Filtration of Algal Suspensions". Ontario Water Resources Commission, Research Publication No. 21, 1968.
- Avnimelech, Yoram, Bill W. Troeger, and Lester W. Reed. "Mutual Flocculation of Algae and Clay: Evidence and Implications". <u>Science</u>, 216 (1982): 63-65.
- Benefield, Larry D., Joseph F. Judkins, and Barron L. Weand. <u>Process</u> <u>Chemistry for Water and Wastewater Treatment</u>. Englewood Cliffs, New Jersey: Prentice-Hall, Inc., 1982.
- Bernhardt, Heinz, Oluf Hoyer, and Bernhard Lüsse. "Untersuchungen zur Beeinflussung der Flockung und Flockenabtrennung durch Algenbürtige Organische Substanzen." <u>Zeitschrift für Wasser-</u> und Abwasser-Forschung, 18 (1985a): 6-17.
- Bernhardt, Heinz, Oluf Hoyer, Helmut Schell, and Bernhard Lüsse. "Reaction Mechanisms involved in the Influence of Algogenic Organic Matter on Flocculation." Zeitschrift für Wasser- und Abwasser-Forschung, 18 (1985b): 18-30.
- Bernhardt, Heinz, Oluf Hoyer, Bernhard Lüsse, and Helmut Schell. "Investigations on the Influence of Algal-derived Organic Substances

on Flocculation and Filtration." In <u>Treatment of Drinking Water for</u> <u>Organic Contaminants</u>. Ed. Peter M. Huck and Peter Toft. Proceedings of the Second National Conference on Drinking Water, Edmonton, Canada, April 7-8, 1986. New York: Pergamon Press, 1986.

- Borchardt, J. A., and Charles R. O'Melia. "Sand Filtration of Algal Suspensions". Journal of the American Water Works Association, 43 (1961): 438-452.
- Cleasby, John L. "Disinfection". Class notes for CE 523. Dept. of Civil and Construction Engrg., Iowa State University, Fall 1985.
- Cohen, J. M., G. A. Rourke, and R. L. Woodward. "Natural and Synthetic Polyelectrolytes as Coagulant Aids." Journal of the American Water Works Association, 50 (1958): 463-478.
- Davis, Eric, and Jack A. Borchardt. "Sand Filtration of Particulate Matter". Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, 92 (1966): 47-60.
- Deb, Arun K. "Theory of Sand Filtration". <u>Journal of the Sanitary</u> <u>Engineering Division, Proceedings of the American Society of Civil</u> <u>Engineers</u>, 95 (1969): 399-422.
- Driscoll, Charles T., and Raymond D. Letterman. "The Chemistry and Fate of Aluminum in Drinking Water." Accepted for publication in the Journal of the Environmental Engineering Division, Proceedings of the American Society of Civil Engineers, ca. 1988.
- Duben, Mark A. "Molecular Size Distribution of Organic Carbon and Trihalomethane Formation in Small Water Treatment Plants That Use Alternative Disinfectant/Oxidant Chemicals." M.S. thesis. Iowa State University, Ames, Iowa, 1987.
- Echelberger, Wayne F., Joseph L. Pavoni, Philip C. Singer, and Mark W. Tenney. "Disinfection of Algal Laden Waters". Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, 97 (1971): 721-730.
- Edzwald, James K., and Desmond F. Lawler. "Mechanisms of Particle Destabilization for Polymers in Water Treatment." <u>Use of Organic</u> <u>Polyelectrolytes in Water Treatment</u>. Proceedings of an American Water Works Association Seminar, Las Vegas, Nevada, June 5-9, 1983.
- Edzwald, James K., William C. Becker, and Steven J. Tambini. "Organics, Polymers, and Performance in Direct Filtration." <u>Journal of</u> <u>Environmental Engineering</u>, <u>Proceedings of the American Society of</u> <u>Civil Engineers</u>, 113 (1987): 167-185.

- Evins, C., and G. F. Greaves. "Penetration of Water Treatment Works by Animals." Water Research Centre, Technical Report TR 115 (1979).
- Fair, Gordon M., J. Carrell Morris, Shih Lu Chang, Ira Weil, and Robert P. Burden. "The Behavior of Chlorine as a Water Disinfectant". <u>Journal of the American Water Works Association</u>, 40 (1948): 1051-1060.
- Foess, G. W., and J. A. Borchardt. "Electrokinetic Phenomena in the Filtration of Algal Suspensions". <u>Journal of the American Water</u> <u>Works Association</u>, 61 (1969): 333-338.
- Folkman, Yair, and Alberto M. Wachs. "Filtration of Chlorella Through Dune-sand". Journal of the Sanitary Engineering Division, <u>Proceedings of the American Society of Civil Engineers</u>, 96 (1970): 675-690.
- Friedman, A. A., D. A. Peaks, and R. L. Nichols. "Algae Separation from Oxidation Pond Effluents." <u>Journal of the Water Pollution Control</u> <u>Federation</u>, 49 (1977): 111-119.
- Golueke, C. G., and W. J. Oswald. "Harvesting and Processing Sewage-Grown Planktonic Algae." <u>Journal of the Water Pollution Control</u> <u>Federation</u>, 37 (1965): 471-498.
- Green, D. E., and P. K. Stumpf. "The Mode of Action of Chlorine". Journal of the American Water Works Association, 38 (1946): 1301-1310.
- Griffin, A. E. "Review of the Progress in Break Point Chlorination". Journal of the New England Water Works Association, 61 (1947): 145-150.
- Guillard, Robert R. L. "Culture of Phytoplankton for Feeding Marine Invertebrates". In <u>Culture of Marine Invertebrate Animals</u>. Ed. W. L. Smith and M. H. Chanley. New York: Plenum Publishing Corporation, 1975.
- Halperin, Lazar, Alberto Wacks, Jacobo Sachs, Pincas Bercovits, and Ilan Rosenstock. "Treatment of Lake Kineret Water by Preozonation and Contact Filtration." Final Report. Mekorot Water Co. Ltd, Water Quality Department, Haifa, 1986.
- Harris, Robert H., and Ralph Mitchell. "The Role of Polymers in Microbial Aggregation". <u>Annual Review of Microbiology</u>, 27 (1973): 27-48.
- Hellebust, J. A. "Extracellular Products". In <u>Algal Physiology and</u> <u>Biochemistry</u>. Ed. W. D. P. Stewart. Berkeley, California: University of California Press, 1974.

- Hom, Leonard W. "Kinetics of Chlorine Disinfection in an Ecosystem." Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, 98 (1972): 183-194.
- Hoyer, Oluf, Bernhardt Lüsse, and Heinz Bernhardt. "Isolation and Characterization of Extracellular Organic Matter (EOM) from Algae". Zeitschrift_für Wasser- und Abwasser-Forschung, 18 (1985): 76-90.
- Ibrahim, J., L. Squires, H. Mitwalli, and M. Tahas. "Chlorine as an Algicide in a Conventional Water Treatment Plant". <u>International</u> <u>Journal of Environmental Studies</u>, 20 (1982): 41-46.
- Ives, Kenneth J. "An Investigation of Engineering Problems of Algal Removal." Ph.D. dissertation, University College, London, 1955.
- Ives, Kenneth J. "The Significance of Surface Electric Charge on Algae in Water Purification." Journal of Biochemical and Microbiological Technology and Engineering, 1 (1959): 37-47.
- Ives, Kenneth J. "Simulation of Filtration on Electronic Digital Computer". Journal of the American Water Works Association, 52 (1960): 933-939.
- Ives, Kenneth J. "Filtration of Radioactive Algae". Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, 87 (1961): 23-37.
- Ives, Kenneth J. "Deep Bed Filters." In <u>Mathematical Models and Design</u> <u>Methods in Solid-Liquid Separation</u>. Ed. A. Rushton. NATO ASI Series E, Applied Sciences, No. 88. Dordrecht, Netherlands: Martinus Nijhoff Publishers, 1985.
- Jacobsen, Samuel, and Marshall S. Wellington. "Introduction of Prechlorination to Slow Sand Filters". <u>Journal of the New England</u> <u>Water Works Association</u>, 63 (1949): 129-147.
- Jalali-Yazdi, Y. "Algal Growth and Flocculation in Inorganic Unialgal Systems." Ph.D. dissertation, University of Missouri, Columbia, 1984.
- Janssens, J. G., H. Van Dijck, J. Meheus, and F. Van Hoof. "Comparative Investigation of Preozonation and Prechlorination in Relation to Removal of Algae by Direct Filtration." In <u>The Role of Ozone in</u> <u>Water and Wastewater Treatment</u>. Ed. R. Perry and A. E. McIntyre. Proceedings of an International Conference, November 13-14, 1985. London: Selper Ltd, 1985.

.

- Johnson, D., M. R. Farley, R. E. Youngman, N. P. Yadav, and J. T. West. "Removal of Algae by Various Unit Processes." Water Research Centre, Technical Report TR 45, 1977.
- Johnson, P. N., and Appiah Amirtharajah. "Ferric Chloride and Alum as Single and Dual Coagulants." <u>Journal of the American Water Works</u> <u>Association</u>, 75 (1983): 232-239.
- Kawamura, Susumu, and Yoshitaro Tanaka. "Applying Colloid Titration Techniques to Coagulant Dosage Control." <u>Water and Sewage Works</u>, 113 (1966): 348-357.
- Kawamura, Susumu, G. P. Hanna Jr., and K. S. Shumate. "Application of Colloid Titration Technique to Flocculation Control." <u>Journal of</u> <u>the American Water Works Association</u>, 59 (1967): 1003-1013.
- Klute, Rudolf, and Uwe Neis. "Coagulation of Algae and Subsequent Removal by Filtration or Flotation." <u>Water Supply</u>, 1 (1983): 157-162.
- Kott, Yehuda. "Chorination Dynamics in Wastewater Effluents." <u>Journal</u> of the Sanitary Engineering Division, Proceedings of the American <u>Society of Civil Engineers</u>, 97 (1971): 647-659.
- Lin, S. D., R. L. Evans, and D. B. Beuscher. "Algal Removal by Alum Coagulation." Illinois State Water Survey, Report of Investigation 68, 1971.
- Ludwig, Daniel Dean. "Filtration and Chlorination of Small Water Supplies". Ph.D. dissertation, Iowa State University, Ames, Iowa, 1961.
- Lüsse, Bernhard, Oluf Hoyer, and Carl J. Soeder. "Mass Cultivation of Planktonic Freshwater Algae for the Production of Extracellular Organic Matter (EOM)". Zeitchrift für Wasser- und Abwasser-Forschung, 18 (1985): 67-75.
- Mackie, W., and R. D. Preston. "Cell Wall and Intercellular Region Polysaccharides". In <u>Algal Physiology and Biochemistry</u>. Ed. W. D. P. Stewart. Berkeley, California: University of California Press, 1974.
- Mangravite, Frank J. "Synthesis and Properties of Polymers Used in Water Treatment." <u>Use of Organic Polyelectrolytes in Water Treatment</u>. Proceedings of an American Water Works Association Seminar, Las Vegas, Nevada, June 5-9, 1983.
- McGarry, Michael G. "Algal Flocculation with Aluminum Sulfate and Polyelectrolytes." <u>Journal of the Water Pollution Control</u> <u>Federation</u>, 42 (1970): 191-201.

- Morris, J. Carrell. "The Acid Ionization Constant of Hypochlorous Acid from 5°C to 35°C". <u>Journal of Physical Chemistry</u>, 70 (1966a): 3798.
- Morris, J. Carrell. "Future of Chlorination". <u>Journal of the American</u> <u>Water Works Association</u>, 58 (1966b): 1475-1482.
- Morrison, Robert Thornton, and Robert Neilson Boyd. <u>Organic Chemistry</u>. 3rd edition. Boston, Massachusetts: Allyn and Bacon, Inc., 1973.
- Morrow, John J., and Emerson G. Rausch. "Colloid Destabilization with Cationic Polyelectrolytes as Affected by Velocity Gradients." Journal of the American Water Works Association, 66 (1974): 646-653.
- Naghavi, B., and R. F. Malone. "Algae Removal by Fine Sand/Silt Filtration". <u>Water Research</u>, 20 (1986): 377-383.
- Narkis, Nava, and Menachem Rebhun. "Inhibition of Flocculation Processes in Systems Containing Organic Matter." <u>Journal of the Water</u> <u>Pollution Control Federation</u>, 55 (1983): 947-955.
- O'Melia, Charles R. "Coagulation." In <u>Water Treatment Plant Design for</u> <u>the Practicing Engineer</u>. Ed. Robert L. Sanks. Ann Arbor, Michigan: Ann Arbor Science Publishers, 1978. 65-82.
- Oron, Gideon, Gedaliah Shelef, Anna Levi, Arie Meydan, and Yossef Azov. "Algae/Bacteria Ratio in High-Rate Ponds Used for Waste Treatment". <u>Applied and Environmental Microbiology</u>, 38 (1979): 570-575.
- Palmer, Mervyn C. <u>Algae and Water Pollution</u>. United States Environmental Protection Agency, Report EPA-600/9-77-036. Washington, D.C.: U.S. Government Printing Office, 1977.
- Pressman, Maurice. "Cationic Polyelectrolytes as Prime Coagulants in Natural-Water Treatment." <u>Journal of the American Water Works</u> <u>Association</u>, 59 (1967): 169-181.
- Raab, Frank. "Taste and Odor Troubles in the Minneapolis Water Supply". Journal of the American Water Works Association, 23 (1931): 430-434.
- Sakthivadivel, R., V. Thanikachalam, and S. Seetharaman. "Head-Loss Theories in Filtration." <u>Journal of the American Water Works</u> <u>Association</u>, 64 (1972): 233-238.
- Sastry, C. A., M. N. Rao, and A. V. Rao. "Studies on Separation of Algae from Stabilization Pond Effluents by Coagulation." <u>Journal of the</u> <u>Institution of Engineers (India)</u>, 57 (1977): 91-94.
- Scheid, Francis. <u>Theory and Problems of Numerical Analysis</u>. Schaum's Outline Series in Mathematics. New York: McGraw-Hill Book Company, 1968.

- Schell, Helmut, and Heinz Bernhardt. "Bestimmung der Ladungskonzentration als Steuergrösse des Flockungsmittelzusatzes, Teil 1." <u>Zeitschrift für Wasser- und Abwasser-Forschung</u>, 19 (1986): 51-59.
- Standard Methods for the Examination of Water and Wastewater, 16th ed. Washington, D.C.: American Public Health Association, 1985.
- Streeter, H. W., and C. T. Wright. "Prechlorination in Relation to the Efficiency of Water Filtration Processes". <u>Journal of the American</u> <u>Water Works Association</u>, 23 (1931): 22-49.
- Stump, Vernon L., and John T. Novak. "Mixing of Polyelectrolytes for Direct Filtration." <u>Proceedings of the American Water Works</u> <u>Association Annual Conference</u>, Anaheim, California, May, 1977.
- Sukenik, A., B. Teltch, A. W. Wachs, G. Shelef, I. Nir, and D. Levanon. "Effect of Oxidants on Microalgal Flocculation." <u>Water Research</u>, 21 (1987): 533-539.
- Taras, M. J. "Effect of Free Residual Chlorination on Nitrogen Compounds in Water". Journal of the American Water Works Association, 45 (1953): 47-61.
- Tenney, Mark W., Wayne F. Echelberger, Ronald G. Schuessler, and Joseph L. Pavoni. "Algal Flocculation with Synthetic Organic Polyelectrolytes". <u>Applied Microbiology</u>, 18 (1969): 965-971.
- Tilton, R. C., John Murphy, and J. K. Dixon. "The Flocculation of Algae with Synthetic Polymeric Flocculants". <u>Water Research</u>, 6 (1972): 155-164.
- Van Olphen, H. <u>An Introduction to Clay Colloid Chemistry</u>. 2nd edition. New York: John Wiley and Sons, 1977.
- Van Vuuren, Lukas R. J., and Frank A. van Duuren. "Removal of Algae from Wastewater Maturation Pond Effluent." <u>Journal of the Water</u> <u>Pollution Control Federation</u>, 37 (1965): 1256-1262.
- Volkova, N. C., N. V. Khominskaya, V. M. Grashchenko, and S. A. Azoyan. "Use of Polyethylene Imines in Flotation and Improving the Filtration of Suspensions of Blue-Green Algae." <u>Hydrobiological</u> <u>Journal</u>, 18 (1982): 59-63.
- Wetzel, Robert G. <u>Limnology</u>. 2nd ed. Philadelphia, Pennsylvania: Saunders College Publishing, 1983.
- White, George Clifford. "Chlorination and Dechlorination: A Scientific and Practical Approach". Journal of the American Water Works <u>Association</u>, 60 (1968): 540-555.

- Whitener, J. S. "Filtration Improvements and Economics with Prechlorination". Journal of the American Water Works Association, 20 (1928): 61-63.
- Wiesner, Mark R., and Pierre Mazounie. "Raw Water Characteristics and the Selection of Water Treatment Configurations for Particle Removal". Presented at a Preconference Seminar on Coagulation at the Annual Conference of the American Water Works Association, Kansas City, Missouri, June, 1987.
- Wight, Jeffrey L., Bruce A. Johnson, J. H. Reynolds, and E. J. Middlebrooks. "How Chlorine Affects Soluble COD in Algal Laden Systems". <u>Water and Sewage Works</u>, 125 (1978): 48-54.
- Yeh, Hsuan-Hsien, and Mriganka M. Ghosh. "Selecting Polymers for Direct Filtration." Journal of the American Water Works Association, 73 (1981): 211-218.

APPENDIX A: COLLOID TITRATION PROCEDURE

(Procedure adapted from Schell and Bernhardt (1986))

Reagents

Potassium polyvinyl sulfate (PPVS), marketed as "polyvinylsulfuric acid potassium salt" by the Eastman Kodak Company (Rochester, New York), and as "poly(vinyl sulfate, potassium salt)" by the Aldrich Chemical Company (Milwaukee, Wisconsin):

Dissolve 32.4 mg in 1 L double distilled water. One mL of this solution is equivalent to 0.0002 meq.

Toluidine blue indicator (TBI):

Dissolve 40 mg in 1 L double distilled water.

Cationic polymer (CP):

Add 100 mg of the product as received to 1 L double distilled water.

Standardize Cationic Polymer

Dilute the CP 10 times to obtain a 10 mg/L solution. Take 100 mL of the 10 mg/L CP solution, add 3 mL TBI to obtain a blue color. Titrate with PPVS standard until blue changes to pink. The cationic charge concentration is calculated from:

CP charge concentration in $\mu eq/mg = (mL PPVS) \times 0.2$

Determine Charge Concentration of Unknown

Take 100 mL of unknown sample, add 5 mL of 100 mg/L CP solution and stir for 5 minutes. Add 3 mL of TBI. Titrate with PPVS standard until

blue changes to pink. The charge concentration of the unknown is calculated from:

charge concentration of unknown in $\mu eq/L$

- CP charge concentration x 5 minus (mL PPVS) x 2

Example

A 10 mg/L solution of cationic polymer requires 18.3 mL of PPVS to change the color from blue to pink. The charge concentration of the cationic polymer is $18.3 \times 0.2 = 3.66 \ \mu eq/mg$.

5 mL of a 100 mg/L solution of the same polymer is then added to an unknown sample. After 5 minutes of reaction time, it requires 6.7 mL of PPVS to obtain the color change. The charge concentration of the unknown is $3.66 \times 5 - 6.7 \times 2 = 18.3 - 13.4 = 4.9 \ \mu eq/L$.

Remark

In this case, where the cationic polymer is only calibrated <u>en route</u> to the determination of the charge concentration of an unknown, no blank correction is required, for it is assumed to be equal in both titrations. If the absolute value of the charge concentration of the cationic polymer is required, it will be necessary to make a blank correction with a 100 mL aliquot of double distilled water.

APPENDIX B: FILTRATION DATA

- Abbreviations
- Hydraulic data
- Chemical dosage data
- Average feed water characteristics
- Measured head loss values
- Measured turbidity values

ABBREVIATIONS USED IN APPENDIX B:

Chemical dosage data:

CHEM	Treatment chemical used
CONC	Concentration of chemical feed solution
TIME	Chemical contact time before next chemical or filtration
DOSE	Chemical dosage concentration
C12	Chlorine
CFT	Catfloc T
573C	Magnifloc 573C

Average raw water characteristics:

PART. VOL.	Particle volume calculated from particle counts
NPOC	Non-purgeable organic carbon
SS	Suspended solids
C	<u>Chlorella</u>
S	Scenedesmus

HYDRAULIC LOADING DATA

,

	RUN		FLOW - FILTER A (mL/min)				FLOW - (ml	FILTER /min)	B	LIQUID (n	DEPTH (m)	
•		RAW	DOSE 1	DOSE 2	TOTAL	RAW	DOSE 1	DOSE 2	TOTAL	#1	#2	
	1	46.68	1.08	1.14	48.90	45.38	1.07	1.15	47.60	5.20	5.06	0.25
	2	59.78	1.08	1.14	62.00	58.08	1.07	1.15	60.30	6.60	6.41	0.25
	3	44.38	1.08	1.14	46.60	43.18	1.07	1.15	45.40	4.96	4.83	0.15
	4	45.88	1.08	1.14	48.10	44.58	1.07	1.15	46.80	5.12	4.98	0.15
	5	47.08	1.08	1.14	49.30	45.78	1.07	1.15	48.00	5.24	5.11	0.15
	6	40.48	1.08	1.14	42.70	39.38	1.07	1.15	41.60	4.54	4.43	0.15
	7	47.78	1.08	1.14	50.00	46.48	1.07	1.15	48.70	5.32	5.18	0.15
	8	49.88	1.08	1.14	52.10	48.38	1.07	1.15	50.60	5.54	5.38	0.15
	9	44.78	1.08	1.14	47.00	44.18	1.07	1.15	46.40	5.00	4.94	0.15
	10	46.68	1.08	1.14	48.90	45.08	1.07	1.15	47.30	5.20	5.03	0.15
	11	45.08	1.08	1.14	47.30	43.78	1.07	1.15	46.00	5.03	4.89	0.15
	12	44.78	1.08	1.14	47.00	43.38	1.07	1.15	45.60	5.00	4.85	0.25
	13	44.78	1.08	1.14	47.00	44.48	1.07	1.15	46.70	5.00	4.97	0.25
	14	47.08	1.08	1.14	49.30	46.18	1.07	1.15	48.40	5.24	5.15	0.10
	15	48.08	1.08	1.14	50.30	47.38	1.07	1.15	49.60	5.35	5.28	0.25
	16	46.38	1.08	1.14	48.60	45.78	1.07	1.15	48.00	5.17	5.11	0.25
	17	45.18	1.08	1.14	47.40	44.58	1.07	1.15	46.80	5.04	4.98	0.25
	18	46.88	1.08	1.14	49.10	45.58	1.07	1.15	47.80	5.22	5.09	0.15
	19	45.48	1.08	1.14	47.70	43.28	1.07	1.15	45.50	5.07	4.84	0.15
	20	48.08	1.08	1.14	50.30	45.88	1.07	1.15	48.10	5.35	5.12	0.15
	21	42.38	1.08	1.14	44.60	40.08	1.07	1.15	42.30	4.74	4.50	0.15
	22	47.18	1.08	1.14	49.40	45.88	1.07	1.15	48.10	5.26	5.12	0.25
	23	42.88	1.08	1.14	45.10	41.68	1.07	1.15	43.90	4.80	4.67	0.10
	24	42.58	1.08	1.14	44.80	41.48	1.07	1.15	43.70	4.77	4.65	0.10
	25	47.28	1.08	1.14	49.50	45.88	1.07	1.15	48.10	5.27	5.12	0.10
	26	50.88	1.08	1.14	53.10	49.38	1.07	1.15	51.60	5.65	5.49	0.10
	27	47.98	1.08	1.14	50.20	46.38	1.07	1.15	48.60	5.34	5.17	0.25
	28	46.58	1.08	1.14	48.80	45.38	1.07	1.15	47.60	5.19	5.06	0.25
	29	39.26	1.12	1.17	41.55	39.63	1.11	1.20	41.94	4.42	4.46	0.25
	30	40.41	1.10	1.19	42.70	39.25	1.10	1.22	41.57	4.54	4.42	0.25

HYDRAULIC LOADING DATA

RUN		FLOW - FILTER A {mL/min}				FLOW - (mL)	FILTER (min)	8	LIQUID (m	DEPTH (m)	
	RAW	DOSE I	DOSE 2	TOTAL	RAN	DOSE I	00SE 2	TOTAL	#L	#2	
31	44.93	1.12	1.18	47.23	44.32	1.08	1.21	46.61	5.02	4.96	0.25
32	46.98	1.12	1.18	49.28	46.57	1.07	1.18	48.82	5.24	5.19	0.25
33	41.58	1.08	1.14	43.80	42.29	1.05	1.16	44.50	4.66	4.73	0.25
34	38.45	1.09	1.16	40.70	39.38	1.06	1.18	41.62	4.33	4.43	0.25
35					41.61	0.00	0.00	41.61		4.43	0.25
36	45.14	0.00	1.16	46.30					4.93		0.25
37	41.82	1.15	1.23	44.20					4.70		0.25
38	44.50	1.12	1.18	46.80					4.98		0.25
39	45.01	1.14	1.20	47.35	47.71	1.10	1.23	50.04	5.04	5.32	0.25
40	46.51	1.16	1.23	48.90	50.18	1.12	1.25	52.55	5.20	5.59	0.25
<u>41</u>	45.67	1.17	1.26	48.10	49.76	1.15	1.29	52.20	5.12	5.55	0.15
42	37.49	1.09	1.20	39.78	40.60	1.08	1.21	42.89	4.23	4.56	0.15
43	43.56	1.01	1.16	45.73	48.17	1.02	1.15	50.34	4.86	5.36	0.15
44	38.26	1.14	1.27	40.67	40.34	1.25	1.24	42.83	4.33	4.56	0.15
45	51.16	1.04	1.14	53.34	55.56	0.95	1.15	57.66	5.67	6.13	0.20
45	53.52	1 20	1.08	55.80	47.14	1,18	1.11	49.43	5.94	5.26	0.20
40	46 51	1.09	1.22	48.82	41.04	1.13	1.20	43.37	5,19	4.61	0.20
47	40.51	1 05	1 18	AR 34	42.27	1.07	1.17	44.51	5.14	4.74	0.20
40	40111	1 10	1 21	45.75	44 10	1 12	1.20	46.42	4.87	4.94	0.20
47	43.43	1.05	1 16	45 54	49 51	1 11	1.20	45.82	4.84	4.87	0.20
50	43.32	1.00	1 10	AG 12	43.31	1 09	1.15	45.72	4.91	4.86	0.20
	43.07	1.03	01.11	40416	73.70	1107					

•

CHEHICAL DOSAGE DATA

.

J

RUN		FILTER	A - DC)SE 1		FILTER	1 A - DO)SE 2		FILTER	B - D()SE I		FILTER	B DOSE	2
	CHEM	CONC (mg/L)	DOSE (mg/L)	TINE (min)	CHEM	CONC (mg/L)	DOSE (mg/L)	TINE (min)	CHEN	CONC (mg/L)	DOSE (mg/L)	TINE (min)	CHEM	CONC (mg/L)	DOSE (mg/L)	TINE (min)
1					Fe	96	2.2	7.4					Fe	73	1.8	7.7
2					Fe	107	2.0	5.9					Fe	134	2.6	6.0
3					Fe	101	2.5	9.0					Fe	88	2.2	9.3
4	C12	233	5.4	7.3	Fe	74	1.8	8.8					Fe	74	1.8	9.0
5	C12	481	10.8	7.1	Fe	90	2.1	8.5					Fe	90	2.2	8.8
6	C12	481	12.5	8.3	Fe	89	2.4	9.9					Fe	89	2.5	10.1
7					Fe	115	2.6	8.4	C12	430	9.7	7.2	Fe	115	2.7	8.6
8	C12	2585	54.8	6.8				8.1								
9									C12	257	6.1	7.6				9.1
10	C12	3009	68.0	7.2				8.6								
11									C12	2673	63.8	1.1			<i>c</i> o 1	9.2
12					C12	2738	66.4	7.7					CIZ	2/38	69.I	8.0
13														1310	32.3	1.0
14					CFT	455	10.5	9.1	CIZ	1782	40.4	1.5		455	10.0	9.3
15	C12	3420	75.1	7.0	CFT	436	9.9	7.2						430	10.1	1.3
16	C12	891	20.3	7.3	CFT	227	5.3	7.5	C12	891	20.3	1.3		221	5.4	1.0
17					CFT	223	5.4	1.1	C12	873	20.5	1.5	CEI	223	5.5	1.8
18	C12	1310	29.5	7.2	CFT	223	5.2	8.6	C12	1310	30.0	0.8	CEL	223	5.4	8.8
19	C12	873	20.3	7.4	CFT	223	5.3	8.8	C12	873	21.1	0.8	CFI	223	5.0	9.3
20	C12	1360	29.9	7.0	Fe	93	2.1	8,4					Fe	93	2.2	8.8
21					Fe	68	1.7	9.4	C12	1340	34.8	0.9	Fe	68	1.8	10.0
22	C12	1340	30.0	7.1	Fe	91	2.1	7.4	C12	1340	30.5	0.8	te .	91	2.2	1.0
23	C12	1310	32.2	7.8	Fe	67	1.7	10.0	C12	1310	32.8	0.9	re	6/	1.0	10.3
24	C12	1310	32.4	7.4	A1	134	3.4	9.5					Al	134	3.5	9.1
25	C12	873	19.5	7.1	A1	45	1.0	9.1					AI.	45	1.1	9.4
26	C12	873	18.1	6.6	Al	67	1,4	8.5					. Al	6/	1.5	8./
27	C12	873	19.2	7.0	Al	45	1.0	7.3	C12	873	19.7	0.8	AI	45	1.1	9.5
28	C12	436	9.9	7.2	A I	45	1.1	7.5	C12	436	10.0	0.8	A1	45	1.1	1.0
29									C12	109	3.0	0.9				8./
30	C12	218	5.8	8.3	CFT	178	5.0	8.5					CFT	178	5.2	8.8

CHENICAL DOSAGE DATA

RUN		FILTER	A - D(DSE 1		FILTER	A - DC)SE 2		FILTER	8 - D(DSE I		FILTER	B DOSE	2
	CHEN	CONC (mg/L)	DOSE (mg/L)	TIME (min)	CHEM	CONC (mg/L)	DOSE (mg/L)	TINE (min)	CHEN	CONC (mg/L)	DOSE (mg/L)	TIME (min)	CHEM	CONC (mg/L)	DOSE (mg/L)	TINE (min)
31 32	C12 C12	109 175	2.7 4.1	7.5 7.2	AT	67	1.7	7.7 7.4					AI	67	1.7	7.8
33	C12	131	3.3	8.1	CFT	131	3.4	8.3					CFT	131	3.4	8.2
34	C12	700	19.3	8.7	AI	68	1.9	8.9					Al	68	1.9	8.7
35																
36					CFT	22	0.6	7.9								
37					A1	87	2.4	8.2								
38								_								
39	C12	175	4.3	7.5	CFT	89	2.3	1.7					CFT	89	2.2	1.3
40	C12	130	3.2	7.2	A1	130	3.3	7.4					AI	130	3.1	6.9
41	C12	436	10.9	7.3	CFT	65	1.7	7.6	C12	436	9.8	6.8	573C	65	1.5	1.0
42	C12	436	12.3	8.9	573C	131	4.0	20.1	C12	436	11.3	8.3	573C	131	3.7	8.5
43					573C	131	3.3	17.5					573C	131	3.0	7.2
44	C12	436	12.6	8.7	573C	131	4.1	19.7	C12	436	13.1	8.3	573C	131	3.8	8.5
45	C12	1090	21.7	6.6	573C	175	3.7	6.8	C12	1090	18.3	6.1	573C	262	5.2	6.3
46					573C	145	2.8	6.5					573C	160	3.6	7.4
47	C12	927	21.2	7.2	573C	93	2.3	7.5	C12	836	22.4	8.2	573C	167	4.6	8.4
48	C12	855	19.0	7.3	573C	64	1.6	7.5	C12	373	9.2	7.9	573C	58	1.5	8.2
49	C12	987	24.2	7.7	573C	82	2.2	8.0	C12	445	11.0	7.6	573C	76	2.0	7.8
50	C12	900	21.5	7.8	573C	170	4.3	8.0	C12	4 44	11.0	7.7	573C	174	4.6	7.9
51	C12	961	22.5	7.7	573C	196	5.0	7.9	C12	924	22.6	0.8	573C	191	4.8	8.0

.

AVERAGE RAW WATER CHARACTERISTICS

·

RUN		TURBIDITY (NTU)	Y	i	PART. VOL (mm3/L)	. .		рH		NPOC (mg/L)	SS (mg/L)	GENUS
	RAW	#1 IN	#2 IN	RAW	#1 IN	#2 1N	RAW	#1 IN	#2 IN	RAW	RAW	
1	3.7	3.7	3.7					7.5	7.6			C
2	2.8	3.0	3.3									C
3	2.0	2.5	2.3					6.5	6.7			C
4	1.9	2.0	2.1									C
5	3.4	4.0	3.9									C
6	1.7	2.9	2.8	5.5	5.1	4.8	7.4	7.3	7.2			C
7	2.0	2.5	2.4	6.8	5.5	8.2						C
8	6.2	5.4	5.7	34.0	32.0	32.0	8.0	9.1	8.1		15.0	S
9	2.1	2.1	2.1	4.4	4.0	3.9	7.9	8.1	9.1			C
10	7.0	11.4	6.7	41.0	42.0	40.0	3.0	3.3	3.1			S
11	1.8	2.1	2.5	4.9	5.1	5.2	6.5	6.5	5.9			C
12	6.4	6.5	8.6	37.0	33.0	36.0	8.7	8.8	6.2			S
13	4.9	4.5	4.7	28.0	28.0	28.0						S
14	2.3	2.5	3.4	5.5	6.0	7.5	7.0					C
15	3.9	4.7	3.5	24.0	24.0	24.0	6.2					S
16	2.6	2.6	2.6	7.8	6.0	6.2	6.6					C
17	3.1	3.1	3.2	18.0	14.0	16.0						S
18	8.4	9.9	10.5	14.0	17.0	16.0	6.3					C
19	3.4	3.1	2.9	16.0	15.0	15.0	8.1	9.0	9.0			S
20	4.8	6.7	6.5	7.6	9.2	9.9	8.1	• • •				C
21	3 2	3.1	3.2	18.0	15.0	15.0	8.0	7.4	7.1			S
22	3.1	3.8	3.9	7.0	6.2	6.4	7.3	6.8	6.8			C
23	1.5	2.0	2.3	9.0	8.2	8.2	3.7	3.7	3.7			S
24	6.1	6.1	5.7	20.0	12.0	18.0	1.7	7.1	7.5			C
25	7 3	7 1	7.4	51.0	55.0	52.0	5.5	5.3	5.5			C
26	6 0	5.7	5.3	40.0	32.0	30.0	4.9	4.7	4.8			S
27	45	<i>A</i> 0	4.0	19.0	16.0	18.0	8.2	7.8	7.7			Č
28	7.3	2.7	67	19.0	38.0	43.0	7.7	7.4	7.3			Č
20		n /										-
29	1.1	9.7	10.6	36.0	33.0	32.0	7.3	7.3	7.4	4.5	26	C

.

AVERAGE RAW WATER CHARACTERISTICS

RUN		TURBIDIT' (NTU)	Y		PART. VO (mm3/L)	L.		pH		NPOC (mg/L)	SS (mg/L)	GENUS
	RAW	#1 IN	#2 IN	RAW	#1 IN	#2 IN	RAW	#1 IN	#2 IN	RAW	RAW	
31	5.3	5.2	5.2	22.0	23.0	24.0	7.3	6.6	6.5	34.7	15	C
32	4.5	3.5	3.5	14.0	13.0	15.0	7.3	7.5	7.4	34.3	12	C
33	4.6	4.5	4.5	13.0	12.0	14.0	7.8	7.8	7.7	33.7	10	C
34	3.0	3.6	3.1	9.4	11.0	10.0	7.6	6.9	6.7	33.9	8.6	C
35	4.3	210	4.0	13.0	14.0	13.0	7.8	7.8	7.7	14.9	9.4	C
36	5.1	4.5		11.0	10.0					10.1	10	C
37	9.4	7.4		17.0	14.0					8.5	16	C
38	95	8.9		33.0	25.0					3.0	25	C
20	8.8	8.8	8.1	29.0	31.0	36.0				3.2	21	C
40	8 2	9.5	8.5	23.0	24.0	38.0	8.3	6.0	6.1	3.1	22	C
A1	2 2	2.5	0.0	2000	2		7.8				8.3	C
42	7 9			10.3			8.0				16	C
42	6 7			6.6			7.3				14	Ċ
43	6.8			9.6			7.9			8.7	15	Ċ
44	12 0			21.7			7.7			5.4	26	C
46	15.2			17 7			8.1			3.5	30	C
40	14.1			17.7			7.8			3.4	30	Ċ
47	10.2			9.9			7 5			3.0	24	Ċ
40	10.2			14 0			7 0			2.6	26	Č
47 60	0.5			10.0			67			3.5	28	Ċ
50	7.0 0 F			10.0			7 8			5.8	25	Č
31	3.3			10.0			1.0				L V	v

RUN #1 TO RUN #51 - MEASURED HEAD LOSS VALUES

RUN	TIME (h)	/A (m)	/B (m)	RUN	TIME (h)	/\ (m)	/B (m)	RUN	TIME (h)	/A (m)	/8 (m)
1	0.00	0.151	0,133	5	0.00	0.089	0.081	9	0.00	0.089	0.088
•	1.00	0.254	0.167	-	1.00	0.161	0.100		1.97	0.085	0.081
	2.00	0.362	0.211		2.00	0.251	0.119		4.18	0.075	0.075
	3.00	0.476	0.269		3.00	0.332	0.135		6.12	0.073	0.070
	4.00	0.614	0.335		4.05	0.424	0.153		8.05	0.072	0.067
	5.00	0.753	0.401		5.17	0.545	0.175		10.05	0.071	0.064
	6.00	0.903	0.469		6.08	0.647	0.191		11.72	0.071	0.062
	7.00	1.079	0.540		7.07	0.793	0.222				
	8.00	1.225	0.610		8.22	0.915	0.261				
	9.00	1.388	0.686		10.08	1.140	0.314				
					11.17	1.269	0.361				
2	0.00	0.176	0.181	6	0.00	0.055	0.048	10	0.00	0.086	0.083
	0.52	0.285	0.312		1.70	0.146	0.151		1.70	0.098	0.111
	1.00	0.412	0.449		4.58	0.267	0.304		2.60	0.099	0.133
	2.00	0.701	0.717		6.80	0.342	0.392		5.78	0.098	0.152
	3.00	0.995	0.984		8.93	0.407	0.471		7.70	0.096	0.167
	4.00	1.269	1.259		11.28	0.464	0.540		11.00	0.099	0.199
	5.00	1.481	1.539		11.90	0.479	0.556				
	6.00	1.701	1.838								
	7.00	1.878	2.103								
	8.00	2.122									
3	0.00	0.091	0.084	7	0.00	0.097	0.099	11	0.00	0.063	0.062
-	1.00	0.281	0.229		1.05	0.282	0.328		1.22	0.063	0.062
	2.00	0.449	0.392		3.07	0.632	0.739		4.38	0.068	0.065
	3.00	0.630	0.585		5.12	0.881	1.029		6.62	0.068	0.065
	4.00	0.809	0.772		7.07	1.007	1.220		9.62	0.063	0.062
	5.00	1.045	0.974		10.10	1.210	1.434				
	6.00	1.315	1.174								
	7.00	1.551	1.444								
	8.00	1.934	1.697								
	9.00	2.229	1.957								
	10.00		2.115								
4	0.00	0.099	0.097	8	0.00	0.094	0.075	12	0.00	0.129	0.129
	1.00	0.231	0.234		0.92	0.092	0.080		1.10	0.145	0.141
	2.00	0.367	0.379		3.33	0.097	0.087		2.17	0.160	0.152
	3.00	0.517	0.542		5.72	0.098	0.095		3.18	0.171	0.158
	4.00	0.663	0.686		7.88	0.099	0.102		5.17	0.182	0.164
	5.00	0.784	0.815		9.60	0.100	0.112		7.25	0.194	0.166
	6.00	0.923	0.959		10.83	0.100	0.119		9.12	0.197	0.162
	7.00	1.060	1.091						11.03	0.201	0.163
	8.00	1.183	1.277								
	9.00	1.314	1.462								

162

RUN	TINE	/A	/B	RUN	TIME	/٨	. /B	RUN	TIME	/A	/8
	(h)	(m)	(m)		(h)	(m)	(n)		(h)	(m)	(8)
13	0.00	0.131	0.130	17	0.00	0.110	0.110	21	0.00	0.057	0.060
	2.42	0.142	0.137		1.93	0.135	0.132		0.25	0.089	0.089
	4.08	0,147	0.153		3.75	0.146	0.166		0.73	0.161	0.164
	5,98	0,150	0.173		5.60	0.163	0.193		3.65	0.699	0.703
	8.12	0.160	0.213		7.33	0.176	0.223		5.48	0.992	1.032
	11.02	0.169	0.243		9.48	0.199	0.254		7.55	1.277	1.415
					10.65	0.210	0.272		9.67	1.623	1.851
									10.95	1.807	2.124
14	0.00	0.045	0.044	18	0.00	0.068	0.066	22	0.00	0.162	0.158
• •	1.53	0.047	0.048		1.57	0.106	0.097		1.43	0.587	0.560
	2,97	0.049	0.050		3.13	0.124	0.118		6.15	1.803	1.767
	4.37	0.050	0.054		5.17	0.137	0.136		7.33	2.095	2.001
	6.33	0.052	0.058		6.92	0.147	0.149		8.13	2.235	2.073
	8.93	0.052	0.061		7.65	0.146	0.150				
					9.23	0.161	0.168				
					11.15	0.171	0.183				
15	0.00	0.150	0.150	19	0.00	0.077	0.073	23	0.00	0.051	0.050
	1.65	0.175	0.158		1.20	0.150	0.097		0.58	0.087	0.077
	3.77	0.244	0.180		2.68	0.268	0.182		2.27	0.130	0.144
	5.78	0.384	0.224		5.03	0.331	0.240		3.27	0.154	0.175
	8.10	0.716	0.356		7.37	0.426	0.456		4.65	0.203	0.221
	10.03	0.840	0.452		9.00	0.498	0.528		6.57	0.274	0.300
					11.27	0.575	0.638		8.28	0.399	0.449
									11.08	0.627	0.645
16	0.00	0.130	0.129	20	0.00	0.119	0.114	24	0.00	0.037	0.037
	1.55	0.134	0.131		2.33	0.386	0.343		2.20	0.043	0.045
	4.12	0.134	0.130		4.55	0.505	0.499		4.91	0.050	0.053
	5.65	0.138	0.130		6.10	0.585	0.610		7.16	0.052	0.064
	7.28	0.140	0.133		7.68	0.628	0.714		9.16	0.058	0.077
	9.69	0.143	0.141		9.68	0.753	0.857		11.88	0.068	0.103
	11.38	0.148	0.148		10.98	0.798	0.939				

RUN #1 TO RUN #51 - NEASURED HEAD LOSS VALUES

163

RUN #1 TO RUN #51 - MEASURED HEAD LOSS VALUES

•

RUN	TINE	/A	/B	RUN	TINE	/A	/B	RUN	TINE	/A	/B
	(h)	(m)	(m)		(h)	(m)	(n)		(ħ)	(m)	(n)
25	0.00	0.030	0.030	29	0.00	0.091	0.120	33	0.00	0.104	0.090
	3.15	0.198	0.377		1.00	0.095	0.124		0.63	0.109	0.096
	5.25	0.277	0.524		2.18	0.102	0.128		1.97	0.122	0.111
	6.79	0.339	0.616		3.75	0.113	0.133		3.22	0.131	0.123
	9.38	0.448	0.788		5.25	0.127	0.137		4.58	0.143	0.137
	11.55	0.572	0.973		6.92	0.145	0.143		5.83	0.152	0.149
					8.38	0.159	0.149		8.08	0.168	0.176
					10.58	0.183	0.156		9.40	0.177	0.198
									10.58	0.183	0.220
									11.40	0.187	0.239
26	0.00	0.058	0.058	30	0.00	0.110	0.080	34	0.00	0.100	0.103
	2.56	0.152	0.204		0.77	0.120	0.090		0.58	0.199	0.232
	4.43	0.175	0.231		1.83	0.135	0.104		2.17	0.446	0.609
	6.31	0.208	0.304		4.00	0.162	0.127		3.70	0.667	0.998
	8.41	0.258	0.893		5.88	0.186	0.150		4.87	0.831	1.287
	10.16	0.320	1.747		7.32	0.208	0.165		6.93	1.108	1.720
					8.70	0.225	0.183		7.93	1.231	1.935
					10.23	0.249	0.204		9.39	1.421	2.235
					11.70	0.273	0.227				
27	0.00	0.109	0.109	31	0.00	0.090	0.090	35	0.00		0.080
	1.35	0.213	0.124		1.05	0.219	0.221		1.62		0.096
	3.30	0.352	0.147		2.08	0.346	0.360		3.68		0.107
	5.58	0.422	0.192		3.28	0.492	0.503		4.90		0.107
	8.68	0.579	0.294		4.15	0.594	0.609		6.70		0.110
	10.46	0.756	0.438		5.43	0.735	0.748		8.13		0.119
		•			6.28	0.824	0.852		9.82		0.126
					7.37	0.936	0.969				
					9.02	1.085	1.127				
					10.13	1.187	1.243				
					11.22	1.281	1.345				
28	0.00	0.106	0.106	32	0.00	0.118	0.113	36	0.00	0.092	
	1.35	0.127	0.155		1.03	0.121	0.115		1.12	0.096	
	3.71	0.195	0.311		2.07	0.123	0.117		2.80	0.102	
	5.98	0.393	0.431		2.73	0.125	0.118		4.72	0.109	
	8.05	0.673	0.598		4.55	0.129	0.123		5.83	0.115	
	10.81	1.065	0.698		6.03	0.133	0.127		7.72	0.126	
					7.62	0.140	0.134		9.10	0.137	
					8.85	0.144	0.139				
					10.13	0.148	0.145				
					10.72	0.151	0.149				

164

.

.

RUN	TINE (h)	/A (m)	/B (m)	RUN	TINE (h)	A/ (m)	/B (m)	RUN	TINE (h)	/A (m)	/B (m)
37	0.00	0.086		41	0.00	0.069	0.077	44	0.00	0.062	0.062
•.	0.83	0.201			1.00	0.076	0.082		1.00	0.063	0.066
	2.00	0.342			2.00	0.082	0.086		2.00	0.069	0.072
	3.82	0.575			3.00	0.090	0.090		3.00	0.076	0.080
	5.23	0.761			4.00	0.095	0.094		4.00	0.084	0.088
	7.80	1.125			5.00	0.100	0.098		5.00	0.090	0.097
	9.83	1.334			6.00	0.105	0.101		6.00	0.096	0.106
					7.00	0.111	0.107		7.00	0.102	0.116
38	0.00	0.096			8.00	0.115	0.112		8.00	0.109	0.123
	0.50	0.097			9.00	0.119	0.116		8.78	0.114	0.128
	2.65	0.098			10.00	0.128	0.124		10.00	0.123	0.136
	4.80	0.101			10.67	0.131	0.127	•			
	7.02	0.104									
	8.80	0.106		42	0.00	0.070	0.070	45	0.00	0.108	0.100
	10.62	0.108			1.00	0.082	0.095		0.50	0.115	0.113
					2.00	0.104	0.132		1.00	0.117	0.122
39	0.00	0.090	0.110		3.00	0.126	0.170		1.50	0.118	0.130
	1.30	0.091	0.110		4.00	0.154	0.208		2.25	0.120	0.141
	2.67	0.092	0.108		5.00	0.174	0.227		3.00	0.123	0.151
	4.98	0.093	0.110		6.00	0.197	0.271		4.00	0.127	0.165
	10.77	0.097	0.110		7.00	0.247	0.302		5.00	0.143	0.216
					8.00	0.269	0.317		6.00	0.150	0.273
40	0.00	0.095	0.100		9.00	0.316	0.325		7.00	0.160	0.326
	0.67	0.184	0.182		10.00	0.355	0.314		8.00	0.182	0.340
	1.62	0.317	0.355		11.00	0.360	0.294		9.00	0.192	0.347
	2.92	0.517	0.689		11.47	0.374	0.285		10.00	0.201	0.356
	4.10	0.743	1.077								
	5.35	1.073	1.526	43	0.00	0.069	0.081	46	0.00	0.089	0.098
	7.37	1.735	2.235		1.00	0.080	0.093		0.50	0.098	0.109
					2.00	0.096	0.123		1.00	0.101	0.112
					3.00	0.111	0.152		2.00	0.106	0.119
					4.00	0.126	0.176		3.00	0.111	0.128
					5.00	0.146	0.210		4.00	0.116	0.135
					6.00	0.149	0.236		5.00	0.122	0.144
					7.00	0.160	0.250		6.00	0.129	0.155
					8.00	0.170	0.275		7.00	0.135	0.168
					9.00	0.183	0.288		8.00	0.141	0.179
					10.00	0.196	0.309		9.00	0.149	0.191
					11.00	0.207	0.338		10.00	0.156	0.201

RUN #1 TO RUN #51 - MEASURED HEAD LOSS VALUES
165

/8 RUN TIME /٨ /8 /**X** RUN TIME (h) (m) (m) (m) (m) (h) 0.00 0.088 0.115 0.094 0.075 50 47 0.00 0.146 0.236 0.156 0.100 1.17 1.00 0.107 0.193 0.114 0.126 2.00 2.00 3.00 0.119 0.398 0.245 0.165 3.00 0.557 0.747 0.287 4.00 0.129 0.227 4.00 5.00 0.136 0.262 5.10 0.333 0.909 0.140 6.05 0.365 0.293 6.00 1.078 7.00 0.401 0.326 7.00 0.147 0.441 0.153 0.352 8.00 8.00 1.455 0.464 0.374 9.00 9.00 0.157 9.90 0.161 0.398 0.00 0.058 0.057 0.108 0.102 51 48 0.00 0.073 0.088 0.066 1.00 1.00 0.125 0.116 2.00 0.074 2.00 0.131 0.123 0.109 3.00 0.143 0.129 3.00 0.084 0.136 0.184 0.096 4.00 4.00 0.169 0.135 0.113 5.00 5.00 0.195 0.142 0.231 6.00 0.263 0.133 0.151 6.38 0.354 0.463 0.152 7.00 7.00 0.247 0.156 8.00 0.176 8.00 0.258 0.163 9.00 0.573 0.203 9.00 0.270 0.165 10.00 0.678 0.232 10.00 0.287 0.170 0.00 0.078 0.079 49 0.083 0.082 1.00 2.00 0.093 0.092 0.098 3.00 0.101 4.00 0.111 0.105 0.123 0.111 5.00 0.135 0.118 6.00 0.125 7.00 0.149 8.00 0.166 0.134 9.00 0.182 0.140 10.00 0.201 0.144

-

RUN #1 TO RUN #51 - MEASURED HEAD LOSS VALUES

RUN	TINE (h)	RAW (NTU)	/A IN (NTU)	/B IN (NTU)	/A OUT (ntu)	/B OUT (NTU)	/A C/Co (-)	/B C/Co (-)
1	1 00				1.05	2.70	0.284	0.730
1	2 00				0.86	2.10	0.232	0.568
	2.00				1.11	2.20	0.300	0.595
	3.00				0.98	2.20	0.265	0.595
	4.UU 8 AA				0.98	2.20	0.265	0.595
	2.00				0.70	2.30	0.265	0.622
	0.00				0.20	2.30	0.249	0.649
	0.00				0.92	2 40	0.243	0.649
	0.00				0.50	2 40	0.227	0.649
	9.00	37	27	37	0.04	2.70	01227	01017
	ave	3.1	3.7	3.1				
2	0.52				0.08	0.05	0.027	0.015
-	1.00				0.07	0.08	0.023	0.024
	2.00				0.12	0.08	0.040	0.024
	3.00	2.9			0.10	0.08	0.033	0.024
	4.00	2.8			0.16	0.07	0.053	0.021
	5.00	2.9			0.19	0.10	0.063	0.030
	6.00	2.7			0.22	0.10	0.073	0.030
	7.00	2.6			0.18	0.10	0.060	0.030
	8.00	2.7			0.21		0.070	
	ave	2.8	3.0	3.3				
					0.05	0.06	0 020	0 026
3	1.80	2.3	5.2	2.0	0.00	0.00	0.020	0.020
	2.00	1.9	2.1	2.2	0.00	0.15	0.024	0.040
	3.00	2.1	2.0	2.2	0.07	0.10	0.020	0.005
	4.00	2.1	2.4	1.9	0.05	0.10	0.020	0.070
	5.00	2.1	2.5	1.8	0.00	0.17	0.024	0.074
	6.00	2.1	2.2	2.3	0.07	0.14	0.020	0.000
	7.00	2.1	2.1	1.9	0.05	0.09	0.020	0.039
	8.00	2.0	2.1	3.6	0.11	0.14	0.044	0.001
	9.00	1.8	2.1	1.9	0.16	0.10	0.063	0.045
	10.00	1.7				0.08		0.035
	ave	2.0	2.5	2.3				
4	1.00	1.7	2.5	2.0	0.17	0.11	0.085	0.052
•	2.00	1.8	2.4	2.9	0.14	0.10	0.070	0.047
	3.00	2.1	1.9	2.1	0.14	0.16	0.070	0.075
	4.00	1.9	1.9	2.2	0.13	0.28	0.065	0.132
	5.00	2.0	1.9	2.0	0.18	0.23	0.090	0.108
	6.00	1.7	1.9	2.0	0.14	0.24	0.070	0.113
	7,00	2.1	1.8	1.9	0.17	0.23	0.085	0.108
	9 00	2 0	1.8	2.1	0.17	0.16	0.085	0.075
	0.0V 0.0V	10	1 9	19	0.12	0.15	0.060	0.071
	10 00	1 0			0.14	0.14	0.070	0.066
	10.00	1 0	2 0	2.1	VI 1 7			
	GAC	117	F + A					

RUN	TIHE (h)	RAW (NTU)	/A IN (NTU)	/8 1N (NTU)	/A OUT (NTU)	/B OUT (NTU)	/A C/Co (-)	/B C/Co (-)
5	1.00			3.7	1.10	1.61	0.275	0.413
•	2.00				1.09	1.52	0.273	0.390
	3.00				1.00	1.54	0.250	0.395
	4.05				0.94	1.41	0.235	0.362
	5.17			-	0.97	1.33	0.243	0.341
	6.08	3.4	4.0	4.1	1.04	1.25	0.260	0.321
	7.07				1.33	1.22	0.333	0.313
	8.22				2.00	1.32	0.500	0.338
	10.08				1.69	1.32	0.423	0.338
	11.17				1.70	1.64	0.425	0.421
	ave	3.4	4.0	3.9				
6	1.70	1.6	2.9	3.7	1.48	1.55	0.514	0.554
	4.58	1.7	2.4	2.3	1.53	1.45	0.531	0.518
	6.80	1.7	2.5	2.6	1.68	1.84	0.583	0.657
	8.93	1.7	2.7	2.7	1.87	1.68	0.649	0.600
	11.28	1.7	3.9	2.7	2.10	1.90	0.729	0.679
	ave	1.7	2.9	2.8				
7	1.05	1.9	2.4	2.3	0.24	0.28	0.096	0.117
	3.07	2.2	2.4	2.8	0.55	0.37	0.220	0.154
	5.12	2.1	2.4	2.3	0.85	0.63	0.340	0.263
	7.07	2.0	2.9	2.3	1.65	0.83	0.660	0.346
	10.10	1.9	2.4	2.3	1.16	1.10	0.464	0.458
	ave	2.0	2.5	2.4				
8	0.92	6.4	4.9	5.5	3.20	2.80	0.594	0.496
	3.33	6.3	5.5	5.6	4.20	3.40	0.780	0.602
	5.72	6.4	5.5	5.7	4.70	3.60	0.873	0.637
	7.88	6.3	6.1	6.2	4.80	4.00	0.892	0.708
	9.60	5.9	5.2	5.5	4.40	3.30	0.817	0.584
	10.83	5.9	5.1	5.4	4.70	2.90	0.873	0.513
	ave	6.2	5.4	5.7				
9	1.97	2.2	2.4	2.0	1.70	2.00	0.797	0.952
	4.18	2.2	2.0	2.3	1.70	1.90	0.797	0.905
	6.12	2.2	2.3	2.1	1.60	2.00	0.750	0.952
	8.05	2.1	2.0		1.50	2.00	0.703	0.952
	10.05	2.0	2.1	2.0	1.40	1.80	0.656	0.857
	11.72	2.0	2.0	2.1	1.60	2.10	0.750	1.000
	ave	2.1	2.1	2.1				

/A C/Co /B C/Co **/B OUT** /8 IN /A OUT RUN TINE RAW /A IN (-) (-) (NTU) (NTU) (NTU) (h) (NTU) (NTU) 0.350 0.165 4.00 10 1.70 7.0 11.0 7.0 1.10 0.195 0.717 2.60 7.1 11.2 6.5 8.20 1.30 11.30 2.50 0.988 0.375 5.78 7.0 11.6 6.6 10.20 0.892 0.420 7.0 12.1 6.5 2.80 7.70 0.830 0.526 ٠ 11.3 6.7 9.50 3.50 11.00 6.9 ave 7.0 11.4 6.7 1.22 2.4 2.7 1.60 2.40 0.780 0.960 1.8 11 0.732 0.960 3.0 1.50 2.40 4.38 1.8 2.1 0.920 2.2 1.70 2.30 0.829 6.62 1.9 2.0 2.10 2.20 1.024 0.880 2.1 9.62 1.8 1.7 2.5 ave 1.8 2.1 2.40 2.40 0.369 0.279 12 1.10 6.7 7.1 9.1 8.7 3.20 3.70 0.492 0.430 2.17 6.1 6.6 0.535 3.50 0.538 9.2 4.60 3.18 6.6 6.3 0.600 0.558 3.90 4.80 5.17 6.2 8.6 6.1 4.90 0.831 0.570 7.7 5.40 9.12 6.6 6.4 0.769 0.581 5.00 5.00 11.03 6.3 6.2 8.3 6.5 8.6 6.4 ave 0.385 0.110 4.7 1.75 0.52 4.5 13 2.42 5.0 0.507 0.120 2.30 4.8 0.57 4.08 4.9 4.5 0.551 0.095 2.50 0.45 4.9 4.6 4.9 5.98 0.114 2.50 0.54 0.551 4.6 8.12 4.9 4.5 0.573 0.112 2.60 0.53 4.7 11.02 4.8 4.6 4.5 4.7 4.9 ave 0.766 0.368 1.26 3.2 1.90 2.5 14 1.53 2.3 0.450 0.766 1.90 1.54 2.97 2.3 2.4 3.4 0.427 1.46 0.762 1.89 3.4 4.37 2.3 2.4 0.750 0.462 1.58 3.4 1.86 6.33 2.4 2.4 0.734 0.456 1.82 1.56 2.4 3.7 8.93 2.7 3.4 ave 2.3 2.5 8 0.124 0.093 1.65 3.6 0.44 0.43 15 4.3 5.0 0.42 0.36 0.089 0.103 3.77 3.8 5.1 3.6 0.051 0.164 0.24 0.57 5.78 3.8 4.6 3.4 0.080 0.044 0.21 0.28 6.95 0.069 0.042 0.20 0.24 8.10 3.9 4.6 3.4 0.061 0.086 10.03 3.9 4.4 3.4 0.29 0.30 3.5 ave 3.9 4.7

RUN	TINE (h)	RAW (NTU)	/A IN (NTU)	/B IN (NTU)	/A OUT (NTU)	/B OUT (NTU)	/A C/Co (-)	/B C/Co (-)
16	1.55	2.4	2.4	2.5	0.44	0.89	0.168	0.349
	4.12	2.6	2.7	2.5	0.54	0.93	0.206	0.365
	5.65	2.6	2.7	2.5	0.54	1.03	0.206	0.404
	7.28	2.7	2.7	2.6	0.65	0.56	0.248	0.220
	9.67	2.8	2.6	2.6	0.85	0.34	0.325	0.133
	11.38	2.6	2.6	2.6	0.86	0.29	0.329	0.114
	ave	2.6	2.6	2.6				
17	1.93	2.9	3.2	3.2	0.36	0.44	0.115	0.138
	3.75	3.0	3.1	3.2	0.29	0.24	0.093	0.075
	5.60	3.4	3.1	3.1	0.24	0.23	0.077	0.072
	7.33	3.1	3.1	3.1	0.28	0.31	0.090	0.097
	9.48	3.0	3.1	3.3	0.30	0.21	0.096	0.066
	10.65				0.24	0.16	0.077	0.050
	ave	3.1	3.1	3.2				
18	1.57	8.4	10.6	11.2	5.70	6.90	0.573	0.659
	3.13	8.3	10.0	10.5	5.80	5.90	0.583	0.564
	5.17	8.4	10.2	10.2	7.00	6.60	0.704	0.631
	6.92	8.5	9.3	10.3	4.80	7.10	0.483	0.678
	7.65	8.4	10.5	10.4	10.40	9.20	1.046	0.879
	9.23	8.4	9.6	10.2	7.10	6.40	0.714	0.611
	11.15	8.6	9.4		7.90	7.40	0.795	0.707
	ave	8.4	9.9	10.5				
19	1.20	3.3	3.0	2.9	0.49	0.65	0.158	0.228
	2.68	3.5	3.0	2.9	0.33	0.33	0.106	0.116
	5.03	3.4			0.25	0.24	0.081	0.084
	7.37	3.2	3.2	2.8	0.19	0.16	0.061	0.056
	9.00	3.4	3.2	2.8	0.18	0.17	0.058	0.060
	11.27	3.4			0.18	0.15	0.058	0.053
	ave	3.4	3.1	2.9				
20	2.33	4.7	6.7	6.5	2.40	1.67	0.361	0.259
	4.55	4.8	6.4	6.4	2.50	2.20	0.376	0.341
	6.10	4.8	6.3	6.3	2.60	2.40	0.391	0.372
	7.68	4.9	7.0	6.3	3.90	3.00	0.586	0.465
	9.68	4.7	6.6	6.3	3.50	3.30	0.526	0.512
	10.98	4.8	6.9	6.9	4.30	4.30	0.647	0.667
	ave	4.8	6.7	6.5				

.

RUN	TINE (h)	RAW (NTU)	/A IN (NTU)	/B IN (ntu)	/A OUT (ntu)	/B OUT (NTU)	/A C/Co (-)	/B C/Co (-)
21	0.73	3.4	3.3	3.5	0.15	0.14	0.048	0.044
21	3 65	3.7	2.9	3.3	0.18	0.12	0.058	0.037
	5.40	2.2	3 0	. 3.2	0 17	0.13	0.055	0.040
	7 66	3.3	2 6	3.2	0.17	0.10	0.106	0.031
	1.00	3.3	2.0	2.0	0.35	0.10	0.219	0.093
	7.0/ 10.0F	3.2	2.0	3.0	1 00	0.50	0 323	0 205
	10.95	3.1	2.0	2.1	1.00	0.00	0.353	01200
	ave	J.2	J•1	3.2				
22	1.43				0.21	0.47	0.056	0.120
	3.28	3.1	3.6	3.8	0.36	0.81	0.095	0.206
	6.15	3.1	3.8	3.6	1.08	0.76	0.286	0.194
	7.33	3.0	3.8	4.2	0.87	0.95	0.230	0.242
	8,13	3.1	3.9	4.1	1.00	0.88	0.265	0.224
	ave	3.1	3.8	3.9		••••		
				9 E	0 22	0 52	0 116	0 229
23	0.58	1.0	2.0	3.3	0.23	0.53	0.110	0.220
	2.21				0.07	0.13	0.035	0.050
	3.27	1.5	1.7	1.7	0.19	0.13	0.090	0.000
	4.65	1.5	1.9	1.9	0.23	0.19	0.110	0.002
	6.57	1.5		. .	0.22	U.14	0.111	0.000
	8.28	1.5	2.1	2.4	0.20	0.10	0.101	0.043
	11.08	1.5	2.2	2.1	0.23	U. 14	0.116	0.000
	ave	1.5	2.0	2.3				
24	2.20	6.1	5.9	5.6	4.40	4.10	0.717	0.722
	4.91	6.1	5.7	5.7	4.20	3.90	0.684	0.687
	7.16	6.1	6.4	5.7	4.90	3.80	0.798	0.669
	9.16	6.1	6.2	5.7	5.10	3.90	0.831	0.687
	11.88	6.2	6.5	5.7	5.50	3.70	0.896	0.651
	ave	6.1	6.1	5.7				
25	2,15	75	7.1	7.8	3.20	1.23	0.454	0.167
25	5 25	7 5	7.1	7.2	4.50	3.90	0.638	0.531
	6 70	7 1	6.9	6.9	4.60	4.90	0.652	0.667
	0.72	7 4	7 1	75	4.40	5.20	0.624 -	0.707
	11 55	6 9		110	A 60	5.30	0.652	0.721
	ave	7.3	7.1	7.4	4100			
26	2.56	5.6	5.5	5.3	2.20	0.54	0.384	0.102
	4.43	6.0	6.0	5.6	2.80	1.64	0.489	0.309
	6.31	6.0			3.20	1.66	0.558	0.313
	8.41	6.2	5.8	5.3	2.80	0.60	0.489	0.113
	10.16	6.1	5.6	5.0	2.30	0.58	0.401	0.109
	ave	6.0	5.7	5.3				

RUN	TINE	RAW	/A IN	/B IN	/A OUT	/B OUT	/A C/Co	/B C/Co
	(h)	(NTU)	(NTU)	(NTU)	(NIU)	(111)	(~)	(-)
27	1.35				1.49	2.20	0.369	0.545
	2 20		A. F	A . 0	1.60	1.90	0.397	0.471
	J.JV 5 50	4.4	7.1	4.0	1 00	1 60	0 471	0 397
	5.00	4.3	3.1	4.0	1.70	1 17	0 360	0.000
	8.68	4.3	4.3	4.0	1.40	1 • 1 7	0.300	0.275
	10.46				1.10	1+11	0.215	0.275
	ave	4.5	4.0	4.0				
28	1.35	7.3	6.3	6.7	2.50	2.00	0.375	0.300
	3.71	7.3	6.8	6.6	1.90	2.20	0.285	0.330
	5.98	7.4	6.7	6.7	1.40	2.20	0.210	0.330
	8.05	6.8	6.9	6.7	1.80	3.10	0.270	0.464
	10 91	6.6		•••	3.20	5.40	0.479	0.809
	20101	7 1	6.7	6.7		••••	•••••	
			•••	•••				
29	1.00	10.0	9.1	10.4	7.80	9.60	0.804	0.906
	2.18	10.2	9.5	10.6	8.40	10.10	0.866	0.953
	2 75	11.3	10.3	10.4	8.90	9,60	0.918	0.906
	5 25	11.5	10.2	10.7	9.00	9,80	0.928	0.925
	2.02	10.7	0.0	10.7	8 50	9 10	0.876	0.858
	0.72	10.7	7.0	10.5	0.00	0 90	0.070	0 025
	0.30	10.0	9.0	10.0	0.00	5.00	0.007	0.043
	10.58	10.7	9.5	10.8	0.40	10.00	0.000	U.74J
	ave	10.7	9.7	10.6				
30	0.77	6.9	7.0	6.4	0.24	0.34	0.035	0.055
	1.83	6.9	7.1	6.3	0.17	0.27	0.025	0.044
	4.00	6.8	7.1	6.1	0.16	0.32	0.023	0.052
	5.88	6.5	7.0	6.3	0.39	0.46	0.057	0.074
	7 32	6 7	6.8	6.2	0.52	0.47	0.075	0.076
	0 70	67	6.0	6 1	0 67	0.51	0 097	0.082
	10 12	6.6	L 7	E 0	0.07	0.51	0 101	0 081
	10.23	0.0	0.1	J.J (1	0.70	0.30	0.139	0.076
	11.70	0.0	0.0	0.3	0.73	0.47	0.130	0.010
	ave	6.1	6.9	6.2				
31	1.05	5.3	5.3	5.3	0.06	0.09	0.012	0.017
	2.08	5.3	5.3	5.3	0.07	0.08	0.013	0.015
	3.28	5.4	5.1	5.3	0.05	0.09	0.010	0.017
	4.15	5.3	5.2	5.3	0.07	0.12	0.013	0.023
	5.43	5.1	5.1	5.1	0.80	0.20	0.154	0.038
	6 29	5 3	5 1	5.2	1.30	0.80	0.250	0.154
	7 37	r J 112	5.1 F 0	5.6	1 90	1 40	0.246	0,269
	1.31	5.2	5.0	7.U E J	2 20	1.40	0.J40 A 193	0.205
	9.02	J.J	3.1	J.2	6.20	1.00	U.46J A 119	0.340
	10.13				2.30	1.00	U.44Z	0.340
	11.22	. -	. -	- -	2.10	2.20	0.213	U.42J
	ave	5.3	5.2	5.2				

•

· •

RUN	TINE	RAW	/A IN	/B IN	/A OUT	/B OUT	/A C/Co	/B C/Co
	(h)	(NTU)	(NTU)	(NTU)	(NTU)	(NTU)	(-)	(-)
32	1.03	4.7	4.1	4.1	3.10	3.10	0.886	0.886
	2.07	4.7	4.0	4.1	3.00	3.10	0.857	0.886
	2.73				3.10	3.20	0.886	0.914
	4.55	4.5	4.1	4.1	2.90	3.00	0.829	0.857
	6.03	4.5	4.0	4.0	2.90	3.00	0.829	0.857
	7.62	4.3	4.0	3.9	2.90	2.90	0.829	0.829
	8.85				2.90	2.90	0.829	0.829
	10.13	4.2	3.9	3.9	2.80	2.80	0.800	0.800
	10.72				2.80	2.80	0.800	0.800
	ave	4.5	3.5	3.5				
33	0.63	5.6	4.5	4.5	0.28	0.31	0.062	0.069
	1.97	5.7	4.5	4.7	0.17	0.17	0.038	0.038
	3.22	5.5	4.6	4.5	0.14	0.15	0.031	0.033
	4.58	5.3			0.17	0.14	0.038	0.031
	5.83	5.0	4.5	4.6	0.21	0.18	0.047	0.040
	8.08				0.19	0.20	0.042	0.044
	9.40	4.6			0.19	0.21	0.042	0.047
	10.58	4.6	4.3	4.2	0.22	0.18	0.049	0.040
	ave	4.6	4.5	4.5				
24	0 50	2 1	27	24	0.06	0 32	0.017	0.103
34	0.00	3.0	27	3.4	0.00	0.13	0.014	0.042
	2.11	7.0	3.1	3+6	0.05	0.10	0.017	0.032
	3.10	3 0	25	3.0	0.00	0.09	0.011	0.029
	4.07	3.0	3.5	2 9	1 00	0.11	0.278	0.035
	7 63	J.U	J • 4	2.5	1 00	0.13	0.278	0.042
	0 20				1 50	0.15	0.417	0.048
	ave	3.0	3.6	3.1	1.50	0115	•••••	
25	0.53	4.6		3.9		3.00		0.750
33	1 62	4.3		3.9		3.00		0.750
	3 68	4.3		4.1		3.10		0.775
	£ 90	A.A				3.00		0.750
	6 70	A.1		3.9		3.00		0.750
	8 13	A 2		5.7		2,90		0.725
	9.92					3.00		0.750
	ave	4.3		4.0				
36	1,12	5.0	4.6		2.60		0.578	
30	2.80	6.2	4.9		2.50		0.556	
	1 79	J.L	4.6		2.20		0.489	
	5 83	4.6	4.3		2.20		0.489	
	7.72	4.6	1.0		2.10		0.467	
	9,10	404	-114		2.00		0.444	
	ave	5.1	4.5				•••••	

'	TETEN NON		• ••••					
RUN	TINE (h)	RAW (NTU)	/A IN (NTU)	/B IN (NTU)	/A OUT (NTU)	/8 OUT (NTU)	/A C/Co (-)	/B C/Co (-)
37	0.83	9.4	8.2		0.09		0.012	
	2.00	10.9	7.9		0.09		0.012	
	3.82	11.9	7.4		0.15		0.020	
	5.23	8.6	7.2		1.20		0.162	
	7.80	7.8	7.0		2.50		0.338	
	9.83	8.0	6.8		3.20		0.432	
	ave	9.4	7.4					
38	0.50	9.6	9.1		8.00		0.899	
	2.65	9.4	8.9		7.90		0.888	
	4.80	9.3	8.9		8.10		0.910	
	7.02	9.8	9.2		7.90		0.888	
	8.80	9.3	8.3		7.70		0.865	
	10.62	9.5	9.1		8.00		0.899	
	ave	9.5	8.9					
39	1.30	9.1	9.3	8.3	8.30	7.40	0.943	0.914
	2.67	8.8	8.9	8.3	8.20	7.10	0.932	0.877
	4.98	8.5	8.6	7.8	8.10	7.10	0.920	0.877
	10.77	8.6	8.3	8.1	7.50	6.80	0.852	0.840
	ave	8.8	8.8	8.1				
40	0.67	8.3	10.2	9.2	0.18	0.10	0.019	0.012
	1.67	8.3	10.2	9.0	0.12	0.12	0.013	0.014
	2.92	8.1	10.0	8.7	1.20	0.19	0.126	0.022
	4.10	8.1	9.3	8.4	1.70	0.36	0.179	0.042
	5.35	8.1	8.9	8.1	1.80	1.30	0.189	0.153
	7.37	8.2	8.4	7.7	2.50	2.40	0.263	0.282
	ave	8.2	9.5	8.5				
41	1.00	3.4			2.90	2.30	0.891	0.707
	2.00	3.9			3.20	2.50	0.983	0.768
	3.00	3.0			2.40	1.90	0.737	0.584
	4.00	3.0			2.60	1.90	0.799	0.584
	5.00	3.0			2.70	2.00	0.830	0.615
	6.00	3.5			2.50	2.00	0.768	0.615
	7.00	3.0			2.20	1.80	0.676	0.553
	8.00	3.4			2.30	1.89	0.707	0.581
	9.00	2.9			2.20	1.60	0.676	0.492
	10.00	3.3			2.20	1.70	0.676	0.522

10.67

ave

3.4

3.3

FILTER RUN #1 TO #51 - MEASURED TURBIDITY VALUES

•

0.615

-

0.768

2.00

2.50

P,

.

FILTER RUN #1 TO #51 - MEASURED TURBIDITY VALUES

RUN	TINE (h)	RAW (NTU)	/A IN (NTU)	/B IN (NTU)	/A OUT (NTU)	/B OUT (NTU)	/A C/Co (-)	/B C/Co (-)
42	1.00	8.0			0.95	1.29	0.121	0.164
	2.00	8.0			0.94	1.25	0.119	0.159
	3.00	7.9			0.89	1.11	0.113	0.141
	4.00	7.7			1.08	1.09	0.137	0.138
	5.00	7.9			1.08	1.09	0.137	0.138
	6.00	7.9			0.89	0.91	0.113	0.116
	7.00	7.7			0.70	0.88	0.089	0.112
	8.00	8.0			0.60	0.99	0.076	0.126
	9.00	7.6			0.58	1.25	0.074	0.159
	10.00	7.9			0.66	7.50	0.084	0.952
	11.00	8.0			1.00	10.00	0.127	1.270
	11.47	7.9			2.10	10.60	0.267	1.346
	ave	7.9						
43	1.00	6.8			2.20	3.10	0.327	0.461
	2.00	7.1			2.30	2.80	0.342	0.416
	3.00	7.0			2.30	2.60	0.342	0.387
	4.00	6.9			2.60	2.50	0.387	0.372
	5.00	6.5			2.70	2.60	0.402	0.387
	6.00	6.8			2.80	2.80	0.416	0.416
	7.00	6.5			2.90	2.70	0.431	0.402
	8.00	6.5			3.20	2.70	0.476	0.402
	9.00	6.7			3.10	2.60	0.461	0.387
	10.00	6.8			3.20	2.60	0.476	0.387
	11.00	6.4			3.20	2.60	0.476	0.387
	ave	6.7						
44	1.00	6.7			1.71	2.60	0.251	0.382
	2.00	7.0			1.75	2.50	0.257	0.367
	3.00	7.0			1.78	2.40	0.261	0.352
	4.00	6.8			2.00	2.30	0.294	0.338
	5.00	6.6			2.20	2.40	0.323	0.352
	6.00	6.9			2.60	2.40	0.382	0.352
	7.00	6.7			2.20	2.40	0.323	0.352
	8.00	6.8			2.40	3.00	0.352	0.441
	8.78	6.9			2.90	3.70	0.426	0.543
	10.00	6.7			3.20	3.80	0.470	0.558
	ave	6.8						

••

•

RUN	TIME (h)	RAW (NTU)	/A IN (NTU)	/B IN (NTU)	/A OUT (NTU)	/B OUT (NTU)	/A C/Co (-)	/B C/Co (-)
45	0.50	12.7			7.30	4.10	0.568	0.319
	1.00	12.9			8.00	4.80	0.622	0.373
	1.50	13.0			8.30	5.20	0.645	0.404
	2.25	13.1			8.80	5.70	0.684	0.443
	3.00	13.0			8.90	6.10	0.692	0.474
	4.00	13.0			8.90	6.90	0.692	0.537
	5.00	12.8			9.30	3.20	0.723	0.249
	6.00	12.8			10.20	4.30	0.793	0.334
	7.00	12.9			9.00	4.50	0.700	0.350
	8.00	12.7			7.10	7.90	0.552	0.614
	9.00	12.6			9.20	9.40	0.715	0.731
	10.00	12.8			10.20	9.80	0.793	0.762
	ave	12.9						
46	0.50	16.0			8.10	4.80	0.534	0.316
	1.00	15.5			8.30	5.30	0.547	0.349
	2.00	16.0			8.30	5.80	0.547	0.382
	3.00	16.0			8.50	6.10	0.560	0.402
	4.00	16.0			8.50	6.70	0.560	0.441
	5.00	16.0			8.40	6.90	0.553	0.454
	6.00	15.5			9.80	6.00	0.646	0.395
	7.00	15.0			9.60	6.20	0.632	0.408
	8.00	14.5			9.40	6.40	0.619	0.422
	9.00	13.5			9.50	6.80	0.626	0.448
	10.00	13.0			9.20	7.30	0.606	0.481
	ave	15.2						
47	1.00	15.0			10.70	6.40	0.759	0.454
	2.00	15.0			10.20	5.20	0.723	0.369
	3.00	14.5			9.10	3.70	0.645	0.262
	4.00	14.5			8.80	3.50	0.624	0.248
	5.00	14.5			8.80	3.80	0.624	0.270
	6.00	15.0			9.80	5.20	0.695	0.369
	7.00	14.0			9.50	5.50	0.674	0.390
	8.00	13.0			9.40	5.90	0.667	0.418
	9.00	13.0			9.60	5.40	0.681	0.383
	9.90	12.5			9.50	5.40	0.674	0.383
	ave	14.1						

RUN	TINE (h)	RAW (NTU)	/A IN (NTU)	/B I n (ntu)	/A OUT (NTU)	/B OUT (NTU)	/A C/Co (-)	/B C/Co (-)
49	1 00	11.0			7.30	3.40	0.719	0.335
40	2 00	11.0			6.90	4.00	0.680	0.394
	3 00	10.5			5.40	4.40	0.532	0.433
	1 00	10.5			3.50	4.70	0.345	0.463
	5 00	10.5			3.70	5.00	0.365	0.493
	6 38	10.0			4.20	5.10	0.414	0.502
	7 00	10.0			4.20	5.70	0.414	0.562
	9 00	9.5			6.30	5.40	0.621	0.532
	9,00	9.5			6.10	5.50	0.601	0.542
	10.00	9.5			5.90	5.50	0.581	0.542
	ave	10.2			••••			
49	1.00	9.0			7.60	4.60	0.854	0.517
	2.00	8.9			6.70	4.70	0.753	0.528
	3.00	9.1			6.20	4.90	0.697	0.551
	4.00	8.9			6.00	5.00	0.674	0.562
	5.00	9.1			6.10	5.10	0.685	0.573
	6.00	8.9			6.30	5.00	0.708	0.562
	7.00	8.9			6.40	5.10	0.719	0.5/3
	8.00	8.7			6.20	5.10	0.697	0.5/3
	9.00	8.8			6.00	5.40	0.674	0.60/
	10.00	8.7			5.70	5.70	0.640	U.64U
	ave	8.9						
50	1.17	10.0			4.40	0.88	0.459	0.092
	2.00	10.3			3.40	0.99	0.355	0.103
	3.00	9.6			2.70	1.14	0.282	0.119
	4.00	9.6			2.50	1.56	0.261	0.163
	5.10	9.8			1.98	2.20	0.206	0.229
	6.05	9.4			1.76	2.30	0.184	0.240
	7.00	9.3			1.36	2.30	0.142	0.240
	8.00	9.4			1.24	3.00	0.129	0.313
	9.00	8.9			1.24	3.00	0.129	0.313
	ave	9.6						
51	1.00	9.6			8.80	7.80	0.922	0.818
	2.00	9.6			8.30	7.60	0.870	0.797
	3.00	9.4			7.60	7.10	0.797	0.744
	4.00	9.8			6.50	6.50	0.681	0.681
	5.00	9.5			3.90	5.80	0.409	0.608
	6.00	9.6			2.20	6.70	0.231	0.702
	7.00	9.6			1.32	5.20	0.138	0.545
	8.00	9.2			1.13	4.90	0.118	0.514
	9.00	9.5			0.97	4.40	0.102	0.461
	10.00	9.6				4.30		0.451
	ave	9.5						

5

•

mean	feed	42A	42B	42A	42B
size	water	out	out	left	left
(µm)	(#/mL)	(#/mL)	(#/mL)	(%)	(%)
1.71	11300	663	1296	5.9	$ \begin{array}{r} 11.5\\ 10.7\\ 12.0\\ 11.6\\ 14.9\\ 19.3\\ 25.3\\ 32.7\\ 49.6\\ 120.4\\ 180.0\\ \end{array} $
2.02	79055	4769	8456	6.0	
2.37	45735	3216	5510	7.0	
2.79	90235	5822	10478	6.5	
3.27	52425	4189	7820	8.0	
3.85	44665	4197	8632	9.4	
4.52	36430	3971	9224	10.9	
5.31	26015	3223	8512	12.4	
6.23	11935	1583	5922	13.3	
7.33	2815	349	3390	12.4	
8.61	1060	133	1908	12.5	
total	401670	32114	71144		
mean	feed	47A	47B	47A	47B
size	water	out	out	left	left
(µm)	(#/mL)	(#/mL)	(#/mL)	(%)	(%)
1.71	36500	28460	9120	78.0	25.0
2.02	233560	176910	60470	75.7	25.9
2.37	133890	92130	29430	68.8	22.0
2.79	287350	198610	60760	69.1	21.1
3.27	146940	93000	27270	63.3	18.6
3.85	101830	58610	17830	57.6	17.5
4.52	55060	25860	9990	47.0	18.1
5.31	21580	8000	4900	37.1	22.7
6.23	8680	2220	2930	25.6	33.8
7.33	4110	710	1630	17.3	39.7
8.61	2630	470	1400	17.9	53.2
total	1032130	684980	225730		

.

APPENDIX C: PARTICLE COUNTS DURING RUN 42A/B AND RUN 47A/B

(Feed water samples taken before treatment chemicals were added)