Studies of the factors influencing the flocculation and sedimentation of microbial cells in the treatment of Kraft mill effluents

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STUDIES OF THE FACTORS INFLUENCING THE 
FLOCCULATION AND SEDIMENTATION OF MICROBIAL CELLS 
IN THE 
TREATMENT OF KRAFT MILL EFFLUENTS.

by Nicholas Dunlop-Jones.

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the 
award of Doctor of Philosophy of the Loughborough University 
of Technology, October 1982.

Supervisor: M.J. Jaycock, Ph.D. (Nottm.), Ph.D. (Cantab.)
Department of Chemistry

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TO
MUM AND DAD
&
HEATHER
ACKNOWLEDGMENTS

The opportunity to do this research arose from a common interest that Mike Jaycock, my supervisor, and Bill Frankle, of International Paper Company, had in the applications of colloid chemistry to the Paper Industry.

Firstly, I would like to thank Mike for the confidence he has shown in me during this work, and his ability to produce a hundred and one solutions to every problem. I would also like to thank Bill Frankle for instigating the project and for having faith in the approaches that we have used to tackle the problem.

I would also like to thank the technical staff at Loughborough University, especially Ray Barton and Bert Bower. There were many at the Corporate Research Center who gave me the benefits of their time and knowledge, especially Bob Crossley, John Hung, Bill Shields and Danny Strizack.

Finally, thanks must go to Heather Norman for driving up to Loughborough after working all week, only to be faced with a weekend of typing.

The project was funded by International Paper Company, USA.

The paper was a gift from the Gestetner Paper Mill, Kilbagie, Alloa, Scotland.
SUMMARY

The treatment of paper mill effluents involves a succession of unit processes to remove the impurities that may vary in size by about six orders of magnitude. The unit process of primary importance in this study was the biological treatment stage, where an understanding of the flocculation and sedimentation of micro-organisms is needed in order to operate it efficiently.

A bench-scale chemostat was constructed to operate as a model treatment plant, and the physico-chemical properties of the effluent were determined. Similarly the properties of pilot-plants and paper mill treatment plants were determined. The results were compared with treatment data available from other International Paper Company mills.

The electrokinetic properties of the predominantly microbial particles in the treatment systems were measured using microelectrophoresis. Details of the natural variation in the electrophoretic mobility were obtained, and the effects of calcium chloride and aluminium sulphate on these systems were measured.

The variation in the mobility of a single population was found to be small for such a heterogeneous population and the implications are that a common material is adsorbed on the particle surfaces.

Estimates for the particle concentration, volume
fraction and Debye-Hückel parameter of the biological effluents were obtained.

Using a multi-equation computer programme, based on DLVO theory and modified to include adsorbed layers, the magnitude of the long-range (>3nm) van der Waals and electrostatic forces were calculated for interacting biological colloids of 0.5-2.0 μm diameter. The effect of adsorbed layers and changes in the particle composition on the stability of these systems appears to be minor. The validity of applying DLVO theory to such heterodisperse and poorly defined dispersions is discussed. Consideration was also given to the role that these forces play in the flocculation of biological effluents.

The rate of sedimentation was measured at constant temperature in precision bore glass columns. Using an interactive computer programme, based on the work of Carstensen & Su (1970a,b), the data was analysed. The validity of using this model for studying effluent dispersions was tested and discussed.

The effect of aluminium sulphate, calcium chloride and sodium chloride on the sedimentation of the effluents was examined with reference to the electrophoretic mobility data for the same systems.

This study has given an idea of the complexity of paper mill effluents and the need for model studies on the individual components of the system.
GLOSSARY AND ABBREVIATIONS

Aeration Stabilisation Basin - consists of a large aerated lagoon which supports the micro-organisms used for biological treatment of the effluent.

Alum - papermakers term for aluminium sulphate.

AS - activated sludge process.

ASB - aeration stabilisation basin.

Biochemical Oxygen Demand - usually measured over a period of five days, and represents the oxygen required by the seed organisms to oxidise the available organic matter in an effluent.

BOD - Biochemical Oxygen Demand.

BSAS - bench-scale activated sludge unit.

CEDED - bleaching sequence. Chlorination-alkaline extraction chlorine dioxide-alkaline extraction-chlorine dioxide.

Chemical Oxygen Demand - a measure of the amount of a strong oxidising agent, such as potassium dichromate, consumed by a waste sample when the two are heated.

COD - Chemical Oxygen Demand.

Colour - colour is determined by visual (spectrophotometric) comparison of the sample with known concentration of a standard solution of potassium chloroplatinate and cobaltous chloride. The sample is first filtered through a 0.8 micron membrane filter.

CRC - International Paper Company's Corporate Research Center, Sterling Forest, New York.
CTAB - cetyltrimethylammonium bromide.

Decker - A screen used to separate the pulp from the pulping liquor.

DLVO Theory - classical theory describing the stability of lyophobic dispersions.

EDTA - 1,2-diaminoethanetetra-acetic acid.

EPA - Environmental Protection Agency.

Facultative - the ability to grow with or without the presence of oxygen. Often used in the wastewater treatment industry to describe a biological operation where aerobic, facultative and anaerobic organisms/regions exist.

Fillers - white inorganic pigments used to improve the finish and opacity of paper. They improve the printing surface and give a smooth white finish.

Filterable solids - a measure of the weight of solid material, in a known volume of effluent, retained by a glass fibre filter (1.2 micron) after drying at 103 °C for 1 hour.

IP - International Paper Company, USA.

Jar test - A simple sedimentation test used qualitatively to determine the effectiveness of a treatment operation. A mixed sample is placed in a measuring cylinder and observed.

Kaolin (China Clay) - used as a filler because it is white, soft, non-abrasive and relatively cheap.
Kraft (Sulphate) Pulping - the "cooking" of wood in a mixture of sodium hydroxide and sodium sulphide in a digester under controlled conditions.

Laser Zee Meter - instrument for determining the zeta potential of particles dispersed in water. Consists of a microelectrophoresis cell in which the particles are illuminated with a helium-neon laser and observed with a microscope.

Lignin - a wood polymer consisting of phenyl propane units with varying amounts of methoxy substitution. It cements the fibre cells together giving them the stiffness usually associated with wood.

LPS - lipopolysaccharide.

LZM - laser zee meter.

Non-combustible solids - the weight of residue remaining after igniting a known volume of effluent at 550°C to constant weight.

NPDES - National Pollutant Discharge Elimination System.

Plug flow - a term used to indicate that the solid material produced in a biological treatment operation is recycled. Degrees of recycle are possible.

Recausticising - recovery of sodium hydroxide.

SS - suspended solids.

Suspended Solids - a measure of the weight of suspended solid, in a known volume of effluent, that is retained by a 1.2 micron filter after drying at 103-105°C.

TDS - total dissolved solids.
TI - Ticonderoga Pulp and Paper Mill, New York, USA.

Titanium Pigments - used in papermaking because of their high optical scattering powers. The main pigments used as fillers are forms of titanium dioxide e.g. "Anatase" and "Rutile".

TKN - Total Kjeldahl Nitrogen.

TOC - total organic carbon.

Total Solids - a measure of the weight of residue remaining after heating a known volume of effluent at 103-105 °C to constant weight.

TSS - total suspended solids.

TVSS - total volatile suspended solids.

White Water - the aqueous paper furnish. Consists of materials such as fibres, fillers, retention aids etc.
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CHAPTER 1

INTRODUCTION
1.1 STATEMENT OF THE PROBLEM

The manufacture of paper requires a large supply of water, and it is estimated that the pulping of wood alone requires 40 000–70 000 U.S. gallons per ton of pulp produced (Pinder & Gauvin 1959). The disposal of this process water has a considerable effect on the natural environments of the receiving waters and so efforts are made to control the amount of pollution it causes.

International Paper Company (IP) operate fifteen mills in the United States, thirteen of which use the alkaline kraft process for pulping wood. The products produced by these mills include fine papers and packaging materials, and as a result, large volumes of effluent are created with characteristics dependent on the processes that are used at a particular mill.

The impetus behind this study resulted from the Federal Water Pollution Control Act Amendments (Public Law 92-500) which was passed in 1972. The law's intent is to eliminate all discharge of pollutants by 1985 and for the first time, a polluter may be fined or receive a jail sentence. The United States Environmental Protection Agency (EPA) was designated to administer the law and a schedule for compliance was set up. By 1977 the "Best Practical Control Technology Currently Available" was to be installed throughout the industry and by 1983 the "Best Available Treatment Economically Achievable" is to be implemented. The EPA issued guidelines for each paper mill which defined
the minimum effluent conditions for 1977 and 1983. It was expected that National Pollutant Discharge Elimination System Permits (NPDES) would be issued at these minimums, but it now appears that the 1983 limits are to be less stringent than was first thought.

IP made a decision to reduce the pollutant effects of their mills in order to meet the proposed guideline limits by 1977 and 1983. The first objective was to reduce the volume of pollution that the mills produced. This was to involve an increase in the re-use of process water and a reduction in the amount of material released into the sewers. The second objective was to improve, upgrade and where necessary implement the latest wastewater treatment technology. This investigation was primarily concerned with the second objective.

The EPA broadly classifies pollutants into eight types: oxygen demanding substances, disease-causing agents, synthetic organic compounds, plant nutrients, inorganic chemicals and mineral substances, sediments, radioactive substances and thermal discharges. A summary of the NPDES permit issued to IP's Ticonderoga pulp and paper mill (TI) in New York, is given in Table 1.1.

The TI mill was chosen as a model on which to base this investigation, as it was within easy reach of the facilities at IP's Corporate Research Center (CRC) and was thought to present most of the problems likely to be encountered at any of the IP mills. The mill produces 15.33 million U.S.
<table>
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<td>Daily Av. Kg day⁻¹</td>
<td>Daily Max. Kg day⁻¹</td>
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<td>Flow</td>
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<tr>
<td>TSS</td>
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<td>9 072</td>
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<tr>
<td>Settleable solids</td>
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<td>no limit</td>
</tr>
<tr>
<td>BOD₅</td>
<td>1 996</td>
<td>3 593</td>
</tr>
<tr>
<td>BOD₂₈</td>
<td>no limit</td>
<td>no limit</td>
</tr>
<tr>
<td>Colour</td>
<td>no limit</td>
<td>no limit</td>
</tr>
<tr>
<td>TKN</td>
<td>635</td>
<td>1 143</td>
</tr>
<tr>
<td>NH₃</td>
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<td>no limit</td>
</tr>
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<td>P (total)</td>
<td>40</td>
<td>72</td>
</tr>
<tr>
<td>Temp.</td>
<td>-</td>
<td>99°F</td>
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<td>pH</td>
<td>5.3</td>
<td>8.5</td>
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* These parameters are defined in the glossary (p.vi).

Table 1.1 Summary of the Ticonderoga Process Wastewater Final Effluent Limitations and Monitoring Requirements, New York State Pollutant Discharge Elimination System. Discharge Permit (91-20-2(5/79)). Issued May 1979.
gallons of effluent a day, which is released into the picturesque Lake Champlain. The lake flows very slowly and diffusion of the effluent is therefore poor, producing a noticeable colouring both north and south of the diffuser outlet. Consequently, much legal pressure is brought to bear on IP concerning the pollution from the TI mill. A diagram and summary of the TI process sewer and wastewater treatment average pollutants are given in Appendix I.

1.2 PULP AND PAPER MILL EFFLUENTS

TI has a bleached kraft pulp mill, which aims to selectively remove the fibre-bonding lignin (Figure 1.1) from the wood with a minimum solution of the hemicelluloses and cellulosces. This process is currently the most widely used for pulping and produces about 80% of the chemical pulp in the United States. The principal active chemicals are sodium hydroxide and sodium hydrogen sulphide. Sodium carbonate is also present in the pulping liquor because the causticising reaction, which produces sodium hydroxide, does not go to completion. Unreduced sodium sulphate, sodium thiosulphate, polysulphides and sodium sulphite can also be present (Bryce 1980). The aim of the process is to selectively remove the fibre-bonding lignin from the wood with a minimum solution of the hemicelluloses and cellulosces.

The reactions that take place with lignin and with the carbohydrates in the kraft process are complex and not
Figure 1.1 Tentative structure of a pine Kraft lignin molecule (Marton 1968).
completely understood. In early investigations (e.g., Hägglund 1949; Enkvist 1954) it was established that thio-
lignins, containing about 2.5% bound sulphur, are formed. It was suggested that the sulphur blocks the reactive groups in lignin which would otherwise take part in condensation reactions and inhibit the dissolution of lignin (Enkvist et al. 1962).

Lignin cleavage reactions are also important and in studies with model compounds (e.g., vanillyl alcohol) the following have been identified:

(i) Cleavage of α-aryl ether bonds, where the phenolic groups formed in the reaction make the lignin more soluble and more susceptible to further degradation (Gierer & Norén 1962).

(ii) Cleavage of β-aryl bonds in the phenolic units (Gierer & Smedman 1965) and in the non-phenolic units (Gierer & Norén 1962) produces phenolic and glycolic groups and breaks the lignin down into more soluble low molecular weight fractions. Condensation reactions also occur in which the various carbanions formed in lignin degradation compete with the nucleophilic anions (S$_2^-$, SH$^-$, and OH$^-$) from the cooking liquor for the active sites in the lignin.

The wood carbohydrates will have one of a number of fates: (i) dissolve in the pulping liquor, (ii) degrade to soluble lower molecular weight products, (iii) remain in the fibre as insoluble degradation products or (iv) remain in their original form. Table 1.2 (Aurell & Hartler 1965)
<table>
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<th>Kraft Pulp</th>
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<td>Pulp yield (% of wood)</td>
<td>100.0</td>
<td>48.6</td>
</tr>
<tr>
<td>Lignin</td>
<td>27.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Carbohydrate composition (% of total sugars)</td>
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<tr>
<td>Xylose</td>
<td>10.2</td>
<td>10.9</td>
</tr>
<tr>
<td>Arabinose</td>
<td>2.9</td>
<td>1.0</td>
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<tr>
<td>Mannose</td>
<td>18.9</td>
<td>7.1</td>
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<tr>
<td>Glucose</td>
<td>62.6</td>
<td>79.7</td>
</tr>
<tr>
<td>Galactose</td>
<td>6.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Polysaccharide content (% of wood)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xylan</td>
<td>8.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Glucomannan</td>
<td>15.3</td>
<td>4.1</td>
</tr>
<tr>
<td>Cellulose</td>
<td>32.3</td>
<td>34.3</td>
</tr>
<tr>
<td>Galactan</td>
<td>4.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Araban</td>
<td>1.1</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 1.2 Sugar analysis of pine kraft pulp compared with that of the original wood.
shows the sugar analysis of a pine kraft pulp and the original wood, and all the sugars listed can be expected in the pulp mill effluent. The degradation reactions are quite complex and include both alkaline hydrolysis and end-group peeling reactions.

An outline of the process flow in the TI kraft mill and recausticising plant is shown in Figure 1.2. The kraft mill effluent can be considered to have three contributors: decker filtrates, condensates and intermittent uncontrolled losses throughout the whole process. These waste liquors contain alkali-lignin and cellulose breakdown materials, incompletely cooked wood fragments, fibre, bark, pitch particles, grit, metallic materials, scale, fly ash and residual amounts of the active chemicals used in the process. Spills, overflows and washups in the mill are an important and unpredictable source of waste load. As a rule-of-thumb they contribute 30-50% of the biochemical oxygen demand (BOD) and suspended solids (SS) arising from the pulp mill.

Referring to Figure 1.2, the pulp proceeds from the digester to the bleach plant. Bleaching chemicals and process water are most commonly used on a once-through basis adding considerably to the pollution load. A wide range of conditions and sequencing is found in pulp mills (see Lorås 1980), but it is normal to alternate between an acid stage, where an oxidising agent is applied, and alkaline extraction stage. For a highly bleached kraft pulp as is required at
Figure 1.2 Schematic Flow Diagram of the Ticonderoga Mill Kraft and Recausticising Processes.
TI, the chlorination-alkaline extraction-chlorine dioxide-alkaline extraction-chlorine dioxide (CEDED) sequence is favoured. At TI, 36% of the BOD, 60% of the colour and 6% of the total suspended solids (TSS) of the entire pollution load of the mill is produced at the bleach plant. The chlorination stage uses the most process water, sometimes equalling that used in the rest of the bleach plant.

Investigations of the spent liquor from the chlorination stage have shown that the aromatic structure of lignin is considerably destroyed (Van Buren & Dence 1970; Bennett et al. 1971). A number of low molecular weight compounds are formed which include methanol, acetaldehyde, and acids such as succinic, malonic and oxalic (Ota et al. 1973). Lindström & Nordin (1976) isolated several chlorinated phenols from the spent liquor. Erikson & Dence (1976) have also detected mono-, di- and tri-chlorolignin oligomers.

The reactions of chlorine with the carbohydrates in the pulp are much slower than with the lignin. Carbohydrates can be attacked by chlorine or other radicals, and the rate of reaction is increased in the presence of light. Non-radical processes such as oxidation and hydrolysis are also likely (Lichtin & Saxe 1955). These reactions lead to the formation of carbonyl and carboxyl groups.

The principal reaction in the alkaline extraction stage is one in which the lignin compounds are dissolved. Kempf & Dence (1970), found that 60–90% of the lignin bound chlorine
is lost at this stage and is partly replaced by hydroxyl groups. Spent extraction liquors contain the same low molecular weight substances and phenolic oligomers found in the chlorination effluent, though the latter have a higher molecular weight.

The chlorine dioxide stage has the advantage that it does not normally degrade the carbohydrates in the pulp. For this reason most of the studies have concentrated on the reaction of the dioxide with lignin. Results from model lignin studies indicate that the chlorine dioxide attacks the phenolic groups leading to chlorine substituted reaction products. An important aspect of the CEDED sequence is that it produces toxic chlorinated aromatic compounds.

A large source of wastewater (31%) in the TI mill arises from the paper machines. When the papermaking stock is run onto the paper machine wire, a certain amount of the solid matter is not retained, and passes through the wire together with most of the water used for suspending the fibres. This "white water" contains cellulose fibres and fines, soluble matter, and a high percentage of non-fibrous suspended material such as kaolin or calcium carbonate, starches, titanium pigments and dyes. Much effort has gone into "closing up" the machine systems and recirculating the maximum amount of white water. The TI mill was operating an 85% recycle in 1981.

The power plant produces only a small fraction of the total mill effluent (6.4%) as the general sewer is viewed as
being recycled. The likely pollutants have all been discussed, but in particular a significant percentage of the BOD (22.7%) and TSS (56%) arises at the power plant.

The wood room produces a small amount of effluent. It usually contains a large amount of silt which settles readily and provides no wastewater treatment problems.

1.3 WASTEWATER TREATMENT

Wastewater pollutants can be removed by physical, chemical and biological means (Table 1.3). The initial treatment stage at the TI mill (Appendix I) is primary sedimentation clarification. The clarifiers are preceded by a bar screen which is designed to remove all suspended material larger than 0.15mm diameter. The effluent is then split and flows into two circular, mechanically cleaned, clarifiers. No chemicals are added at this stage as the solids usually have good settling characteristics, most mills achieving 80-90% TSS removal (Knapp et al. 1964). At TI, primary clarification removes 83.5% of the TSS.

After primary clarification, the effluent flows to secondary biological treatment. There are many ways of biologically treating the effluent and in the pulp and paper industry the aerated lagoon is the most widely used. Different types of aerated lagoon exist and different definitions appear in the literature, but they can be considered to include: (i) large storage oxidation basins, (ii) aerated stabilisation basins (ASB), and (iii) the
<table>
<thead>
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<th>Treatment</th>
<th>Primary</th>
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<td>suspended solids</td>
<td>dissolved organics, suspended solids, colour</td>
<td>dissolved organics, suspended solids, colour</td>
</tr>
<tr>
<td>Objectives</td>
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<tr>
<td>Processes</td>
<td>sedimentation</td>
<td>activated sludge, aerated lagoon, sedimentation</td>
<td>granular carbon, filtration, chemical coagulation sedimentation</td>
</tr>
<tr>
<td></td>
<td>↓ sludges</td>
<td>↓ sludges</td>
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</table>

Table 1.3 Wastewater treatment sequences.
activated sludge (AS) processes. They all provide an environment for micro-organisms to grow and convert the colloidal and dissolved carbonaceous organic matter into various gasses and cell tissue. The effectiveness of the process relies on the removal or degradation of the micro-organisms. An accompanying reduction in plant nutrients, colour and inorganic materials is also achieved.

The storage oxidation ponds are usually very large having hydraulic retention times from 20 to over 60 days. They have been largely superceded by the ASB process where the rate of biological activity is increased by having a higher dissolved oxygen concentration. This is brought about by the use of surface or diffusion aerators. The ASB may be operated as a completely mixed system, a plug flow system, or a compromise between the two.

The TI ASB covers 14 acres, holds 67 million U.S. gallons of effluent and is aerated and mixed by 18 floating aerators (Figure 1.3). It is a facultative lagoon in that it is not completely mixed and anaerobic regions exist. The pH of the lagoon effluent is reduced from an average of 6.84 to an average of 5.1 using sulphuric acid. This reduction in pH is to improve the settling of the solids in the secondary clarifiers (Figure 1.5) and to minimise the addition of alum at the tertiary treatment stage.

In order to meet the final effluent requirements (Table 1.1) a tertiary treatment system was constructed. At an estimated cost of $2.5 million, two 182ft. diameter reactor
Figure 1.3 Ticonderoga Mill Aeration Stabilisation Basin showing the surface aerators (a).

Figure 1.4 Two Stage Facultative Pilot Plant Bastrop, Louisiana.
Figure 1.5 Ticonderoga Mill Secondary Treatment Sedimentation Clarifiers.

Figure 1.6 Tertiary Treatment Reactor Clarifiers under construction. Ticonderoga Mill.
clarifiers (Figure 1.6) were installed along with the equipment necessary for the addition of alum, a polymer flocculent and sodium hydroxide for the adjustment of pH. This treatment stage became operational in September 1979 and is very costly; the treatment reagents in 1981 alone totalled $2.12 million (Cawrse 1982). Therefore improvements in any of the treatment stages could result in considerable savings if the tertiary treatment is reduced. Alum (180-360mg dm$^{-3}$) is added as a 50% slurry at a junction box before the effluent flows to a mixing box. At this point, sodium hydroxide is added to maintain the pH in the range 4.8 to 5.0. The effluent is then split and flows to the two reactor clarifiers. As the effluent enters the clarifiers, a high molecular weight cationic polymer (Nalcoflo® 7129; 4-6mg dm$^{-3}$) is added. Finally, the effluent flows to a foam trap where the pH is raised to 5.3 before being discharged into Lake Champlain.

All the sludge produced at the tertiary clarifiers is pumped into one of three holding lagoons. It remains there until it is transferred to a belt press where a major part of the water is removed. Later it is transported to a landfill site.

Opportunities arose to carry out comparative investigations on other treatment systems. These were:

(i) the facultative lagoon, Bastrop, Louisiana,
(ii) a two stage facultative pilot plant, Bastrop, Louisiana (Figure 1.4), and
(iii) an AS pilot plant, Ticonderoga, New York.  
Data was also available from the wastewater treatment plant at IP's Androscoggin pulp and paper mill in Maine.

Interest arose in the AS process as an alternative to an inadequate ASB system. Typically, the AS plant is relatively small, it has a lower retention time and is completely mixed. Nutrients are usually added in the form of nitrogen and phosphorous to maintain a higher growth rate and concentration of micro-organisms. The main deterrent to more extensive use of the AS process is its high capital and operating costs, which can be twice that of ASB systems. These smaller systems are also more sensitive to fluctuations in effluent character and may not give the required reduction in temperature that the longer retention processes provide.

1.4 APPROACHES TO THE PROBLEM

There are a number of possible approaches to the problem and the ultimate merits of each will depend on the final effluent limitations and their long term cost effectiveness. A first approach could be to reduce the volume of effluent produced by the mills. Among the factors encouraging the paper industry to save water are (i) reduced losses of fibre, fines and filler, (ii) reduced cost for purchasing or processing fresh water, and (iii) reduced cost of heating process streams. The paper industry has made many efforts to reduce process water consumption. For
example, in the manufacture of bleached kraft pulp in the southern states of America, the amount of water used was reduced from 100,000 U.S. gallons per ton of production to 40,000 U.S. gallons over the period from 1946 to 1956 (Springer et al. 1976). The TI mill was thought to be down to about 20,000 U.S. gallons per ton in 1981.

Many of the heavily contaminated sewers have relatively low flow rates and therefore a further approach could be to treat these separately. Equipment and treatment chemicals would have to be purchased and this would have to be financially justified. To give an example, the feasibility of using an ion-exchange process for removing the colour from the bleach plant effluents was investigated by Sethy & Tait (1980).

Fluctuations in the physical and chemical nature of the influent to the biological treatment stage often disturbs the microbial population, despite the large buffering capacity of the lagoons. A direct relationship exists between the quality and quantity of spills and overflows in the mills and the quantities of SS escaping from the clarifiers (Frankle & Crossley 1977). These shock loadings could be prevented by incorporating an equilibration stage. To save on capital expenditure the possibility of segmenting the present lagoons exists, with the first segment being used for equilibration.

A number of possibilities for the improvement of the wastewater treatment processes have been investigated, as
part of the CRC "End of Pipe Treatment Technology Development Program" (Frankle 1979). The feasibility of introducing single stage or multi-stage AS processes has been investigated (Tait 1981) and a pilot plant AS investigation is currently underway at TI (Shields 1982). The flocculation of the effluent with a number of ionic and polymeric species has been studied by Hung (1981).

As part of this CRC programme it was agreed that the following would be carried out:

(i) the application of fundamental colloid and surface science to wastewater treatment,

(ii) the investigation of the physical and chemical characteristics of typical pulp and paper mill waste streams, and

(iii) the proposal of optimisation schemes for the flocculation, sedimentation and filtration of wastewaters. More specific direction was given at later stages in the investigation, resulting in the abandonment of some of the initial aims as it became more clear as to what the 1983 legislation would require. This work was ultimately concerned with the flocculation and sedimentation of microbial cells in the treatment of kraft mill effluents.
CHAPTER 2

THEORY OF THE FLOCCULATION OF MICROBIAL CELLS
2.1 INTRODUCTION

Many industrial processes utilise the properties of micro-organisms and, with the recent surge of interest in biotechnology, they have become of great economic importance. The efficient operation of these processes usually relies at some stage on the interaction of the micro-organisms to form flocs. To give an example, in brewing by the batch process the yeast cells must flocculate at the end of the growth phase to allow easy separation by sedimentation (bottom beers) or flotation (top beers). A review of the part played by micro-organisms in industry has been given by Ash (1979).

This work is concerned with the biological treatment of pulp and paper mill effluents where a principal aim is to produce an easily settled, flocculated population of micro-organisms. For convenience the interactions between the suspended organisms will be considered in three sections: the long-range surface interactions occurring at particle separations > 3nm; the short-range interactions at < 3nm; and the interactions that result from the hydrodynamic forces present in treatment operations.

2.2 LONG-RANGE INTERACTIONS

The now classical DLVO theory (Derjaguin & Landau 1941; Verwey & Overbeek 1948) was developed to account for the stability of aqueous dispersions of lyophobic colloids in the presence of simple electrolytes. It gives a static
account of colloidal interactions and does not consider the time dependent processes that may be involved (metabolism, locomotion, rheology etc.). The basic premise is that the total energy of interaction, \( V_t \), between two particles consists of two additive terms: one, \( V_A \), due to the van der Waals forces, and one, \( V_R \), due to the overlap of electrical double-layers associated with charged groups present on the surface, therefore:

\[
V_t = V_A + V_R \tag{2.1}
\]

In making predictions based on this theory it is necessary to define the composition, the charge at the surface and the dimensions of the interacting particles.

Microbial cells can be considered as discrete colloidal particles and their long-range interactions treated according to DLVO theory. However this approach has been criticised by some workers (e.g., Rutter & Vincent 1980; Bleir & Matijević 1978) because micro-organisms are far from being ideal particles, having neither a simple geometry, nor a simple uniform molecular composition. Despite the limitations, it is considered necessary to account for the long-range interactions. Calculations of their order of magnitude can give an insight into their function in the flocculation of wastewater dispersions and they can be useful in optimising the operation of a treatment process (Grutsch 1981).
2.2.1 Composition and Structure of Microbial Cells

The primary aim of this section is to outline the current state of knowledge of the composition and structure of microbial cells. However, information concerning algal, fungal and protozoal surfaces is scant when compared with that available for bacteria.

A considerable fraction of the solid material in a biological treatment system is due to bacteria, the majority of which are Gram-negative (Boyle 1979). Bacteria also make up the smaller range of the biological solids which are, in theory, the most difficult to flocculate. For these reasons the following description will only concentrate on the structure and composition of bacterial species. Certain aspects of the structure and chemistry of fungal walls can be found in the reviews edited by Burnett & Trinci (1979), and for protozoa causing tropical disease, in Tropical Disease Research Series:2 (1979).

Bacteria are prokaryotic organisms which can be seen as three morphological types — spheres, straight rods and curved rods (0.5 – 1.5μm diameter; 1 – 2μm in length). The majority of bacteria stain readily with aniline dyes and their ability to retain stain during washing has been used to divide them into two groups; Gram-positive if they retain the stain or Gram-negative if they do not. Therefore it is possible to broadly classify bacteria according to their morphology and response to the Gram-stain.
In Figure 2.1 the principle structures of a "typical" bacterial cell are shown. Not all the structures will occur in all organisms and some - flagella, pili and capsules - will only be present under certain conditions.

2.2.1.1 Extracellular Appendages

The flagella and pili are appendages which extend from the surface of many organisms into the surrounding environment. Their structure and function have been reviewed by Gibbons (1968), Ottow (1975), Sokatch (1979) and Burchard (1981).

Pili have been implicated in the adhesion of certain bacteria to both mammalian tissue and inert surfaces. They are generally 5 to 25nm in width, and up to 1 - 2 µm in length. On any one organism several hundred pili may be present, usually arranged peritrichously. Analysis of a purified preparation of type 1 pili of *E. coli* showed them to consist almost entirely of the protein pilin, having a subunit with a molecular weight of 16 000. Pilin has a low number of basic amino acids, fewer free carboxyl groups and a relatively high proportion of hydrocarbon side chains. This composition would result in the pili having hydrophobic properties and may explain their general adhesiveness.

Flagella are unbranched helical filaments which are about 20nm thick but are longer than pili, reaching lengths of up to 200µm. More than 98% of their total dry weight is protein. They are primarily responsible for the motility of
Figure 2.1 Diagram of a 'typical' bacterial cell showing the following features:

a) capsule, b) cell wall,
c) cytoplasmic membrane, d) inclusion,
e) flagella, f) nucleus,
g)pili, and h) microcapsule
bacteria and hence their ability to respond to a chemotactic stimulus.

2.2.1.2 Capsule

Many bacteria produce a secretion of viscid material around the external surfaces of their cell walls, which may be from fractions of a micron up to $10\mu$m thick. It may adhere closely to the cell wall (capsule) or be copious in quantity and relatively loosely associated (slime layer). There is considerable interest in their structure because of the part that these extracellular materials play in adhesion and flocculation. In general they are polysaccharides although a few organisms produce polypeptide and protein capsules. The major component of capsules and slime layers is water.

The polysaccharides may be conveniently divided into:
(i) homopolysaccharides, that is polymers of a single sugar or amino acid sugar residue and; (ii) heteropolysaccharides where more than one type of residue is present. Examples of polysaccharide capsule materials are given in Figure 2.2 and of a polypeptide capsule polymer in Figure 2.3.

The majority of bacterial exopolysaccharides are made of more than one type of sugar residue and often contain uronic acids and/or pyruvyl ketal groups which give the polymers an overall negative charge. Acetyl groups are also common substituents. A more detailed account of the structure and other aspects of bacterial capsules has been
Figure 2.2 Repeating unit of (a) the homopolysaccharide cellulose (Acetobacter xylinum), and (b) the heteropolysaccharide hyaluronic acid (Streptococcus A and B).

Figure 2.3 Dipeptide fragment of Bacillus anthracis poly-D-glutamic acid capsule.
given by Sutherland (1977), Berkeley et al. (1979) and Troy (1979).

2.2.1.3 Cell Wall

The cell walls of Gram-positive and Gram-negative bacteria have very different structures and may be from 10-50nm thick. Gram-negative cell walls are the more complex but both, with the exception of Archaebacteria, contain peptidoglycan as their main structural component.

The structure and location of this heteropolymer has been studied in detail by Ghuysen (1968) and Schleifer & Kandler (1972). In Gram-negative organisms peptidoglycan represents as little as 5% of the cell wall, whereas in Gram-positive bacteria the material may account for as much as 80% of the total dry weight of the cell wall. Values of 40 to 50% are more commonly found. As its name implies, it consists of glycan chains with peptide constituents. The glycan chains contain alternating residues of muramic acid and glycosamine in β-1-4 linkage (Figure 2.4).

The location of peptidoglycan as a separate layer inside the cell walls of Gram-negative organisms, makes it unlikely that it will react with macromolecules in the external environment. This was almost conclusively proved by Rapske (1958), who showed that it can only be attacked by lysozyme after the outer membrane has been disrupted with chelating agents such as EDTA. In contrast, some peptidoglycan is exposed at the surface of Gram-positive
Figure 2.4 Generalised structures of the peptidoglycans. a) Found in Gram-negative bacteria and many Bacillus species. b) From Staphylococcus aureus.
bacteria, even when the full complement of secondary cell wall polymers is present. This has been proved by, for example, the finding that peptidoglycan antibodies result in the agglutination of Gram-positive cells (Hughes et al. 1971). Exposed peptidoglycan would give portions of the cell surface amphoteric properties.

The second most abundant secondary wall polymers found in Gram-positive bacteria are the teichoic acids. This is a general term used to describe phosphate-containing wall polymers. Some examples are given in Figure 2.5 but, for a detailed description of these polymers, reference should be made to Archibald (1974) and Baddiley (1972). In bacteria not producing capsules these polymers may represent the outer surface and thus be in direct contact with the environment (Archibald 1980). They are highly negatively charged linear polymers, characteristics which make them hydrophilic and relatively flexible. The majority of Gram-positive organisms also contain a form of teichoic acid linked to a glycolipid. This polymer appears to penetrate the cell wall and become exposed at the cell surface.

The cell walls of Gram-negative organisms contain, protein, lipid and complex polysaccharide material, in addition to peptidoglycan. Teichoic acids are rarely found in this group. Electron micrographs have shown that the envelope consists of several layers (Figure 2.6). Outside the peptidoglycan is the outer membrane which in section has the appearance of a unit membrane. Typically the wall
Figure 2.5 Examples of the structures of teichoic acids: a) ribitol teichoic acid, b) glycerol teichoic acid, c) glucosylglycerol phosphate teichoic acid, and d) teichuronic acid.
Figure 2.6 Diagrammatic representation of the Gram negative cell wall.
cl=peptidoglycan peptide cross link, pp=peptidoglycan polysaccharide, pl=phospholipid, lps=lipopolysaccharide, cc=capsular carbohydrate, cp=capsular protein, es=enzyme located at the cell surface, p=outer membrane protein, ep=periplasmic enzyme, lp=lipoprotein, s=cytoplasmic membrane, em=cytoplasmic membrane enzymes involved in synthesis of components of the surface structure, ps=permeases, ec=cytoplasmic membrane enzymes whose activity is directed towards the cytoplasm.
(Costerton 1975).
consists of 25% phospholipid, 25-30% lipopolysaccharide (LPS) and 45-50% protein. Muhlradt & Golecki (1975) and DiRienzo et al. (1978), have shown that LPS can be found at the outer surface. Moreover, using a specific-labelling reagent, it has been shown that fifteen of the eighteen proteins examined by Kamio & Nikaido (1977), were exposed to the environment. Of particular relevance to microbial interactions is the work of Shands (1966), which demonstrated that the LPS of *E. coli* and *S. typhimurium* may extend up to 150nm from the surface.

2.2.1.4 Other Constituents

Beneath the cell wall and enclosing the cytoplasm is the cytoplasmic membrane. This is a unit membrane about 7.5nm thick that accounts for approximately 10% of the cell’s dry weight and consists mostly of lipid (16 - 19%) and protein (40 - 75%). The structure of the unit membrane has received a lot of attention in the literature (e.g., Danielli & Davson 1935; Robertson 1967; Singer 1974) and that of the fluid mosaic model, as shown in Figure 2.6, is reasonably representative of current thinking. Since it is deeply buried in the cell wall it is unlikely to affect the initial interaction of the particles.

About 80% of the cytoplasm and 75% of the total weight of the cell is water. This is important to remember when applying DLVO theory as account should be taken of the total composition of the interacting particles. The
remaining 20% of the cytoplasm consists of small intracellular inclusions, such as the nucleus, and are not considered here.

2.2.1.5 Model Bacterial Cell

Faced with the complex composition and structure of bacteria it is necessary to define a model cell before applying DLVO theory. With reference to the previous discussion the following simplifying assumptions are made:

(i) the cell is spherical having a diameter of 0.5-2.0 μm,

(ii) it consists of an inner cytoplasm of water surrounded by a 10-50nm sheath of various amounts of polysaccharide, protein and phospholipid, and

(iii) there are no surface appendages.

2.2.2 Origin of Surface Charge

When particles are suspended in an aqueous medium they can attain a charge on their surface by the following mechanisms:

(i) The dissociation of any ionogenic groups present at the particle surface, e.g., carboxyl groups, which would give the particle a negative charge at high pH.

(ii) The unequal dissolution of oppositely charged ions of which the particle may be composed.

(iii) Adsorption of ionic species from solution.

When considering microbial cells only (i) and (iii) are
expected to contribute to the charge on the surface. However, the charge on the surface of inorganic filter and filler materials may arise from (ii).

In extensive microelectrophoretic studies of wastewater treatment streams, Grutsch (1981) found that under normal operating conditions (pH 6-8) microbial cells always have a negative charge. This is a characteristic of most naturally occurring macromolecules in the environment and is attributed to the existence of a chemical predator, the hydrated electron. This species was present during the evolution of these natural polymers, and is considerably more reactive toward those with a positive charge (Scott 1973, 1979).

There have been a number of studies to determine the types of ionogenic groups present at bacterial surfaces (see the review by James 1982). Under controlled conditions of growth and measurement, microelectrophoresis has been used for this purpose. By varying the pH at constant ionic strength the typical curves shown in Figure 2.7 have been obtained. Curve I is typical of non-ionogenic surfaces which are not expected to be found in a microbial population. Curve II is typical of a surface at which the charged groups are anionic (carboxyl, phosphate). Mixed amino-carboxyl surfaces give curves of type III. From studies such as these it has been confirmed that amino, carboxyl and phosphate groups may be found on bacterial surfaces.
Figure 2.7 Typical pH-mobility curves: I) Nujol oil droplets (Douglas & Shaw 1958), II) \textit{K. aerogenes} (Gittens & James 1967), III) \textit{B. megaterium}, \textit{B. subtilis} (Douglas & Shaw 1958), and \textit{Strep. pyrogenes} (James et al. 1965).
Fuller classification and possible identification may be achieved by specifically reacting the surface groups with chemicals or enzymes. For example, surface carboxyl groups can be esterified by diazomethane or acidified methanol (Gittens & James 1963; Maccacaro & James 1959). After esterification, cells of *K. aerogenes* had a zero mobility at pH values below 7 and in more alkaline solutions the methyl ester is hydrolysed. Neihof & Echols (1978) reacted the carboxyl groups with a mixture of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride and a nucleophile (e.g. propylamine) at pH 5. The resulting surface was positive due to the remaining amino groups. This was confirmed by then treating the surface with fluorodinitrobenzene which produced a material of near zero mobility over a wide pH range.

Enzymic treatments of bacterial cell surfaces are not common in the literature but they have been used to study other biological surfaces (e.g. Seaman et al. 1967; Glaeser & Mel 1966).

There is a natural variation in the surface properties of a population of the same cell type which increases when mixed microbial populations are considered. In the latter case the detail in the pH-mobility curves (Figure 2.7) will not be as pronounced, but the same ionogenic groups can be expected on the surfaces. The majority of micro-organisms have isoelectric points in the range pH 2–3, reflecting the significant contribution of carboxyl groups (James 1982).
The adsorption of ions or polyelectrolytes from solution also influences the surface charge. Stern (1924) was the first to analyse the specific adsorption of ions at the solid/liquid interface and, using a method similar to that used to derive the Langmuir isotherm, obtained an expression for the charge density, $\sigma_i$, in the Stern plane:

$$
\sigma_i = \frac{N_i Z_+ e}{1 + \frac{N_A}{n_i M} \exp \frac{Z_+ e \phi_s + \phi_+}{kT}}
$$

$$
\sigma_i = \frac{N_i Z_- e}{1 + \frac{N_A}{n_- M} \exp \frac{Z_- e \phi_s - \phi_-}{kT}}
$$

[2.2]

where $N_i$ is the available number of adsorption sites per cm$^2$, $Z_+$ and $Z_-$ the valencies of the ions of concentration $n_+$ and $n_-$ respectively, $\phi_s$ the Stern potential and $\phi_+$ and $\phi_-$ the specific adsorption potentials of the ions. $M$ is the molecular weight of the solvent and $N_A$ is the Avogadro number. Proceeding from [2.2], the following relationship can be obtained for a dilute solution where only counter-ion adsorption is considered:

$$
\sigma_i = n_i e z = \frac{N_i e z}{1 + \exp (\Delta \theta_0 / kT)}
$$

[2.3]

where $n_i$ is the number of ions adsorbed per cm$^2$ and $x$ is the
mole fraction. The free energy of adsorption can be split into two parts as follows:

\[ \Delta G_0 = \Delta G + z e \phi_d , \quad \text{(2.4)} \]

where \( \Delta G \) is the chemical component and \( z e \phi_d \) is the electrical component.

From (2.4) it can be deduced that even when the electrical term \( z e \phi_d \) is positive it is possible for adsorption to occur, so long as \( \Delta G \) is negative and larger than the electrical term.

Stern's approach has been criticised for neglecting:
(i) the effect of lateral repulsion between adsorbed ions;
(ii) the discreetness of charge effect, and (iii) the influence of the adsorbed particle on the medium in the Stern layer.

There is no knowledge of anion adsorption occurring on microbial surfaces, but the important role of divalent cations has been postulated by a number of authors (e.g. Tenney & Stumm 1965; Armstrong 1966; Friedman et al. 1969; Tezuka 1969; Bangham & Pethica 1960).

The adsorption of polymeric material (Section 2.3.1) onto cell surfaces can alter the electrophoretic mobility and when in excess the cells will assume the electrophoretic characteristics of that material.

Two theoretical approaches have been used to describe polymer adsorption (Vincent 1974). The first was based on
the random walk concept (Flory 1953; Frisch et al. 1953; Frisch & Simha 1957), where the adsorption isotherm was determined from considerations of the changes in conformation that occur when a typical Gaussian coil was placed in contact with a reflecting wall. This approach has been criticised for overestimating the number of possible conformations, but DiMarzio & McCrackin (1965) and Clayfield & Lumb (1966a,b; 1968, 1974) have described how this can be overcome, using Monte Carlo computer simulations.

The second approach, introduced by Silberberg (1962a,b), made use of the concept that the polymer segments exist in two energy states at an interface: (i) runs of segments lying immediately adjacent to the surface ("trains") and; (ii) runs of segments extending into the bulk solution ("loops" or "tails"). The most probable conformation of the polymer at the interface was then calculated. For example, by equating the chemical potential of the macromolecules in the adsorbed state and the bulk solution, the adsorption isotherm may be determined.

The early work was primarily concerned with the adsorption of isolated molecules but more recent papers have extended the theory to account for lateral interactions when there is high surface coverage (Silberberg 1968; Hoeve 1970, 1971). Multilayer adsorption (Silberberg 1972) and polyelectrolyte adsorption (Hesselink 1972) have also been considered. As yet there is no theory that accounts for the kinetics of polymer adsorption.
Comprehensive theories describing the adsorption of polyelectrolytes at the solid/liquid interface that takes into account the various variables such as the charge density of the surface, the degree of dissociation of the polyelectrolyte, the effect of charge screening etc., are not yet available. In addition to the lack of theoretical knowledge, systematic studies of the adsorption of polyelectrolytes are limited. Tadros (1979) studied the adsorption of lignosulphonates onto two pesticides, but the conclusion he drew from the work was that the adsorption process was very complex and model studies would be needed. Tadros did deduce that the adsorption of the lignosulphonates was weak and in most cases reversible.

2.2.3 Structure of the Double-Layer

When microbial cells are dispersed in aqueous media they tend to carry an electric charge (Section 2.2.3). This charge influences the distribution of ions in solution near the surface forming an ionic double layer. The charge is neutralised by the counter-ions in solution such that the overall system is electrically neutral, and no net coulombic force exists between particles at large distances of separation.

The structure of the double-layer has been considered in detail by Overbeek (1952) and has been extensively reviewed (see Parsons 1954; Bockris et al. 1963; Sparnaay 1972; Hunter 1981). The structure that is widely accepted
is that developed by Grahame (1947) which embodies the principles put forward by Helmholtz (1879), Perrin (1904), Gouy (1910, 1917), Chapman (1913) and Stern (1924).

The current thinking is that the space charge in the electrolyte solution surrounding a particle is divided into two regions. Firstly the compact or inner Stern region, very near the cell wall. There the charge and potential distribution are determined chiefly by the geometrical restriction of ion and molecule size, and the short range interactions between ions, the wall and adjoining dipoles. Secondly a diffuse layer, further out from the wall, where a solution to the Poisson-Boltzmann equation may be expected to give a reasonable representation of the potential distribution. Among the simple ions that have been studied at the mercury-solution interface, specific adsorption is more common among anions, presumably because they are less strongly hydrated. The potential distribution near a metal electrode (and some colloidal particles) is therefore likely to look like Figure 2.8.

The double-layer of microbial cells however, is difficult to define. The surface charge is not located within an infinitely thin shell, but is spread throughout a layer (cell wall with/without a capsule) which is permeable to water, ions and small molecules (Parsegian and Bingell 1973). The charge is not uniformly distributed but is arranged in zones of varying density. In addition there may be appendages, that are likely to be charged (Section
Figure 2.8 Structure of the double-layer according to Bockris et al. (1963).
2.2.1.1), which protrude from the surface. These and other short-range effects (Section 2.3) further complicate the double-layer.

Haydon (1961, 1964) has considered the structure of the double-layer for a surface that is permeable to counter-ions as well as effect of having a fixed layer of ionogenic groups below the surface. However, the situation is infinitely more complicated when the permeable layer may have the variety of structure and composition shown in Figure 2.6.

Therefore at present it is possible to do no more than divide the microbial double-layer into two regions. (i) The inner Stern region close to the outer surface which is immobile and undefined, possibly containing adsorbed ions, polymer chains and cell appendages. There is now strong evidence for the presence of boundary layers of water in this region (Israelachvilli & Adams 1978). (ii) Outside the immobile region is the diffuse part of the double-layer where the charge distribution can be adequately described by a solution to the Poisson-Boltzmann equation.

It can be argued that the potential which determines the electrostatic stability of a microbial dispersion is that at the hydrodynamic radius of the particles undergoing Brownian diffusion. It is then possible to equate this potential with the zeta-potential obtained from electrokinetic measurements (see Section 2.2.4).
2.2.4 Zeta-Potential

In all electrokinetic phenomena a fluid moves relative to a particle or solid surface. In this study, where electrophoresis is used, the microbial cells move along the lines of force of an externally applied electric field. Details of the experimental procedure are given in Section 4.3, but in short, the electrophoretic mobility of a particle is measured and then, using one of several available formulae, the zeta-potential, $\zeta$, is calculated. Zeta is the potential at an imaginary surface of shear which is considered to be close to the solid surface and within which the fluid is stationary. All the material inside the sheath forms the kinetic unit, so that the particle moves along with a certain quantity of its surrounding liquid.

The kinetic unit of a microbial cell will be the cell plus any extracellular material attached to the surface. If the surface is hydrophilic then there is evidence for the presence of a structured layer of water which will increase the hydrodynamic radius. The presence of surface appendages will likewise move the surface of shear to a position further from the surface.

Calculation of the zeta-potential from the electrophoretic mobility has been extensively reviewed. Overbeek (1950) and Booth (1948, 1953) covered the early work and the modern theory has been reviewed by Overbeek & Wiersema (1967), Dukhin & Derjaguin (1974), Overbeek & Bijsterbosch (1979). More recently a thorough account has
The first equation relating electrophoretic mobility, \( \nu_e \), to \( \zeta \) was due to Helmholtz (1879) and Smoluchowski (1905, 1921) who equated the electrical forces with the viscous forces giving the Smoluchowski equation:

\[
\nu_e = (4\pi \varepsilon_0) \cdot \frac{D \zeta}{4\pi \eta} = \varepsilon \frac{\varepsilon}{\varepsilon_0} ,
\]

where \( D \) is the (dimensionless) dielectric constant \( (D = \varepsilon / \varepsilon_0 \) where \( \varepsilon_0 \) is the permittivity of free space and \( \varepsilon \) is the relative permittivity), and \( \eta \) is the viscosity of the medium. This equation is applicable to an impenetrable particle of definable shape or orientation. The more penetrable a particle is by counterions, the more inaccurate the calculation of \( \zeta \) is from \( \nu_e \) (Haydon 1964).

After the publication of the Debye-Hückel theory for strong electrolytes, Hückel (1924) derived a significantly different equation for the electrophoretic mobility of a spherical particle (only):

\[
\nu_e = (4\pi \varepsilon_0) \cdot \frac{D \zeta}{6\pi \eta} = \frac{2e\zeta}{3\eta} ,
\]

of which a more rigorous derivation has been given by Overbeek & Bijsterbosch (1979).

The reason for the discrepancy between [2.5] and [2.6] was found to arise from the different ways in which account was taken of the electric field in the neighbourhood of the particle (Henry 1931). Hückel had disregarded the
deformation of the applied field by the presence of the particle and Smoluchowski had assumed the field to be uniform and everywhere parallel to the particle surface. These assumptions are only justifiable in the extreme cases where $\kappa a \ll 1$ and $\kappa a \gg 1$ respectively.

The unitless parameter $\kappa a$ is the product of the particle radius, $a$, and the Debye-Hückel parameter given by:

$$\kappa^2 = \frac{4 \pi e^2 \rho N \sum c_i z_i^2}{(4 \pi \varepsilon_0)^2 D k T} \frac{\sum c_i z_i^2}{k T e}$$  \hspace{1cm} (2.7)

where $c_i$ is the concentration (mol dm$^{-3}$) and $z_i$ the valency of the ion $i$; $k$ the Boltzmann constant, $e$ the electronic charge, $N_A$ the Avogadro number and $\rho$ the density of the medium. The distance $1/\kappa$ is referred to as the thickness of the double layer.

Henry derived a formula that showed a smooth transition from the Hückel to the Smoluchowski equation as $\kappa a$ was increased (see Overbeek 1952). In the transition region account was taken of the electrical force on the particle, and also both the frictional force and the electrophoretic retardation, since all are comparable in magnitude for $\kappa a \sim 1$ (Dukhin & Derjaguin 1974). The electrophoretic retardation results from the force exerted by the d.c. field on the ions surrounding the particle. This force is transferred to the solvent molecules resulting in a flow of liquid in an opposite direction to the
The following equation was given by Henry:

\[ v_E = (4\pi \varepsilon_0) \frac{D \phi}{6\pi \eta} f_i(\kappa a) = \frac{2\varepsilon_0}{3\eta} f_i(\kappa a) \quad [2.8] \]

The function \( f_i(\kappa a) \) depends on the shape of the particle and for a sphere was given by,

for \( \kappa a < 1 \):

\[ f_i(\kappa a) = 1 + \frac{(\kappa a)^2}{16} - \frac{5(\kappa a)^3}{48} - \frac{(\kappa a)^4}{96} + \frac{(\kappa a)^5}{96} \]

\[ \frac{[ (\kappa a)^4 - (\kappa a)^5 ] e^{\kappa a}}{8} \int_0^{\kappa a} e^{-\tau} d\tau \quad [2.9] \]

and for \( \kappa a > 1 \):

\[ f_i(\kappa a) = \frac{3}{2} - \frac{9}{2\kappa a} + \frac{75}{2\kappa^2 a^2} - \frac{330}{\kappa^3 a^3} \quad [2.10] \]

Values for the exponential integral in [2.9] are given in tables of mathematical functions (e.g., Jahncke & Emde 1945).

It can be shown that \( f_i(\kappa a) \) approaches 1 for small \( \kappa a \) and \( 3/2 \) for large \( \kappa a \). This calculation is based on the assumption that the external field can be superimposed on the field due to the particle and the latter can be described by the linear Poisson-Boltzmann equation. Therefore the treatment is only valid for particles of low potential (< 25 mV).

The Henry equation fails to account for the distortion of the field induced by the movement of the particle. A finite relaxation time is required for the distorted ion atmosphere to regain symmetry, and in most cases this effect decreases the mobility of a particle. Generally the effect of relaxation is appreciable for \( \zeta > 10 \text{mV} \) and \( 1 < \kappa a < 10 \).
To obtain an expression for the mobility which is valid for all values of $\kappa a$, the geometric effect considered by Henry (1931) and both the relaxation and retardation effects have to be taken into account. This involves solving several differential equations simultaneously. Solutions were obtained by Overbeek (1943) and Booth (1950) for spherical particles. They showed that for intermediate values of $\kappa a$ the electrophoretic velocity varies as an infinite power series in $\zeta$. Due to the complexity of the problem only the first coefficients were calculated. Wiersema et al. (1966) provided a computer solution for zeta-potentials of up to 150mV, which showed that Overbeek (1943) and Booth (1950) overestimated the magnitude of the relaxation correction for intermediate values of $\kappa a$ ($0.2 < \kappa a < 50$).

The calculation of zeta-potential from electrophoretic mobility using the Wiersema et al. procedure is not an easy task, especially if one has to consider anything other than a simple electrolyte system. Tables based on the Wiersema et al. procedure showing the relation between $\zeta$ and mobility have been prepared by Loeb et al. (1961) and Ottewill & Shaw (1972), but they are strictly for simple electrolyte systems and are of limited value when dealing with wastewater treatment streams.

Recently O'Brien & White (1978) provided a more rapid computer solution to the electrophoretic problem. Using a computer programme available from O'Brien & White it is
possible to input any arbitrary collection of ion valencies, concentrations and limiting ionic conductivities (the latter measured at any temperature) and to calculate $\zeta$ for any given particle radius. The problem lies in defining all these parameters for a particular wastewater stream. If the assumption is made that the ionic concentration arises only from sodium sulphate then this solution can be used for order of magnitude calculations.

The effect of conductivity on $\zeta$ has been neglected in these treatments. Although the effects of high particle conductivity have been demonstrated (Henry & Brittain 1931), all particles may be assumed to be insulators (Hunter 1981). The exception is the liquid metallic dispersion of mercury. On the other hand the effect of surface conductance can lead to significant errors (>5%) if the Hückel or Smoluchowski equations are used except for values of $K\alpha \ll 0.1$ and $K\alpha \gg 500$ respectively. This is particularly the case for large values of $\zeta$. In the other more rigorous solutions mentioned earlier, the effects of surface conductance are taken into account in the treatment of the relaxation effect.

It has been assumed that the permittivity and coefficient of viscosity are the same in the double-layer as they are in the bulk medium. However, the viscosity of water rises steeply at a field strength of $10^5 \text{V cm}^{-1}$ due to some ordering of the solvent dipoles (Andrade & Dodd 1951). The permittivity falls off as the potential increases and several estimates of this effect are available (Grahame...
1950; Conway et al. 1951). Both effects reduce the particle mobility for a given zeta-potential. Lyklema & Overbeek (1961) conclude that the effect of field strength on the permittivity can probably be neglected, but the effect on the viscosity may be more serious. The variation of $\eta$ with field strength may be represented by:

$$\eta = \eta_0 \left(1 + f_0 (d\psi/dx)^2\right), \quad [2.11]$$

where $\eta_0$ is the viscosity at zero field strength. The value of the viscoelectric constant $f_0$ is not known with any certainty. Lyklema & Overbeek used $f_0 = 10^{-11}$ cm$^2$ V$^{-1}$ but it now appears to be fifty to one hundred times lower (Smith 1973). A reduction in $f_0$ would make the approximation $\zeta = \psi_0$ more valid. The general practice among colloid chemists of neglecting the viscoelectric effect will be adopted in this investigation.

It has been found that typical $K_\alpha$ values for biologically treated bleached kraft mill effluents lie in the range 100-600, and if coagulants such as aluminium sulphate are added a will be higher. The O'Brien and White approach is the most rigorous and suitable for this range, especially for $K_\alpha < 500$, although in the majority of cases the limiting Smoluchowski equation is adequate (Section 5.3).
2.2.5 Interaction of Spherical Double-Layers

The mutual approach of two charged microbial cells is accompanied by a repulsive energy, $V_r$, that arises from the overlap of their diffuse double-layers. The treatment of this repulsive energy requires certain simplifying assumptions and depends on the geometry of the interacting particles.

Mathematical treatments are only available for certain well defined geometries (sphere, flat plate, cylinder) and in this study, the assumption will be made that interacting microbial cells approximate to spheres. Where an interacting surface can best be represented by a plate-model the sphere model will be retained with the radius of curvature considered infinitely large.

The aqueous colloidal dispersions found in paper mill effluents may contain particles of different surface charge for a given solution condition. Therefore only a treatment that can account for the interaction of dissimilar double-layers will be considered.

In calculating $V_r$, it is necessary to make a restricting assumption as to whether the interaction takes place at constant charge, or at constant potential. Both will be considered, although for biological systems the interaction may be a compromise between the two. Ninham & Parsegian (1971) have given a mathematical description of $V_r$ in which both the charge and electrostatic potential vary, at
constant chemical potential. However, a value has to be assigned to the chemical potential at the surface, which was not possible for the systems we studied.

2.2.5.1 Interaction at Constant Potential

Derjaguin (1954) was the first to consider the interactions of dissimilar double-layers. There have been several attempts since then but all of the results require tedious graphical or numerical integration and are not easily applicable to practical systems (e.g., Devereaux & de Bruyn 1963). When considering heterodisperse systems, the popular simplified equation derived by Hogg et al. (1966) may be used. These workers followed the method adopted by Derjaguin (1934, 1939) who assumed each interacting sphere to consist of a series of rings of radius \( h \) and thickness \( dH \), each of which could then be considered as a flat plate. Thus, providing the thickness of the double-layers is small compared to the particle radii, \( a_1 \) and \( a_2 \), the energy, \( V_R \), of interaction at constant surface potential is given by:

\[
V_R = \frac{2\pi a_1 a_2}{a_1 + a_2} \int_H^2 V_1(H_0) dH.
\]

where \( H_0 \) is the separation of the theoretical flat plates and \( H \) is the minimum separation of the particles. \( V_1 \) represents the potential energy of interaction of two parallel, infinite, flat plates. Hogg et al. simplified the calculation of \( V_1 \) by using the Debye-Hückel approximation for low surface potentials (<25mV), making no attempt to
account for such effects as dipole and specific chemical interactions. They arrived at the following expression:

\[ V_1 = \frac{(4\pi \varepsilon_0).D.K}{8\pi}\left\{\left(\phi_0^2 + \phi_1^2\right)(1-\coth 2kd) + 2\phi_1\phi_2 \text{cosech } 2kd\right\}, \tag{2.13} \]

where \(2d\) is the distance of separation of the plates. As \(H\) is identical to \(2d\), [2.12] was solved analytically giving:

\[ V_{\psi} = \frac{(4\pi \varepsilon_0).D.a_1.a_2 (\phi_1 + \phi_2)}{4(a_1+a_2)} \left[\frac{2\phi_1\phi_2}{(\phi_1^2+\phi_2^2)} \ln\left(\frac{1+\exp(-KH)}{1-\exp(-KH)}\right) + \ln(1-\exp(-2KH))\right]. \tag{2.14} \]

Verwey and Overbeek (1948) have shown that Derjaguin's (1934, 1939) method is reasonable if \(Ka>5\), and gives a good approximation if \(Ka>10\). Using the Debye-Hückel approximation, [2.14] holds exactly for \(\phi_0\) and/or \(\phi_2\) of less than 25mV, although Hogg et al. have shown that the equation holds for surface potentials of less than 50-60mV.

Since the completion of this project a paper by Ohshima et al. (1982) has appeared in the literature in which corrections have been made to the Hogg et al. equation. The improvements enable the extension of the calculation of \(V_{\psi}\) to moderate potentials. However, for the low potentials encountered in this study there would be no advantage in using the improved equations.
2.2.5.2 Interaction at Constant Charge

Wiese & Healy (1970) followed the method of Frens (1968) and derived an equation for the energy, $V_R^\sigma$, of interaction of spheres of dissimilar double-layers at constant charge:

$$V_R^\sigma = V_R^\psi - \frac{(4\pi \varepsilon_0)D a_1 a_2}{2(a_1+a_2)} \ln(1-\exp(-2KH)) \tag{2.15}$$

where $V_R^\psi$ is the energy of interaction given by [2.14].

According to Frens & Overbeek (1972) the difference between $V_R^\sigma$ and $V_R^\psi$ tends to decrease with surface potential however, for small potentials $V_R^\sigma$ deviates markedly from $V_R^\psi$ for KH<1. For KH<0.5, $V_R^\sigma$ becomes increasingly higher than $V_R^\psi$ as H decreases. Generally $V_R^\sigma$ is larger than $V_R^\psi$ and the two are only identical at large separations. Jones & Levine (1969) have concluded that neither the constant charge nor the constant potential approach is applicable for KH<0.5.

2.2.6 London-van der Waals Interactions

The interaction between neutral atoms was first appreciated by van der Waals (1873) in explaining deviations from the ideal-gas law. It was London (1930a) however, who first expressed the interaction forces in quantum-mechanical terms. As summarised by London (1937) the interaction of two neutral atoms can be expressed by $-\beta/\Lambda^2$ where $\Lambda$ is the distance between the molecules and $\beta$ is a constant to which three forces contribute: dipole-dipole (Keesom 1921),...
dipole-induced dipole (Debye 1921) and induced dipole-induced dipole (London-van der Waals dispersion). In general these forces are attractive, although when macroscopic bodies are separated by a fluid, repulsion may occur. There are a number of publications that review dispersion force theory (e.g., Parsegian 1975, Richmond 1975, Mahanty & Ninham 1976).

One of the main purposes of this section is to describe the methods of estimating these forces of interaction for macroscopic microbial cells. Nir (1979) has given a detailed account of the problem for cells of biological interest. It was thought (Bangham & Pethica 1960) that these forces would be small and therefore unimportant in biological dispersions but their significance was soon realised (Curtis 1960).

The calculation of $V_A$ between two particles, composed of a large number of molecules, was originally (Hamaker 1937) assumed to be given by the sum of all possible interactions between pairs of molecules in different particles. In essence the interactions were assumed to arise from the largely temperature independent ultraviolet contribution to the London-van der Waals dispersion energy. Casimir & Polder (1948) demonstrated that at large separations the forces are retarded, leading to an inverse seventh power dependence on the distance of separation rather than the inverse sixth power predicted by London. Therefore solutions based on the Hamaker approach have
appeared for two cases:

(i) those applicable to unretarded interactions only, which are considered to be valid for separations of \( H < \lambda/2 \); and

(ii) solutions applicable to all particle separations and therefore allowing for retardation.

In this study \( \lambda \) has been taken to be equal to the conventional value of 100nm; 72nm for diamond and 134nm for silicon bromide are the extremes.

The Hamaker theory however, is recognised to be inadequate for the following reasons (Parsegian & Ninham 1971):

(i) The highly polar nature of liquid water ensures that much of the dispersion force comes from polarisation at infrared and microwave frequencies rather than the ultraviolet.

(ii) It is incorrect to think of the pairwise additivity of individual interatomic interactions in condensed media.

(iii) By virtue of the low frequency contributions the dispersion force also contains a temperature dependent component.

(iv) That the liquid between the interacting particles can be dealt with by the insertion of an arbitrary dielectric constant at a single frequency.

Progress in the theory of London-van der Waals dispersion theory can be traced back to Lifshitz (1955,
1956) and Dzyaloshinskii et al. (1961) who gave a framework for calculating dispersion interactions for any combination of dielectric media from measurements of their spectral properties. These theories were difficult to apply and colloid chemists had to wait for the semi-classical approaches of G. van Kampen et al. (1968), Ninham & Parsegian (1970a, 1970b), Parsegian & Ninham (1969, 1973) and others (see Richmond 1975) to appear. The Hamaker and Lifshitz approaches will be considered separately.

2.2.6.1 The Microscopic Hamaker Approach

In general the London-van der Waals interaction energy, $V_A$, takes the form given by Vold (1961):

$$ V_A = -\frac{1}{12} \sum_{i=1}^{n} f(A_i) \, G_i , \quad [2.16] $$

where $f(A_i)$ is a function of the various Hamaker constants involved and $G_i$ is a function of the geometry of the system.

The Hamaker constant, $A_{ii}$, for two bodies of material 1 acting across a vacuum is given by:

$$ A_{ii} = \pi^2 N_1 \beta_1 , \quad [2.17] $$

where $N_1$ is the number of atoms or molecules per cm$^3$ and $\beta$ is the constant in London's (1930) equation.

For the interaction between two dissimilar materials:

$$ A_{12} = N_1 N_2 \beta_{12} , \quad [2.18] $$
provided that:

\[ \beta_{12} = (\beta_{11} \cdot \beta_{22})^{\frac{1}{2}} \quad [2.19] \]

[2.19] is Bertholet's (1899) principle where the interaction constant of two different particles equals the geometric mean of the interaction constant of the individual particles (providing the ground state electronic frequencies of the molecules are equal). Therefore \( A_{12} \) is given by:

\[ A_{12} \sim (A_{11} \cdot A_{22})^{\frac{1}{2}} \quad [2.20] \]

The Hamaker constant \( A_{131} \) for two bodies of the same material suspended in medium 3 is given by:

\[ A_{131} = A_{12} + A_{33} - 2A_{13} \quad [2.21] \]

and if the bodies suspended in the medium 3 are of a different composition then:

\[ A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad [2.22] \]

Using [2.20], [2.21] and [2.22] can be approximated as:

\[ A_{131} \sim (A_{11}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})^2 \quad [2.23] \]

and

\[ A_{132} \sim (A_{11}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})(A_{22}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}}) \quad [2.24] \]

According to Schenkel and Kitchener (1960), the right hand sides of [2.23] and [2.24] should be divided by \( \varepsilon \), the dielectric constant of the medium 3. But Visser (1972) disagreed because the numerical results of Krupp et al. (1972) indicated that [2.23] and [2.24] should be written
as:

\[ A_{131} = c_1 (A_{11} + A_{33} - 2A_{13}) \]  \[2.25\]

and

\[ A_{132} = c_2 (A_{12} + A_{33} - A_{13} - A_{23}) \]  \[2.26\]

where \( c \) is a constant equal to 1.6 when material 3 is water.

Hamaker (1937) suggested that \( V \) could be repulsive rather than attractive, and it has been shown (Israelachvili 1973; van Oss et al. 1979) that \( A_{132} \) becomes negative when:

\[ A_{11} > A_{33} > A_{22} , \]

or when

\[ A_{11} < A_{33} < A_{22} . \]

These net-repulsive forces have been implicated in the interaction of biological systems (van Oss et al. 1980).

At this point it is convenient to consider the calculation of Hamaker constants, reviews of which have been given by Gregory (1969), Visser (1972) and Nir (1979). One method is to assign a value to the London constant, \( \beta \), for the materials of interest. Notable among the expressions for \( \beta \) is that of Slater & Kirkwood (1931):

\[ \beta_{H} = \frac{3}{4} \frac{\hbar^2}{\pi} \frac{1}{\nu_0} \alpha_0^2 \]  \[2.27\]

where \( z \) is the number of electrons in the outer shell of the molecule, \( \hbar \) is Planck's constant, \( \nu_0 \) is the frequency of the electron in the ground state, and \( \alpha_0 \) is the static

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polarisability of the molecule. Moelwyn-Hughes (1961) modified (2.27) by replacing \( \nu_0 \) with \( \nu_p \), the characteristic frequency of the molecule. Although the Moelwyn-Hughes expression is widely used, it tends to give Hamaker constants that are too high (Gregory 1968). On the other hand, Visser has reported good agreement with this approach when comparing it with constants derived from both the Slater-Kirkwood expression and the Lifshitz approach (Section 2.2.6.2).

There are more direct methods of estimating Hamaker constants. Important examples are the static dielectric constant approach of Tabor & Winterton (1969) and Gregory (1969), and the method used by Fowkes (1968) based on interfacial tension data. Tabor & Winterton and Gregory show that the Hamaker constant of material 1 is given by:

\[
A_{11} = \frac{27}{64} \nu_p \left( \frac{\varepsilon_{10} - 1}{\varepsilon_{10} + 2} \right)^2
\]

where \( \varepsilon_{10} \) is the static dielectric constant obtained from the square of the refractive index at the characteristic frequency, \( \nu_p \).

Fowkes (1968) gives the following equations for calculating the Hamaker constant:

\[
A_{11} = 12.2d^2 \gamma_d/\lambda
\]

and,

\[
A_{131} = \frac{12.2\{d_1 (\gamma_1^d)^{\frac{1}{2}} - d_3 (\gamma_3^d)^{\frac{1}{2}}\}}{\varepsilon_3 \lambda_{13}}
\]

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where $\gamma_{13}^{d}$ is the dispersion contribution to the surface tension of the solids 1,3; $d$ is the separation of atomic centres at contact and is 0.4nm for inorganic materials, 0.43nm for water and 0.46nm for organic molecules; $\lambda_{13} = 0.9$ and $\varepsilon_3$ is the dielectric constant of material 3. When 3 is water $\varepsilon_3 \lambda_{13}$ is equal to 1.6.

Vold (1961) derived an equation based on [2.16] and [2.20] for the general case of two spherical particles, radii $a_1$, $a_2$ and Hamaker constants $A_{11}$ and $A_{22}$, having adsorbed layers of thickness $\delta_1$ and $\delta_2$ and Hamaker constants $A_{44}$, $A_{55}$ in a medium of Hamaker constant $A_{33}$:

$$V_a = -\frac{1}{12}\left\{g_{45}\left(A_{44}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}}\right)\left(A_{55}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}}\right)\right. + g_{12}\left(A_{11}^{\frac{1}{2}} - A_{44}^{\frac{1}{2}}\right)\left(A_{22}^{\frac{1}{2}} - A_{55}^{\frac{1}{2}}\right)$$

$$\left. + g_{15}\left(A_{11}^{\frac{1}{2}} - A_{44}^{\frac{1}{2}}\right)\left(A_{55}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}}\right) + g_{24}\left(A_{22}^{\frac{1}{2}} - A_{55}^{\frac{1}{2}}\right)\left(A_{44}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}}\right)\right\}. \quad [2.31]$$

If $A_{11} = A_{44}$ and $A_{22} = A_{55}$ then [2.31] reduces to a form for the interaction of two spheres without adsorbed layers.

Hamaker (1937) arrived at an expression for $G$ by calculating the interaction energy between two volumes $dV_1$ and $dV_2$ of two spheres and then summing over the total
volume $V_1$ and $V_2$. For particles of radius $a_1$ and $a_2$:

$$G = \frac{y}{x^2+xy+x} + \frac{y}{x^2+xy+y} + 2 \ln \left[ \frac{x^2+xy+x}{x^2+xy+y} \right], [2.32]$$

where for:

- $G_{45} : \Delta = H, \quad r_1 = a_1 + \delta_1, \quad r_2 = a_2 + \delta_2$
- $G_{12} : \Delta = H + \delta_1 + \delta_2, \quad r_1 = a_1, \quad r_2 = a_2$
- $G_{13} : \Delta = H + \delta_1, \quad r_1 = a_1, \quad r_2 = a_2 + \delta_2$
- $G_{24} : \Delta = H + \delta_2, \quad r_1 = a_1 + \delta_1, \quad r_2 = a_2$
- $x = \Delta / 2r_1, \quad y = r_2 / r_1$

$H$ is the distance of separation of the outer surfaces of the particles. This equation is only valid for $\Delta \ll \lambda / 2$. It is common practice to neglect retardation between colloidal particles, as even for particle radii of up to 0.2 µm, the distances over which the attractive forces act are of the order of 10 nm. However, with bacterial cells of 2.0 µm diameter the range of interaction may be much greater. In addition it is necessary to consider the role of secondary minimum flocculation (Section 2.2.7) which could occur at separations of the order of $\lambda / 2$. For these reasons [2.32] is of limited use in this study.

Schenkel and Kitchener (1960) have proposed equations based on an approximate form of the Hamaker function. Although they have been extensively used because of their simplicity, Vincent (1973) has pointed out that they are inadequate, especially for small particles. They are also limited in their application to practical systems as they can only be used for spheres of equal radii.
Using an integration technique similar to that used by Hamaker, Vincent derived analytical expressions for the retarded $G$ function, separating it into a long range function $G_L$ and a short range function $G_s$. At a critical separation, $\Delta^*$, there is a transition from one to the other, where for $\Delta<\Delta^*$, $G_s$ is used and for $\Delta>\Delta^*$, $G_L$ is used. Vincent gave the following:

$$G_s = b \left[ \frac{y + y + 2 \ln \left( \frac{u}{u+y} \right)}{u} \right]$$

$$+ \frac{8c r^2}{d} \left[ 2y + (2u+y) \cdot \ln \left( \frac{u}{u+y} \right) \right]. \quad [2.33]$$

$$G_L = \frac{b'}{10d} \left[ \frac{y(1+y)^2}{u^2} + \frac{y(1-y)^2}{u+y} - \frac{2(y^2+y+1)}{u} \right]$$

$$+ \frac{2(y^2-y+1)}{u+y} + 4 \ln \left( \frac{u+y}{u} \right)$$

$$+ \frac{c'}{ \frac{60r^2}{u+y} } \left[ \frac{2 - 2 + y^2+y+1 - y^2-y+1}{u^2} \right]$$

$$- \frac{y(1+y)^2}{u^2} - \frac{y(1-y)^2}{u+y} \right]. \quad [2.34]$$

The constants $b$, $b'$, $c$ and $c'$ have the following values:

$$b = 1.01 \quad c = 0.14(2\pi/\lambda)$$

$$b' = 2.45(\lambda/2\pi) \quad c' = 2.04(\lambda/2\pi),$$

where $u = x^2 + xy + x$, and $d = r_1 + r_2 + \Delta$. The definitions of $x$, $y$, $r_1$, $r_2$ and $\Delta$ are those given for [2.32].

Vincent has given a polynomial for the rapid calculation of $\Delta^*$ but Nazir (1977) has shown that this can be grossly in error. For this reason, an iterative
technique has been used to locate $\Delta \times$. Examples of the transition from $G_s$ to $G_L$ are shown in Figures 2.9 to 2.17. Figures 2.9 to 2.13 show the effect of increasing the radii of equal size particles. The smoothness of the transition from $G_s$ to $G_L$ decreases as the radii of the particles increases and is poor for particle radii $>1\mu m$ (Figure 2.12). However, providing that one of the interacting particles is small, a smooth transition is maintained (Figures 2.14 to 2.17). The implications of this behaviour are that these equations are suitable for calculating $V_R$ for sphere-sphere interactions and for approximating sphere-plate interactions. They are however, not suitable for calculating the interaction between two plates when the radii would be assumed to be infinitely large.

Clayfield et al. (1970) integrated analytically Overbeek's simplification of the Casimir & Polder (1948) equation for the retarded interaction between two atoms, and gave an expression for the dispersion force between spherical particles:

$$ G = \frac{12}{r_1 + \Delta + r_2} \cdot I $$

[2.35]

Five expressions were given for $I$ depending on the values for $r_1$, $r_2$, $\Delta$ and $\rho$ where $\rho = 3\lambda/2\pi$. The equations for $I$ are complicated and will not be reproduced here, but direct reference will be made to them using the numbering system.
Figure 2.9 The behaviour of Vincents' short and long range geometric functions for small particles of equal radii.
Figure 2.10 The behaviour of Vincent's short and long range geometric functions for particles of equal radii.
Figure 2.11 The behaviour of Vincents' short and long range geometric functions for particles of equal radii.
Figure 2.12 The behaviour of Vincents' short and long range geometric functions for large particles of equal radii.
Figure 2.13  The behaviour of Vincents' short and long range geometric functions for large particles of equal radii.
The behaviour of Vincents' short and long range geometric functions for particles of unequal radii.
Figure 2.15 The behaviour of Vincents' short and long range geometric functions for particles of unequal radii.
The behaviour of Vincents' short and long range geometric functions for particles of unequal radii.

Figure 2.16
Figure 2.17 The behaviour of Vincents' short and long range geometric functions for particles of unequal radii.
of the original paper:

(i) For $p<\Delta$, $I = I_{s1}$; Equation 27

(ii) For $\Delta+2r_1 > p > \Delta$, $I = I_{s2}$; Equation 28

(iii) For $\Delta+2r_2 > p > \Delta+2r_1$, $I = I_{s3}$; Equation 29

(iv) For $p > \Delta+2r_1 + 2r_2$, $I = I_{s4}$; Equation 30

(v) For $\Delta+2r_1 + 2r_2 > p > \Delta+2r_2$, $I = I_{s5}$; Equation 31

Equations 27-31 have been coded in Prime FORTRAN66 and can be found in Subroutine CLUM (Appendix II).

Vincent (1973) compared the calculation of the geometric functions using equations [2.32]-[2.35] and found good agreement between the more rigorous Clayfield et al. approach and the Vincent equations at large separations. At $\Delta$ less than 5-10nm the Vincent equations broke away, underestimating the calculation of $G$. However this comparison was only carried out for two spheres of 500 nm radius where a smooth transition from $G_s$ to $G_L$ is obtained with the Vincent equations. The non-retarded Hamaker equation coincided with the short range Vincent equation for $\Delta<1$nm but, as would be expected, overestimated the calculation of $G$ at larger distances of separation.
2.2.6.2 The Macroscopic Lifshitz Approach

In Lifshitz theory it is usual to define the dispersion energy, \( V_{132}(H,T) \), between flat media separated by a distance \( H \) as:

\[
V_{132}(H,T) = -\frac{A_{132}(H,T)}{12\pi H^2},
\]

where \( A_{132}(H,T) \) is more appropriately referred to as the Hamaker function and represents the summation of contributions from fluctuations over the entire frequency range.

The non-retarded Hamaker function, \( A_{132}(H,T) \), is given by:

\[
A_{132}(H,T) = -\frac{3kT}{2} \sum_{n=0}^{\infty} \int_{0}^{\infty} dx \ln \left[ 1 - e^{-\Delta_{132} e^{-x}} \right],
\]

where

\[
\Delta_{132} = \frac{\epsilon_i(\mathbf{i}\xi_n) - \epsilon_r(\mathbf{i}\xi_n)}{\epsilon_r(\mathbf{i}\xi_n) + \epsilon_i(\mathbf{i}\xi_n)},
\]

\[
\xi_n = \frac{n 2mkT}{h},
\]

and

\[
x = 2kH,
\]

where \( h \) is the Planck constant, \( k \) is the Boltzmann constant and \( H \) is the thickness of material 3. Hough & White (1980) have shown that since \( \Delta_{13} \Delta_{32} e^{-x} < 1 \), the integral in [2.37] can be performed by expanding the log term in a power series and integrating term by term to obtain:

\[
A_{132}(H,T) = \frac{3kT}{2} \sum_{n=0}^{\infty} \sum_{s=0}^{\infty} \left( \Delta_{13} \Delta_{32} \right)^s,
\]
where \( s \) is the number of terms used in the summation. Therefore in order to solve (2.41), values for the functions 
\( \varepsilon_j(i\xi) \), \((j=1,2,3)\) evaluated at \( \xi=n(2\pi k T/m) \) have to be obtained. The function \( \varepsilon(i\xi) \) has no direct physical significance and arises purely from mathematical considerations in the evaluation of the free energy of a dispersive system.

Ninham & Parsegian have represented \( \varepsilon(i\xi) \) in terms of experimentally accessible quantities, namely relaxation frequencies, \( \omega_l \), and oscillator strengths, \( f_i \):

\[
\varepsilon(i\xi) = 1 + \sum_{i=1}^{N} \frac{C_i}{1+(\xi/\omega_i)^2}, \quad [2.42]
\]

where 
\[
C_i = \frac{2}{\pi} \frac{f_i}{\omega_i}, \quad [2.43]
\]

Mitchell & Ninham (1972) outlined an expression for the interaction of two spheres which did not include retardation effects. Even with this approximation the formula is rather complicated and an estimate of the contribution of the different terms is still lacking.

2.2.3 Choice of Approach and Hamaker Constants

The microscopic approach has been chosen to calculate the London-van der Waals interaction between microbiological cells. Both the Vincent and the Clayfield et al. equations, with and without the adsorbed layer formula of Vold have been used. The limitations of this method were outlined at
the beginning of Section 2.2.6, but it has been indicated (Lips & Jessup 1979) that theoretical predictions based on the simple Hamaker theory may not be as much in error as has sometimes been implied. The low frequency contribution is sensitive to electrolyte concentration and is screened according to $e^{-2KH} (KH)^{-1}$ where $1/K$ is the Debye-Hückel screening length given by [2.7] (Richmond 1975). For a 1:1 electrolyte at 298K $1/K$ lies approximately between 10nm and 1nm for electrolyte concentrations in the range $10^{-5}$ to $10^{-1}$ mol dm$^{-3}$; for a very dilute effluent stream at $H>10$nm the low frequency term makes no effective contribution. Nevertheless, it should be realised that a major contribution to the Hamaker constant of hydrocarbon media acting across water originates from fluctuations in the infrared frequencies and not solely from the visible and ultraviolet regions.

Though the Lifshitz approach is considerably more complex than the Hamaker theory, Hough & White (1980) have shown that using available refractive index/wavelength data and spectral data that $V_A$ and Hamaker functions can be constructed for a number of interacting materials using the Lifshitz approach. But although attempts have been made to describe the interaction of relatively simple cells it was not thought justified to use this theory for bacterial cells which are poorly defined both chemically and structurally.

There are a number of literature sources of Hamaker constants (e.g., Gregory 1969, Visser 1972, Nir 1979, van
Oss et al. 1977) from which values have been selected. In making energy calculations only energy derived Hamaker constants have been used. For the model bacterial cell, materials were selected with Hamaker constants typical of the proteins, sugars and lipids. $A_{i1}$ and $A_{i3}$ values for these compounds as well as those for filler and filler materials are listed in Table 2.1.

In the past, workers have agreed that the $A_{i3}$ value for interacting cells of biological origin lies between $8 \times 10^{-21}$ J and $2 \times 10^{-20}$ J (Curtis 1967; Wilkins et al. 1962; Parsegian & Gingell 1973). This is still thought to be the case (Pethica 1980). The significance of a representative range of Hamaker constants and the effect of adsorbed materials on the surface of interacting bacterial cells was investigated.

2.2.7 Total Energy of Interaction

The total energy of interaction is given by [2.1] and the typical variation of $V_T$ with particle separation is shown in Figure 2.18. The computer programme DLVO (Appendix II) was written to enable the rapid calculation of $V_T$ by the selected methods discussed in this Chapter. By convention the calculated energies were divided by the product $kT$, where $k$ is the Boltzmann constant and $T$ the absolute temperature, and given in a dimensionless form. $V_T$ decreases approximately exponentially with distance and has a range of the order of the thickness of the double-layer.
### Table 2.1 Hamaker constants considered during this study

<table>
<thead>
<tr>
<th>System</th>
<th>$A_{11} / 10^{-21} J$</th>
<th>$A_{132} / 10^{-21} J$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>54.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipalmitoyl lecithin</td>
<td>96.7</td>
<td>6.0</td>
<td>Nir (1979)</td>
</tr>
<tr>
<td>Galactose</td>
<td>123.7</td>
<td>14.0</td>
<td>Nir (1979)</td>
</tr>
<tr>
<td>Bovine serum albumin</td>
<td>102.8</td>
<td>7.6</td>
<td>Nir (1979)</td>
</tr>
<tr>
<td>Titanium Dioxide</td>
<td>110</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Kaolin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td></td>
<td>22.3</td>
<td>Hough &amp; White (1980)</td>
</tr>
</tbody>
</table>
Figure 2.18 The potential energy of interaction as a function of the separation of two particles.
\( V_a \) decreases as an inverse power of the separation, (i.e. proportional to \( H^{-x} \) where \( x \) varies from 1 to 7), between the particles and has a range comparable to the particle size. At close separations \( V_a \) dominates and there is a deep primary minimum, although in microbial systems other forces probably dominate in this region. At high surface potentials and low ionic strength a primary maximum occurs at intermediate particle separations. It is this potential barrier that contributes to the stability of the system. Since for a given separation and particulate system \( V_a \) is constant, the magnitude of \( V_T \) depends mainly on \( V_R \) and therefore on the surface potential and ionic strength of the medium. For large particles it is possible for the attractive term to dominate at large distances of separation and a resulting secondary minimum to occur.

In practice it is found that when \( V_T < 5kT \) the flocculation process is diffusion controlled. As \( V_R \) is increased the dispersion becomes increasingly stable. Likewise, if a secondary minimum of the same order of magnitude is present, the particles may form a more loosely structured floc. The DLVO description of flocculation was considered in conjunction with other possible particle interactions that are known to occur, particularly at short separations.
2.3 SHORT-RANGE INTERACTIONS

There are a number of processes that are important in the interaction of biological cell surfaces at short distances of separation (Pethica 1961). Although the long-range forces may control the approach of two particles, it is the short-range forces that ultimately determine the formation and structure of a floc. However, few of them have been explored (Pethica 1980).

2.3.1 Polymer Mediated Interactions

A number of natural polymers have been shown to be involved in the flocculation of micro-organisms (see Harris & Mitchell 1973). These polymers may originate from various sources in a paper mill biological treatment system: (i) the protein and polysaccharide capsular material (Section 2.2.1.2); (ii) macromolecular material produced by protozoa (Watson 1945); (iii) complex materials released on lysis of the cells (Pavoni et al. 1970); and (iv) polymeric lignins and celluloses in the influent. Although it may be difficult to determine the structural characteristics of these polymers it is important to consider the types of particle interactions that they may be involved in. This area has been reviewed by Vincent (1974).

The major effect of macromolecules present in the continuous phase is a hydrodynamic one (Section 2.4): the rate of flocculation is reduced as a result of the increase in solution viscosity. However, at high concentrations of
free polymer it has been observed (Vrij 1976; Cowell et al. 1978; Vincent et al. 1980) that weak reversible flocculation can occur by a mechanism akin to a "phase separation" process that happens in mixed polymer solutions. Also, Feigin & Napper (1980) have described a depletion stabilisation of particles by free nonionic polymers.

If there is a high polymer coverage on both interacting surfaces then a steep repulsive steric interaction, $V_s$, comes into play when the separation of the particles is less than the sum of the thicknesses of the adsorbed layers. The origins of this repulsion are thought to arise from two mechanisms: (i) the entropic or volume restriction effect where a macromolecule adsorbed on a particle loses configurational freedom on the approach of a second particle, and (ii) the mixing or osmotic effect where the layers of adsorbed molecules interpenetrate, the higher segment density in the overlap region leading to a local osmotic pressure. Adsorbed polyelectrolytes provide additional electrical double-layer repulsive forces. A comparison between theoretically computed and experimentally measured pressures between interacting sterically stabilised particles has been given by Cairns et al. (1981). However, the form of this interaction is complex and still the subject of much debate, even for uncharged adsorbed polymers (Vincent & Whittington 1982; Napper 1977).

On the other hand, if there are available adsorption sites on one of the particle surfaces then it is possible
for bridging to occur by polymers being simultaneously adsorbed on the two particles. Sufficient electrolyte is necessary so that the thickness of the polymer layer is greater than $\sim 2/k$, otherwise electrical double-layer repulsion will prevent the particles approaching sufficiently close enough. Under normal operating conditions (pH 6-9) the net charge on the macromolecules in a biological treatment system will be of the same sign as the microbiological surfaces, and yet bridging may occur. For anionic microbiological surfaces this is aided by the presence of multivalent cations (e.g. $Ca^{2+}$) where the attachment of the polymer to the surfaces is thought to be via a carboxyl-cation-carboxyl complex (Section 2.2.2). Bridges may also conceivably be formed by extended segments entangling with one another, but the evidence in the literature suggests that polymer-polymer interactions of this sort will be of a limited extent.

2.3.2 Hydration Forces

There is now considerable evidence for the existence of close range hydration forces. Israelachvilli and Adams (1978) observed a short-range repulsive force at a hydrophilic mica/water interface which prevented adhesion contact. In contrast, on hydrophobic surfaces such as CTAB coated mica, attractive forces were measured (Pashley & Israelachvilli 1981). But although there is a growing case for the existence of hydration forces there is still much controversy as to their magnitude and range.
2.3.3 Chemical Bonds

Since the formation of bonds (e.g., electrostatic, covalent, hydrogen) depends upon interacting atoms sharing electrons, very close approach is required. If the electronic orbitals of two opposed atoms are filled, then the repulsion between the orbitals (Born repulsion) will prevent their close approach. Prediction of whether or not a bond will be formed requires detailed knowledge of the surface, which is lacking for the systems encountered in this study (Section 2.2.1).

2.3.4 Dipole Interactions

At short separations between particles dipole-dipole (Keesom), dipole-induced dipole (Debye) and ion-dipole interactions become significant. These interactions depend on the stereochemistry of the approaching cells and are only accessible to calculation if the chemical structure of the approaching surfaces is known.

2.4 HYDRODYNAMIC INTERACTIONS

The DLVO theory does not account for the time dependent processes such as Brownian motion and the bulk flow of the suspending medium. Both have a considerable effect on the rate of flocculation and stability of a colloidal suspension.
The first serious quantitative study of these effects was given by Smoluchowski (1917). He initially considered the limiting case of two equal sized spheres moving solely under the influence of Brownian motion. The coagulation was found to follow a simple second-order kinetic expression where the number concentration of particles, $N_T$, of all sizes was given by:

$$\frac{dN_T}{dt} = \frac{4kT}{3\eta} N_T^2,$$

where $\eta$ is the viscosity of the medium. The solution to (2.44) can be expressed in terms of a half-life, $t_\frac{1}{2}$:

$$t_\frac{1}{2} = \frac{3\eta}{4kTN_0},$$

so that:

$$\frac{N}{N_T} = 1 + \frac{t}{t_\frac{1}{2}},$$

$N_0$ being the initial number concentration of the particles.

Smoluchowski also considered the case where coagulation was caused solely by bulk flow in a laminar shearing field and arrived at:

$$\frac{N_T}{N_0} = e^{-\beta t},$$

where $\beta = \frac{4\gamma \phi}{\pi}$; $\phi$ being the volume fraction of the particles, and $\gamma$ a suitable scalar measure of the shear rate.

Equations (2.46) and (2.47) are then used as limiting
cases against which more realistic analyses are traditionally normalised. The frequency with which a test particle is bombarded can be derived from [2.46] as:

\[ J_b^0 = \frac{8kT N_r}{3\eta} \]  

[2.48]

The corresponding result for shear-induced coagulation is:

\[ J_b^0 = \frac{8\varphi \dot{\gamma}}{\eta} \]  

[2.49]

Departure of the coagulation rates from these extremes is given by the stability ratio, \( W \), defined as:

\[ W = J^0 / J \]  

[2.50]

where \( J^0 \) can be either a Brownian or shear induced limit.

Fuchs (1934) was the first to show the effect of interparticle forces on Brownian coagulation, by relating it to the total energy of interaction, \( V_r \), (Section 2.2.7). He arrived at the following expression for the stability ratio:

\[ W = 2 \int \frac{\exp(V_r/kT)}{s^2} \, ds \]  

[2.51]

where \( s = 2(a_1 + a_2 + A)/(a_1 + a_2) \). As \( V_r \to 0 \), \( W \to 1 \). This does not take into account the long range force of attraction
which when introduced gives (McGown & Parfitt 1967):

\[
W = \frac{\int \exp(V_f/kT) \, ds}{\int \exp(V_A/kT) \, ds} \frac{s^2}{s^2} \quad [2.52]
\]

Thus having calculated the energy distance curve, \( W \) can be determined by a graphic or numeric integration, and in the computer programme DLVO (Appendix II) the method of Clenshaw & Curtis (1960) was used.

In wastewater treatment systems one would wish ideally to deal with flocculation due to a combination of Brownian and shear effects. Early work (e.g. Swift & Friedlander 1964) on this problem considered the effects to be additive but since then the more sound fluid mechanical approaches have shown this to be an oversimplification.

Curtis & Hocking (1970) considered the trajectories of equal-sized spheres in a laminar shear flow when the spheres were subjected to London-van der Waals forces, but this analysis failed at small particle separations. The problem was overcome independently by van de Ven & Mason (1976a, b) and Zeichner & Schowalter (1977). The former considered the implications of primary and secondary doublets and the dynamics of multiplets; the latter took account of the role of vorticity in determining colloid stability and computed coagulation kinetics in terms of binary collisions. Initially Brownian motion was neglected and the situation...
was analysed as a linear superposition of hydrodynamic and colloidal forces.

At present much remains to be done before these theories can be applied to coarse industrial dispersions. The analyses to date are restricted to binary coagulation of equal-sized spheres, but the agreement of theory and experiment for the case of rapid coagulation is encouraging (Schowalter 1982). The complications produced by double-layers of finite thickness and asymmetric forces and geometry are not yet within reach of the theoreticians. The state of the theory of hydrodynamic colloidal interactions has recently been covered in a series of papers edited by Ninham et al. (1982).
CHAPTER 3

SEDIMENTATION THEORY
3.1 INTRODUCTION

Sedimentation processes are of importance in a number of industries, particularly as a means of solid/liquid separation and an extensive bibliography has been published (Poole & Doyle 1966). In wastewater treatment, sedimentation is one of the most widely used unit operations, where the primary purpose is to produce a clarified effluent. In addition it is usually necessary to produce a sludge with a concentration that can be easily handled and treated. Therefore a fundamental understanding of the sedimentation and compaction of suspended matter is important in the design and efficient operation of a treatment system. The theory of sedimentation has been primarily developed for dilute systems which are not flocculated.

3.2 DILUTE DISPERSIONS

The sedimentation velocity, $U_o$, of a single rigid sphere of radius $a$, in an infinite Newtonian fluid of viscosity $\eta$ in the absence of inertial forces has been known for over a century (Stokes 1856):

$$U_o = \frac{2a^2 (\rho_s - \rho_m) g}{9\eta}$$  \hspace{1cm} [3.1]

where $\rho_s$ is the density of the particle, $\rho_m$ is the density of the medium and $g$ the acceleration due to the earth's gravitational field.
The settling of more concentrated suspensions is more complex as the particles then settle at a rate that depends not only on their size, shape and excess weight, but also on their volume fraction, \( \phi \). The dependence of the settling velocity of a hard sphere on concentration is partly due to a hydrodynamic interaction that arises from a velocity distribution generated in the fluid surrounding each moving particle. In the absence of particle agglomeration of the kind reported by Kaye & Boardman (1962) the settling velocity, \( \bar{U} \), is found to be less than if an individual particle was settling in an infinite fluid.

The problem of determining the effect of concentration on the settling velocity of small rigid spheres began with Smoluchowski (1912) and the early work has been reviewed by Happel & Brenner (1965). The theoretical investigations fall into three groups depending on the assumptions made about the spatial distribution of the spheres and the nature of their interaction.

The first group decided, for mathematical convenience, to consider the centres of the spheres to be in a regular geometric pattern such as some form of cubical array. The second group made calculations using a "cell" model where the average hydrodynamic effect on one sphere of all the other spheres in the dispersion is equivalent to that of a boundary, usually taken as spherical, enclosing the sphere under consideration. These two approaches predict that for a dilute dispersion (\( \phi \ll 1 \)) the fractional reduction in the
sedimentation rate due to particle hydrodynamic interactions is proportional to $\varphi$, with a constant of proportionality that is of the order of unity.

The third group (Burgers 1942; Puyn & Fixman 1964; Batchelor 1972, 1976) adopted the more realistic approach of assuming the particles to be randomly distributed throughout the liquid and, by using statistical analytical methods, showed that the sedimentation velocity is proportional to the volume fraction. Using a systematic and rigorous procedure that overcame the difficulty of non-convergent integrals that are inherent in the derivation, Batchelor arrived at the expression:

$$\bar{U} = U_0 + \bar{V}' + \bar{V}'' + \bar{W} \quad [3.2]$$

$\bar{V}'$, $\bar{V}''$ and $\bar{W}$ were evaluated from a probability density of the location of one sphere relative to a second sphere in a statistically homogeneous dispersion, and from the flow field due to two spheres falling through an infinite fluid. They have the following values:

$$\bar{V}' = -\frac{11}{22} \varphi U_0 \quad [3.3]$$

$$\bar{V}'' = \frac{1}{2} \varphi U_0 \quad [3.4]$$

$$\bar{W} = -1.55 \varphi U_0 \quad [3.5]$$

Substituting [3.3], [3.4] and [3.5] into [3.2], the mean translational velocity of a sphere in a dispersion of
identical rigid spheres at low volume fraction was found to be:

\[ \bar{U} = U_0 (1-K\phi) \]  

where \( K \) is the sedimentation coefficient equal to 6.55. In deriving this equation diffusion was neglected and it was assumed that the initial particle distribution was preserved during the course of sedimentation. The size of the spheres was assumed to be small so that the Reynolds number of the fluid flow was then low and inertial forces could be neglected.

Burgers (1942) and Puyn & Fixman (1964) obtained the same relationship between \( \bar{U} \) and \( \phi \) but their values for the constant \( K \) were 6.88 and 7.16 respectively. Batchelor (1972) has shown that these differences are due to the non-systematic statistical methods used by Burgers and Puyn & Fixman and their failure to satisfactorily overcome the convergence difficulties.

The previous treatments have only been concerned with the hydrodynamic interactions between sedimenting monodisperse particles, whereas in a colloidal system there are likely to be additional non-hydrodynamic interactions. These may be attractive or repulsive, or a combination of both (see Chapter 1). Dickinson (1980) has considered the implications of Batchelor's work and estimated a rule-of-thumb for the effect of double-layer forces on the sedimentation rate of monodisperse particles. In doing so
he neglected any explicit electrical effects (Levine et al. 1976). A hard sphere model was assumed and the sedimentation constant, $K$, was then given by:

$$K \approx 1.5a_0^2 + 3.75a_0^3 - 1.32$$ \[3.7\]

where $a_0$ is the radius of an infinitely steep repulsive barrier surrounding the particle and effectively measures the radius of the double-layer.

It can be shown that the sedimentation velocity in a 2-3% dispersion can be reduced by up to 5-10% using [3.7]. The reasoning behind this is that, because pairs of interacting particles are not permitted to approach closely, a given particle is unable to take advantage of the greater downward flux in the fluid, near the surfaces of other particles. Therefore the particle is more influenced by the diffuse upward current which balances the downward flux in the inaccessible shells around each sphere. These conclusions agree with the predictions of Reed & Anderson (1976, 1980) who obtained a limiting value of 5.80 for interacting hard spheres.

Account may also be taken of the effect of the ionic atmosphere on the sedimentation rate. This so-called Dorn (1878) effect in a dilute suspension of spheres has been considered by Booth (1954), whose expression for the corrected settling velocity $\bar{U}$ takes the form:

$$\bar{U}_0 = U_0 \left(1 - a_0^n \left(0.0037 + \phi \right) \right) \times \left(e\zeta/\kappa T\right)^2 + \phi(\zeta)^2$$ \[3.8\]
where $\zeta$ is the zeta-potential, $e$ is the electronic charge, $q_\beta$ is a parameter dependent on the electrolyte and $\beta$ is a parameter dependent on the geometry of the suspension. Dickinson (1980) has calculated that for $\zeta$ of 50mV in sodium chloride at 298 K near the top of a thin cylindrical container ($\beta = 2\pi/3$), [3.8] gives a 5% reduction in the settling velocity for a dispersion of 0.03 volume fraction. Although the exact values calculated from [3.7] and [3.8] should be treated with some caution because of the many assumptions involved, the impact of the Dorn Effect and double-layer repulsive interactions on $\bar{U}$ are comparable.

A further characteristic of colloidal dispersions is that they are polydisperse in varying degrees. Batchelor (1982) has recently considered the sedimentation of two spheres of different size and density settling in a stable dispersion. The method he used was based on that which led to [3.6], however its complexity limits its extension to heterogeneous wastewater dispersions.

In a coagulating dispersion, where the net non-hydrodynamic forces are attractive, an increase in sedimentation rate is expected as the flocs effectively behave as single large particles. The initial sedimentation rate will then depend on the rate and processes involved in forming a particular floc structure. The additional problems created by polydispersity then relate to the floc size rather than to the particle size. It has been demonstrated by Cornell et al. (1979) that secondary minimum
effects can become important before the onset of coagulation, and association to form transient doublets and/or triplets would be expected to cause an increase in $\tilde{U}$, even though the particles are not in physical contact.

To experimentally verify (3.6), the velocity of a particular sphere in a dispersion has to be measured over a long time, which is not easy. Many observers have therefore used other types of average value for the particle velocity, such as measuring the initial descent of the relatively sharp boundary of a cloud of sedimentary particles. Maude & Whitmore (1958) examined some early experimental data and found that, over a wide range of volume fractions, the mean settling velocity of identical spheres could be represented by an empirical equation of the form:

$$\tilde{U} = U_0 (1-\psi)^\beta,$$  \hspace{1cm} (3.9)

where the value for the constant $\beta$ is uncertain but about 5. Neglecting all but the first two terms, (3.9) reduces to (3.6) for dilute dispersions, giving a value of 5 for the constant $K$.

In sedimentation studies using ultracentrifugation Cheng & Schachman (1955) found a value for $K$, in (3.6), of 5.1 for stable monodisperse polystyrene latices having a radius of 130nm.

With the advantage of having a well characterised monodisperse model latex system Buscall et al. (1982) found that a stable system sediments according to (3.6), with
value for K of 5.4, providing the volume fraction was less than 0.085. They point out that in dilute dispersions the distribution of particles is not likely to be random since approaching particles are slowed down by their hydrodynamic interactions and this gives rise to transient diffusional doublets (Cornell et al. 1979). Hence the value for K should be less than the 6.55 obtained by Batchelor (1972, 1976).

Consideration has been given to the effect of hydrodynamic and non-hydrodynamic interactions on the sedimentation of model systems. However there are considerable limitations in applying these theoretically derived equations to poorly characterised industrial systems. These systems are polydisperse and may be heterogeneous having particles of different density, composition, surface potential, shape and size. In addition, the particles may have rough surfaces; in the case of certain microbial cells, have appendages that protrude into the bulk solution; and, as described in Section 2.3.1, they may have adsorbed macromolecules at the surface. These latter characteristics contribute to a decrease in the sedimentation rate unless of course they result in flocculation. Therefore it is widely recognised that a theoretical understanding of the sedimentation process is at present in a very unsatisfactory state, except for dilute suspensions and then only when they are monodisperse (Davies et al. 1976).
3.3 CONCENTRATED DISPERSIONS

As the initial concentration of a stable monodisperse system of hard spheres is increased a volume fraction is reached (~0.1\(\phi\)) where the theoretical treatments described in the previous section are no longer valid. The sedimentation results of Buscall et al. (1982), for a well characterised monodisperse stable polystyrene latex, show that at volume fractions greater than 0.085 a plot of \(\bar{U}/U_0\) against \(\phi\) becomes non-linear. At the highest volume fraction investigated (0.5), the value for \(\bar{U}/U_0\) tended to zero as the particles approached the region of close packing.

To theoretically explain this region of non-linearity it is necessary to arrive at a solution for the multi-body forces that exist when the particles are in close proximity to one another. This is a problem that has not been satisfactorily solved for sedimenting particles. Dickinson (1980) has indicated that for stable systems, the probability of close-touching configurations is negligible, due to electrostatic repulsion. This makes it possible to tackle the multi-body force problems in terms of pair contributions.

Glendinning & Russel (1982) have given a pairwise additive description of sedimentation and diffusion for all volume fractions of monodisperse spheres. Approximations are required for the multiparticle hydrodynamic and potential interactions plus knowledge of the suspension microstructure. The theory was compared with the
experimental data of Lundh (1980), Kitchen et al. (1976) and Buscall et al. (1982), but good agreement was only obtained for \( \phi < 0.02 \).

The difficulties in applying theoretical models to industrial dispersions were outlined at the end of Section 3.2, and because of these problems the majority of workers have resorted to using empirical expressions to account for observed sedimentation behaviours.

Various authors have attempted to modify Stokes equation [3.1]. Steinour (1944) multiplied the Stokes velocity by a factor that is only dependent on the concentration, giving the relationship:

\[
\bar{U} = U_0 \frac{\epsilon}{(1-\epsilon)^2}, \tag{3.10}
\]

where \( \epsilon \) is the proportion of the total volume of the suspension occupied by the liquid and is analogous to porosity. Equation [3.10] is valid over the range \( 0.5 < \epsilon < 0.7 \) and its validity has been demonstrated by Steinour for uniform glass spheres.

Richardson & Zaki (1954) obtained the following equation for the rate of sedimentation:

\[
\bar{U} = U_0 \epsilon^{-4.65} \tag{3.11}
\]

On the other hand, Garner et al. (1953) and Bischoff (1964) assumed the sedimentation rate, \( d\bar{U}/dt \), to be a linear function of the difference between the instantaneous volume, \( V_0 \), and the ultimate volume, \( V_u \). They arrived at the
following expression:

\[ \bar{U}(t) = V_0 + \left( V_0 - V_e \right) \exp(-kt) \]  \hspace{1cm} [3.12]

where \( k \) is the rate constant.

In the above treatments, no account has been taken of the interactions which occur between particles, especially in concentrated suspensions. In particular, consideration has to be given to the effect of flocculation. Despite their heterodispersity, such dispersions usually settle with a sharp interface, which Steinour (1944) described by the following expression:

\[ \bar{U} = U_0 \frac{0.123(\epsilon - W_1)}{(1 - W_1)^2(1 - \epsilon)} \]  \hspace{1cm} [3.13]

where \( W_1 \) is the volume of liquid that is considered immobile in the flocs. Steinour indicated that [3.13] is similar to an earlier equation derived by Powers (1939).

If flocculation occurs in forming the plug, the rate and mechanism of flocculation will affect the initial sedimentation rate. Smellie & La Mer (1956) studied the sedimentation of phosphate slimes and observed two types of curves, depending on whether the flocculation was initially rapid or very slow (Figure 3.1). In the case of slow flocculation, the subsidence rate was initially slow and gradually increased, indicating that the particle size progressively grew as a result of flocculation. Eventually a floc size was reached where the settling rate remained constant for a period (Type I curve). If the flocculation
Figure 3.1 The two types of sedimentation pattern observed by Smellie & La Mer for sedimenting phosphate slimes.
was rapid a constant subsidence rate was reached immediately (Type II curve) and, providing the initial volume fraction was high enough, the rate could be represented by an empirical equation of the form:

\[
\frac{t}{H_0 - H} = \alpha + \beta t ,
\]

[3.14]

where \( H_0 \) is the initial sediment height, \( H \) is the height of the sediment after a time \( t \) and \( \alpha \) and \( \beta \) are constants independent of time. A Type I curve could also indicate the initial resistance to liquid flow through the plug, which then rearranges to produce channels of lower resistance. Another more likely explanation of the Type I behaviour was given by Carstensen & Su (1970a) and will be discussed in Section 3.4.

A Type II curve is also observed for intermediate concentrations of non-flocculated suspensions, and the transition to Type I sedimentation has been used as a method of determining the isoelectric points of minerals (Sadowski & Laskowski 1980).

The structure of the sedimenting plug depends on the flocculation processes described in Chapter 2. Michaels & Bolger (1962) studied the sedimentation of flocculated kaolin dispersions and postulated a loosely formed structure, where initially the particles flocculated to form small clumps, which loosely bonded to form aggregates and then settled as a plug. Sutherland (1967) provided a theoretical model for the formation of a floc, and his
predictions are in agreement with the experimental results of Michaels & Bolger.

In general, flocs produced by polymer flocculation form a plug with a more open texture than those formed by electrostatic coagulation. This results in a more rapid flocculation rate and both Types I and II curves have been observed (Smellie & La Mer 1956; Eckenfelder & Melbinger 1957).

In this and Section 3.2, consideration has only been given to the initial sedimentation of a dispersion. However, in wastewater treatment operations it is important to understand the sedimentation process over a long time scale. As the height of the settling plug decreases a time is reached when processes other than those governed by gravitational and bouyancy forces become important. With a non-flocculated suspension the particles rearrange to form a closely packed bed, although voids may be be present as surface roughness prevents the particles from sliding over one another.

If the particles are electrostatically flocculated then the compaction rate is determined by the rearrangement and collapse of the aggregates forming the plug. This rate will therefore be slower than is the case for a non-flocculated suspension.

With polymer flocculated suspensions a further compaction process may be envisaged. This is due to a
repulsive force arising from the compaction of the polymeric material between the particle surfaces. In general the final sedimentation volume of these systems is large. However Vincent (1974) quotes the results of Fleer (1971), who has shown that for silver iodide sols, flocculated with the optimum dosage of poly(vinyl alcohol) plus electrolyte, the sediment volume is less than that after coagulation by electrolyte alone. No explanation was offered for this behaviour.

3.4 COMPREHENSIVE TREATMENTS OF SEDIMENTATION

Kynch (1952) developed an expression that describes the sedimentation of monodisperse particles throughout the entire process. He assumed that the velocity, \( U \), of any particle is only a function of the local concentration, \( n \), of particles in its immediate vicinity. The particle flux, \( S \), is then given by:

\[
S = nU
\]  [3.15]

Kynch assumed the concentration to be the same across any horizontal layer. Expressions were derived for the decrease in height of the suspension with time, which was characterised by three sections (Figure 3.2): (i) AOB where \( n_0 \) is the same as the initial concentration, (ii) OCD where the concentration is at a maximum, \( n_u \), and (iii) OBC where there is a continuous and rapid increase in concentration. Thus, the suspension falls as a constant density plug (Section AOB), depositing a plug of maximum density on the
Figure 3.2 Fall of the Surface of a Dispersion according to Kynch (1952).

bottom (Section OCD). For suspensions that are not flocculated, Kynch predicted that the settling rate was constant in the first stage, becoming logarithmic in the final stage, with a transition between the two in the intervening period. However, the method of testing data is cumbersome and complete analytical solutions cannot be obtained. Kynch's analysis does not account for the obvious change in sedimentation rate with concentration that arises from hydrodynamic interactions, and at present there is not an adequate solution to this problem. He also neglects the effect that the initial increase in sediment forming at the base of the vessel has on the region AOB.

On the other hand, Carstensen and Su (1970a,b) have offered a comprehensive treatment for sedimenting
flocculated suspensions. Whilst not as rigorous as the work described in earlier sections of this chapter it does permit the complete analysis of an entire experiment and draws quite heavily on the work so far. The initial sediment was regarded as a plug of height $H$, moving downward with an increasing velocity $\bar{u}$, until a certain critical height was reached, when the rate of change in height decreased abruptly (Figure 3.1, Type I curve.). Because the probable mechanisms are likely to be totally different, the initial and final sedimentation regions will be considered separately.

The initial pattern is analogous to that described by Michaels & Bolger (1962) and Gaudin & Fuerstenau (1959) where at time $t$, the height of the sediment, $H$, is given by the sum of the height of a plug, $x$, containing the initial volume fraction of solids, $\phi$, and the height of a cake, $y$, of volume fraction, $\phi_c$. Using the data of Michaels & Bolger for the sedimentation of a 1.9% calcium oxide suspension an empirical equation of the form:

$$x = H_0 \exp(-kt)$$ \hspace{1cm} [3.16]\

was found to give a good representation of the rate of fall of the plug. To describe the dependence of $H$ on time it is necessary to define how $y$ changes with time. Gaudin & Fuerstenau (1959) have shown that the height of the cake, decreases exponentially:

$$\frac{dy}{dt} = -\omega y$$ \hspace{1cm} [3.17]
where $\omega$ is an exponential decay constant for the cake. In the initial phase the cake also experiences a build up from the temporal contribution of the descending plug. By carrying out a materials balance, Carstensen & Su (1970a) arrived at an expression for the volume fraction of solids in the cake, :

$$\phi_c = \frac{(H_0 - x)\phi}{y}, \quad [3.18]$$

The total change in $y$ with time is then:

$$\frac{dy}{dt} = k \frac{\phi_c}{\phi} x - \omega y, \quad [3.19]$$

Substituting [3.16] and [3.18] into [3.19] and solving for $y$ results in:

$$y = C \{1 - \exp(-kt)\} \exp(-\omega t), \quad [3.20]$$

The expression for the height of the initial sediment at a given time is obtained by combining [3.16] and [3.20] to give:

$$H = H_0 \exp(-kt) + C(1 - \exp(-kt))\exp(-\omega t), \quad [3.21]$$

which when rearranged gives an equation for a straight line of the form:

$$\ln \left( \frac{H - H_0 \exp(-kt)}{1 - \exp(-kt)} \right) = -\omega t + \ln C, \quad [3.22]$$

Using an iterative technique, the optimum value for $k$ can be found giving values of $\omega$ and $C$ from the slope and the intercept of the straight line.
An obvious approximation was made in assuming the cake to be of uniform concentration along the entire length $y$, but attempts to present $\phi$ as a function of $H$ lead to equations that cannot be solved analytically. That the approximation is not unrealistic is supported by the X-ray transmittance data of Gaudin & Fuerstenau (1959). The empirical equation obtained for the height of the plug, $x$, was obtained for a relatively dilute calcium oxide solution. However, when [3.16] is applied to more concentrated dispersions, one still obtains a linear relationship. Deviation from linearity near the critical height demonstrates the limit of the model where other processes become rate determining.

Carstensen & Su (1970b) observed that the decrease in height for the final sedimentation region followed a linear combination of two exponential decays. No previous treatments have lead to such a pattern for concentrated suspensions, although the data in several examples in the literature (Robinson 1926; Haines & Martin 1961; Michaels & Bolger 1962), imply such a relationship.

In order to determine the start of the final sedimentation region the critical height, $H_c$, and time, $t_c$, have to be found. This is done by a graphical interpolation of the sedimentation curve between the two sedimentation regions. The time axis is then redefined at $T=0$ where $T=t-t_c$. 
The forces exerted on the compacting sediment are gravitational, reactional and electrical in nature. The gravitational force acts in a downward direction and is of magnitude \( M(1-(\rho_s/\rho_m))g \), where \( \rho_s \) and \( \rho_m \) are the densities of solid and liquid, \( M \) is the mass of the sediment and \( g \) is the gravitational acceleration. The frictional forces act in the opposite direction and are related to the viscosity and the geometry of the vessel. They are described as a viscosity dependent \((-B(\eta,R)dy/d\tau)\) and a viscosity independent \((-\psi(R))\) component, where \( R \) is the radius of the tube. The electrical force is assumed to be repulsive and also has a component in an upward direction. The size of the force increases as the particles approach one another and is of the form \( \theta y \). The sum of all the forces then equals the mass of the sediment times its acceleration:

\[
M(1-(\rho_s/\rho_m))g - B(\eta,R)dy/d\tau - \psi(R) - \theta y = Md^2y/d\tau^2. \quad [3.23]
\]

This may be written as:

\[
d^2y + B(\eta,R)dy + \theta y = (1-(\rho_s/\rho_m))g - \psi(R) \quad [3.24]
\]

Looking at [3.23] and [3.24], it can be seen that:

\[
y^* = (1-(\rho_s/\rho_m))g - \psi(R)/\theta \quad [3.25]
\]

is a solution to the differential equation. The remaining solutions are found by inserting an expected solution of the form \( y=-Ae^{-\omega T} \) into the homogeneous equation corresponding to
When the expression in brackets is equal to zero, [3.26] is satisfied with the following roots:

\[ \omega = \frac{B(\eta, R)}{2M} \pm \sqrt{\frac{B(\eta, R)^2}{2M^2} - \frac{\theta}{M}} . \]  

These roots can be simplified if \( B(\eta, R)/M > \theta/B(\eta, R) \), giving:

\[ \omega_1 = \frac{B(\eta, R)}{M} \]  

and \( \omega_2 = \frac{\theta}{B(\eta, R)} \).

The complete solution of [3.23] and [3.24] in terms of \( y \) is:

\[ y = M(1 - (\rho_m/\rho_s))g - \psi(R) - A_1 e^{-\omega_1 T} - A_2 e^{-\omega_2 T} . \]  

From [3.30], \( \gamma^* = M(1 - (\rho_m/\rho_s))g - \psi(R)/\theta \) corresponds to \( \gamma_s \) and is therefore related to the ultimate height by the relationship \( \gamma_s = \gamma^* = (H_c - H_u)/2 \). Inserting this into [3.30] and rearranging these equations, the solution for the rate of change in \( H \) with time in terms of the forces considered is:

\[ H - H_u = A_1 e^{-\omega_1 T} + A_2 e^{-\omega_2 T} , \]  

where \( A_1 = 2A_1 \) and \( A_2 = 2A_2 \). From the assumptions leading to these equations, \( \omega_1 \gg \omega_2 \) and the first term on the right hand side of [3.31] should predominate at small values of \( T \) and the last term at high values of \( T \).
An estimate of the ultimate height of the sediment, $H_u$, and first estimates of $\omega_2$ and $A_2$ are obtained from the long tau data where the $A_2 e^{-\omega_2 T}$ predominates, in which case [3.31] reduces to:

$$\ln(H - H_u) = -\omega_2 T + \ln A_2.$$  \hfill [3.32]

This is solved iteratively for $H_u$.

With the estimates for $A_2$ and $\omega$ the value of $(H - H_u) - A_2 e^{-\omega_2 T}$ can be determined for the short tau data, so the two other parameters may be estimated by rearrangement of [3.31]:

$$\ln((H - H_u) - A_2 e^{-\omega_2 T}) = -\omega_1 T + \ln A_1.$$  \hfill [3.33]

This equation may be treated as a linear equation and solved iteratively for $A_2$, that is for a value that results in the smallest residual sum of squared errors.

Analysis of the long time data yields values for: (i) the exponential decay constants and, (ii) the pre-exponential factors in the descent of the sedimentation boundary $A_1$ and $A_2$, and (iii) the ultimate height of the sediment, $H_u$.

The computer programme SEDIMENT (Appendix III) was written to enable rapid analysis of the data and behaviour of this model when applied to these systems is discussed in Chapter 5.
CHAPTER 4

EXPERIMENTAL METHODS
4.1 INTRODUCTION

The purpose of this project was to study the flocculation and sedimentation of kraft mill effluents, particularly at the biological treatment stage. As a fresh supply of effluent was not available in England, the first task was to produce a continuous source of a model effluent. The model system was used to determine the feasibility of using various approaches to the problem and for carrying out controlled experiments. The results were compared with those obtained from full-scale and pilot-plant treatment plants.

Two major experimental techniques were used to study the effluent dispersions: (i) the electrophoretic mobilities of the heterogeneous particle populations were determined by microelectrophoresis, and (ii) as the aim was to achieve a flocculated dispersion that settled readily, the rate of sedimentation was measured and the data analysed using a computer model. The results from the two methods were correlated with data available from pulp and paper mill treatment systems, and an understanding of the flocculation and sedimentation processes was reached.

4.2 WASTEWATER ANALYSIS

A number of analyses were carried out on effluent samples, and the methods and terminology used in the wastewater treatment industry were adopted. Analyses for Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand
(COD), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Total Volatile Suspended Solids (TVSS), Colour and Dissolved Oxygen (DO), were carried out in accordance with the procedures outlined in Standard Methods for the Examination of Water and Wastewater (1975).

4.3 BENCH SCALE ACTIVATED SLUDGE UNIT (BSAS)

The biological treatment processes used for wastewater treatment were outlined in Chapter 1. To produce a continuous source of model effluent, completely mixed continuous-flow stirred tank reactors were constructed. The intent was to operate them under the average conditions found by La Voie et al. (1980) at the Ticonderoga Mill (TI) Aeration Stabilisation Basin (ASB). Data for the TI treatment system is given in Appendix I.

4.3.1 General Design

Biological reactors were constructed with particular reference to Ludzack (1960), Tempest (1965,1967) and Bisogni (1971). Two types were made: Type I had an operating capacity of 3 dm$^3$ and was used for preliminary investigations; when the sedimentation experiments were started a larger scale (12dm$^3$) Type II reactor was necessary.

A plan of the Type I bioreactor is shown in Figure 4.1. The growth vessel consists of a length (24cm) of Pyrex tubing (Q.V.F. Ltd.) with an internal diameter of 13.5cm.
Figure 4.1 Type I continuous flow bench-scale activated sludge unit (BSAS).
The top plate (0.6cm Perspex), is separated from the glass tubing by a neoprene gasket and has seven holes (5x2.4cm, 1x2.7cm and 1x1.7cm diameter) drilled to accept neoprene bungs. An eighth hole (2.8cm diameter), at the centre, has a carbon-black gland which receives a stainless steel impeller. The base plate is aluminium (1cm thick, 17.5cm diameter) and has six stainless steel tie rods (0.5cm diameter) located 0.8cm from the edge. The other ends of the tie rods locate with and pass through the clearance holes (0.6cm diameter) in the top plate, the whole assembly being held together by six nuts on the tops of the rods. The base plate is separated from the culture medium and glass tubing by a sheet of 0.2cm Teflon which serves as a gasket and prevents the micro-organisms adhering to the bottom of the vessel. A piece of Perspex (11x17x0.4mm) is attached to the inner walls of the glass tubing, forming a baffle to allow a settling region in the mixed culture liquor, and to enable one to control the concentration of solids in the reactor.

The Type II bioreactor is shown in Figure 4.2. The growth vessel consists of a rectangular glass container (36x23x23cm) with an operating capacity of 12 litres. A plastic overflow tube (19mm i.d.), is located above a quiescent region, partially enclosed by a Perspex baffle. There is no top to the reactor vessel but it was housed in a Brassaire environmental cabinet (John Bass Ltd., Crawley, Sussex), to prevent the contamination of the laboratory.
Figure 4.2 Type II continuous bench-scale biological reactor

a) titrant pumps           b) pH controller

b) pH controller           c) environmental cabinet

c) environmental cabinet   d) temperature controller

d) temperature controller  e) 12 inch ruler

e) 12 inch ruler           f) stirrer speed controller

f) stirrer speed controller g) air humidifier

h) air pump

i) influent pump           j) stirrer motor

j) stirrer motor           k) media and titrant inlets

k) media and titrant inlets l) pH electrode

l) pH electrode            m) immersion heater

m) immersion heater        n) reactor vessel

n) reactor vessel          o) air diffuser stone

o) air diffuser stone      p) thermistor probe

p) thermistor probe        q) effluent outlet

q) effluent outlet
4.3.2 Mixing and Aeration

The culture had to be sufficiently agitated to permit near perfect mixing, and the aeration had to be capable of keeping the Dissolved Oxygen (DO) concentration above the limit required to maintain growth. The aeration and mixing mechanisms were the same for the Type I and Type II reactors.

An impeller driven by a variable speed, 1/30 horse power, a.c., induction electric motor (Voss Instruments, Maldon, Essex) was used to stir the liquor. Additional mixing was caused by the turbulence from the aerator.

Constant aeration was maintained with an air pump (Rena 301, France) coupled via a simple air-flow meter to a diffuser stone. The aeration rate was adjusted to give a minimum DO level of 2mg dm$^{-3}$ (Bisogni 1971). To reduce evaporation the air was saturated with water. The Type I reactor was completely sealed and the excess air exhausted into the laboratory through an air filter (Whatman Inc., USA). The Type II reactor was enclosed in an environmental cabinet and the air vented through a cotton wool filter.

4.3.3 Control of Medium Flow Rate

Steady-state conditions were maintained by having a influent of a constant composition added continuously at an unvarying rate. A peristaltic pump (Crouzet, France), was used to deliver the influent through short feed lines (silicone rubber tubing, 0.4cm i.d.). To reduce the amount
of microbial growth, the tubing was autoclaved twice a week, and a medium inlet assembly was used (Tempest 1965). The medium flow rate was checked every 2-4 days and the greatest variation was found when new peristaltic tubing was used and a "bedding-in" period was needed.

The flow-rate was selected to give a hydraulic retention time, $\theta_h$, of three days. At TI, $\theta_h$ is 4.37 days if the original dimensions of the ASB are assumed (67 million US gallons). However, there has since been a considerable build up of solid material which has reduced the effective volume of the lagoon, and therefore a shorter retention time was used.

4.3.4 Control of Culture Temperature

The Type I reactor was immersed in a water bath and thermostatted at $30 \pm 1^\circ$C. The temperature of the mixed liquor in the Type II reactor was automatically kept at $30 \pm 0.5^\circ$C with a thermister controlled 75 Watt immersion heater (Jaeger, West Germany). This temperature was thought to be representative of the TI ASB where the yearly temperature of the influent varies between 25-48$^\circ$C. The temperature of the final effluent lies between 17.8 and 34.6$^\circ$C.

4.3.5 pH Control

The pH was controlled automatically by a controller consisting of a GK2401C combination electrode (Radiometer, Copenhagen, Denmark) linked to solenoid switch that
selectively operated two peristaltic pumps (Crouzet, France). When activated, the titrant was pumped into the culture medium until the required pH was reached. 2 mol dm$^3$ sodium hydroxide and 1 mol dm$^3$ sulphuric acid were used to maintain the pH at 6.8 ± 0.2.

When the electrode was placed in the turbulent culture medium, rapid oscillations were produced in the output pH signal due to charged particles hitting the probe surface. To overcome this, a length of glass tubing of greater diameter and length was placed over the electrode. However, the rate at which it became coated with micro-organisms was then increased. Nevertheless, by cleaning and calibrating the electrode every two days the culture medium was kept at a constant pH.

4.3.6 Control of Volume and Solids Concentration

In both types of reactor, the height of the culture liquid was kept constant by drawing the liquid off from the required height with a Crouzet peristaltic pump. The pump ran continuously at ten times the rate of that supplying the influent.

The stirrer and aerator produced fluctuations in the liquid level that had to be damped if this method was to be used successfully. This was achieved, to some extent, by floating 1.0 cm diameter plastic balls on the surface. Furthermore, the height of the liquid was a function of the rate of aeration and mixing (Section 4.3.2).
The concentration of suspended solids in the mixed liquor (MLSS) under constant growth conditions and hydraulic retention times, is determined by the amount of solids removed by the effluent line. The effluent was taken from a section of liquid that was surrounded by a baffle. By raising and lowering the baffle the turbulence and concentration of solids in the immediate vicinity of the removal pipe could be controlled. The TSS concentration was kept at 3 000 ± 200 mg dm\(^3\).

4.3.7 Synthetic Growth Medium

The synthetic growth medium used in this study was developed by Shields (1979) to model the TI ASB influent. Its composition was as follows:

- black liquor concentrate: 14.5g
- starch: 2.0g
- calcium carbonate: 0.3g
- clay: 0.2g
- phosphoric acid: 0.08X10\(^{-3}\) dm\(^3\)
- ammonium hydroxide (58%): 0.9X10\(^{-3}\) dm\(^3\)
- conc. sulphuric acid: 1.0X10\(^{-3}\) dm\(^3\)

The total volume using tap water was 10 dm\(^3\).

The aim was to mimic the TI influent with respect to BOD, Colour, calcium carbonate and clay concentrations, as well as provide sufficient nitrogen and phosphorous to give a BOD:N:P ratio of 100:5:1. Initially the BOD was adjusted by adding increasing amounts of black liquor, but on reaching the target BOD of 250-300ppm the Colour was found
to be too high. Therefore the black liquor concentration was reduced to give the correct colour transmittance and starch was supplemented to raise the BOD to the required concentration (Crossley 1979).

To prevent microbial growth and subsequent changes in the COD of the influent with time, the synthetic media was prepared daily and kept at 3 ± 1°C. Figure 4.3 shows the effect of storing the media for three days at room temperature. An influent COD of 900-1010 mg dm⁻³ was used.

4.3.8 Start-up and Operation

A completely mixed population of micro-organisms was required as a seed for the reactor culture. A good source is the sludge return from a municipal sewage works. A sample (1dm³) was obtained from the Trent Water Authority, Loughborough, and made up to the volume of the reactor with a 1% glucose solution. After six hours, when the population was growing rapidly, the reactor was operated continuously by allowing the synthetic media to flow.

The aim was to produce a continuous supply of a relatively constant mixed population of micro-organisms. Therefore, steady-state growth conditions had to be maintained in the reactor. The steady state-kinetics (dS/dt=0) of a mixed microbial population can be
Figure 4.3 A graph showing the decrease in COD of the synthetic media if stored at room temperature.
conveniently described by the Monod (1949) equation:

\[ S_0 - S - \frac{kxS}{k_s + S} = 0 \]  \[ (4.1) \]

where:  
- \( S_0 \) = influent substrate concentration (measured as COD/mg dm\(^{-3}\)),
- \( S \) = effluent substrate concentration, mg dm\(^{-3}\),
- \( \theta \) = hydraulic retention time, where \( \theta = V/Q \),
- \( x \) = concentration of micro-organisms in the reactor, mg dm\(^{-3}\),
- \( k_s \) = half velocity constant of substrate removal,
- \( k \) = maximum rate of substrate utilisation per unit of micro-organism,
- \( V \) = reactor volume, and
- \( Q \) = flow rate.

The reactor was operated keeping \( S_0 \), the temperature and \( x \) constant with the aim of obtaining a constant \( S \).

When starting up the reactor using the municipal sewage as a seed, it is was not possible to achieve a steady-state for around 48 days (Figure 4.4). This is because a period is needed for the selection of a population suited to the synthetic media. This is not as great a problem if the seed can be taken from a kraft mill biological treatment system. For a detailed discussion of mixed microbial population dynamics, the reader should refer to the review by Daigger & Baudy (1981). For convenience the daily COD was used to monitor the operation of the reactor.
Figure 4.4 Variation in the COD when starting up the reactor with a municipal sewage seed
4.4 EXPERIMENTAL APPROACH

Effluents from the following locations were examined:

(i) Continuous bench-scale activated sludge units,
(ii) Ticonderoga Mill aerated stabilisation basin,
(iii) Ticonderoga activated sludge pilot plant,
(iv) facultative lagoon, Bastrop Mill, Louisiana, and
(v) the Bastrop Mill, pilot plant.

Although it was possible to control the operation of the bench-scale activated sludge units, the physical and chemical composition of the influent to the pilot and full-scale processes varied continuously. To gain an insight into the possible electrokinetic and sedimentation properties of the effluents, the experiments were carried out over the range of pH values normally encountered at TI (Appendix I). The conductivity, pH, TSS and COD were monitored and further information was obtained from optical and electron microscopic examination. Due to limitations in the time spent in the USA, experiments on mill and pilot plant systems were performed for periods of approximately one week. They were repeated on different occasions so that the mean and the range of properties could be determined for each effluent source.

Having collected information under normal operating conditions, the effects of changes in the ionic environment on the sedimentation and electrokinetic properties of the cells was examined. Aluminium sulphate, calcium chloride and the relatively inert electrolyte, sodium chloride, were
A sedimentation model that was developed by Carstensen & Su (1970a,b) to analyse the sedimentation of pharmaceutical suspensions was applied to sedimenting biological effluents. The validity and behavior of this model was investigated over the range of conditions that were found in the treatment systems that were studied.

4.5 MICROELECTROPHORESIS

The majority of microelectrophoresis measurements were made with a Model 400 Laser Zee Meter (Pen Kem Inc., Croton-on-Hudson, New York). However, the instrument is not easily transported and a more portable conventional flat cell instrument (Ingenjörsmässan Repap, Stockholm, Sweden) was used at certain mill locations. The Laser Zee Meter (LZM) was preferred as it is possible to collect frequency distribution curves for mobilities of particles in a fraction of the time required for the conventional apparatus. Both instruments have cells of rectangular cross-section and were calibrated before use.

The theoretical and experimental aspects of microelectrophoresis have been reviewed by Hunter (1981) and the subject has been approached from a biological angle by James (1979).
4.5.1 Theory of a Closed Cell

The walls of microelectrophoresis cells assume a charge relative to the contained liquid, and on applying an electric field the liquid flows along the walls. In a closed system there is a return flow through the centre of the cell. The variation of the liquid velocity with cell depth is however difficult to analyse for rectangular cells. If it is assumed that the top and bottom walls are of an equal charge, then Komagata (1933) and Allen (1934) have shown, using the nomenclature in Figure 4.5, that:

\[ V(0,y) = V_\circ - 1.5 \left( 1 - \frac{y^2}{b^2} \right) / \left( 1 - \frac{192b}{\pi^2 a} \right) \]  

where \( V(0,y) \) is the liquid velocity along the y axis where \( x=0 \). \( V_\circ \) is the electro-osmotic velocity of the liquid and \( 2a \) is the breadth of the cell.

The electrophoretic velocity of the particle, \( v_e \), is obtained by direct observation at the so-called stationary levels where \( V(0,y) \) is zero. The distance of these levels from the centre of the cylinder, \( y \), can be obtained from [4.2], so that:

\[ y = b \left( 2(0.5 + \frac{192b}{\pi^2 a}) / 3 \right)^{\frac{1}{2}} . \]  

The observed velocity, \( V_\circ \), of a particle is the sum of the electrophoretic velocity, \( v_e \), and \( V_\circ \), and has a parabolic profile which is symmetrical about the line \( x=0, y=0 \).

This fact is used to check whether there are any anomalies in the hydrodynamic flow pattern due to...
Figure 4.5 Velocity profiles in a rectangular microelectrophoresis cell. Full line parabola represents the liquid velocity; broken line represents the apparent particle velocity.
differences in the electro-osmotic character of the cell walls or due to convection currents caused by temperature gradients in the fluid. A plot of $V_{ob}$ versus $y^2/b^2$ should give two straight lines intersecting at $(x=0, y=0)$. At the very least one should check that the particle mobilities at the two stationary levels are the same within permissible experimental error.

4.5.2 The REPAP Meter

The REPAP meter is a conventional microelectrophoresis apparatus consisting of a microscope with a calibrated graticule for the observation of the velocity of the individual particles. A thin flat quartz cell with an a/b ratio of 10:1 is immersed in a water bath to avoid convection currents in the sample. There are two platinum blacked measuring electrodes. The light source is arranged with phase contrast illumination. The cell is mounted in a vertical position which allows measurement on settling particles.

Basic instrument components include a d.c. power supply unit with a Voltage adjustable up to 100V, and a d.c. voltmeter. A digital timer ($\pm 0.01$s) is provided to measure the time of migration of individual particles. The whole instrument conveniently packs into a 0.25x0.25x0.55m box.

The microelectrophoresis cell was calibrated as follows. First the voltmeter was tested using an external Solatron d.c. voltmeter and good agreement was obtained over
the entire voltage range. The cell was cleaned by immersing in chromic acid for 24 hours, three washes in tri-distilled water, a thorough steam clean, further washing and then drying in an oven. Two solutions (0.01 and 0.1 Demal) of analytical grade potassium chloride in tri-distilled water were then prepared (Parker & Parker 1924). The potassium chloride being hygroscopic had been dried overnight at 180°C. The cell was filled with one of the solutions, placed in an oil bath at 25.00 ± 0.02°C and allowed to reach thermal equilibrium. The electrodes were fitted into the cell, then connected across a Wayne Kerr B224 a.c.bridge and the resistance measured. The procedure was repeated for the second solution and an average effective cell length of 6.86cm was calculated.

The next step in the calibration was to determine the mobility-depth profile of the cell (Section 4.5.1). A dispersion of AT-rutile in water (0.1 g dm³) was prepared. This pigment was chosen because it has a high refractive index and a relatively homogeneous distribution of mobility values. The cell was filled with the dispersion and the electrodes placed in position, making sure that there were no air bubbles in the cell. The apparent depth of the cell (2b) was measured, using the vernier scale on the microscope racking mechanism, by determining the distance between the inner front and inner back walls (see Figure 4.5). The current flow was kept constant and the velocity of the particles at different levels of the suspension was measured. Twenty particles were timed in each direction,
reversing the polarity after each measurement. The final focusing adjustment was always made from below the observed particle i.e., with the objective moving away from the cell, to avoid backlash in the fine adjustment mechanism.

Figure 4.6 shows a typical velocity-depth curve obtained for the REPAP meter, showing that the hydrodynamic flow was satisfactory. A summary of the calibration values for the cell are given in Table 4.1.

4.5.3 The Lazer Zee Meter (LZM) Model 400

The LZM was designed to overcome the most time-consuming aspects of microelectrophoretic measurements, which stem from having to monitor the velocity of a number of particles (20 -60) in order to obtain a suitable average. The apparatus has a prism between the microscope eye-piece and objective, which rotates with a speed controlled manually by the operator. The motion of the particles is just compensated by the prism rotation so that they appear to be stationary. The control knob can be directly calibrated or the zeta-potential (assuming the Smoluchowski equation [2.5] and a temperature of 20 °C) displayed digitally. This makes it possible to obtain an average value for all those particles in the field of vision (ca. 200), in just a single measurement.

As well as the advantages of its speed and statistical accuracy, the LZM has a helium-neon laser illumination system that can be focussed with an accuracy of 1 μm, so
Figure 4.6 Cell parabola for the REPAP Meter
<table>
<thead>
<tr>
<th></th>
<th>CRC</th>
<th>LUT</th>
<th>REPAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>0.1441cm</td>
<td>0.1611cm</td>
<td>0.0483cm</td>
</tr>
<tr>
<td>b</td>
<td>0.0720cm</td>
<td>0.0805cm</td>
<td>0.0241cm</td>
</tr>
<tr>
<td>2a</td>
<td>1.5321cm</td>
<td>1.5169cm</td>
<td>0.5016cm</td>
</tr>
<tr>
<td>a</td>
<td>0.7660cm</td>
<td>0.7585cm</td>
<td>0.2508cm</td>
</tr>
<tr>
<td>a/b</td>
<td>10.6248</td>
<td>9.4159</td>
<td>10.4067cm</td>
</tr>
<tr>
<td>A</td>
<td>0.2209cm²</td>
<td>0.2444cm²</td>
<td>0.0242cm²</td>
</tr>
<tr>
<td>y</td>
<td>0.0440cm</td>
<td>0.0459cm</td>
<td>0.0147cm</td>
</tr>
<tr>
<td>b-y</td>
<td>0.0280</td>
<td>0.0310cm</td>
<td>0.0094cm</td>
</tr>
<tr>
<td>b-y/2b</td>
<td>0.1947</td>
<td>0.193</td>
<td>0.1946</td>
</tr>
<tr>
<td>L₁</td>
<td>---</td>
<td>4.99cm</td>
<td>---</td>
</tr>
<tr>
<td>L₀</td>
<td>10.11cm</td>
<td>10.58cm</td>
<td>6.86</td>
</tr>
<tr>
<td>L₀/L₁</td>
<td>---</td>
<td>2.12</td>
<td>---</td>
</tr>
<tr>
<td>V₀/V₁</td>
<td>---</td>
<td>2.05</td>
<td>---</td>
</tr>
<tr>
<td>D</td>
<td>0.001916cm</td>
<td>0.0014285cm</td>
<td>0.0102cm</td>
</tr>
</tbody>
</table>

Table 4.1 Calibration details for the microelectrophoresis cells used in this study. The symbols are those used in Figure 4.5.
eliminating any errors due to the depth of field of the microscope objective.

Goetz & Penniman (1975) have given a detailed description of the LZM and suggest its suitability for industrial applications. Being the designers, they show obvious optimism. A description of the calibration and operation of the instrument has been given by Nazir (1977) and Kayem (1978), who have obtained a favourable correlation between results obtained from the LZM and a conventional rectangular-cell apparatus described by Pearson (1973). Therefore this discussion will be limited to those aspects of direct relevance to this study.

The disadvantages of the LZM lie in its cell and electrode system. The cell is made of acrylic (Plexiglass® II) which cannot be cleaned by conventional methods and tended to scratch. The cleaning procedure involved forcing a coarse suspension of cellulose fibres through the cell and then placing the cell, filled with a detergent solution, in an ultrasonic bath for 15 minutes. This was followed by at least 10 rinses with tri-distilled water (30 cm³).

However, the acrylic cell does have an advantage over the conventional REPAP cell, in that the velocity gradient in the cell is not as steep and therefore the error in focussing at a stationary level is reduced.

The electrode system consists of a molybdenum anode and platinum cathode. The latter did not need much attention
but the anode rapidly oxidised with the molybdenum oxide layer leaching into solution if not removed at least every 48 hours. The electrodes were cleaned with a whiting paste supplied by Pen Kem Inc.

At this point it must be mentioned that two LZM instruments were used, one at Loughborough University (LUT) and the other at the International Paper Corporate Research Center, New York (CRC). These instruments were calibrated in a number of stages.

The digital display of zeta-potential is calculated electronically and it is assumed that the voltage drop across the liquid between the electrodes is linear. This is not the case when polarisation occurs, and if not detected, it can lead to a large error in the measurement. Therefore the LUT cell was modified to include a set of platinum blacked stainless steel sensing electrodes, located ~5cm apart between the existing pair. The electrodes were ground flat with the inner top surface so as not to affect the flow characteristics of the cell. If the outer electrodes are not polarising while making a measurement then the ratio between the voltages across the inner, $V_1$, and outer, $V_0$, electrodes should remain constant. $V_1/V_0$ should be also be equal to the ratio of the "electrical" lengths between the inner and outer electrodes $L_1/L_0$.

The circuit shown in Figure 4.7 was used to measure $L_1$, where the current was supplied by a constant d.c. Solatron source. The method of using an a.c. bridge (Section 4.5.2)
cannot be used in this case as it causes a distortion of the parallel lines of conduction in the region of the inner

defines.

Figure 4.7 Diagram showing the circuit used to determine $L_i$ electrodes. The cell was filled with an 0.01 Demal potassium chloride solution having a specific conductivity, $L_s$, of $1.4078 \times 10^{-3}$ ohm$^{-1}$ cm$^{-1}$ at 25°C (Parker & Parker 1924). A current was applied to the circuit and the voltages across the resistor, $V_r$, and the inner electrodes, $V_i$, were measured with a high impedance Keithly 616 digital electrometer. From a derivation of Ohm's law it can be seen that:

$$ L_i = \frac{V_i}{V_r} L_s AR $$  \hspace{1cm} [4.4] 

where $R$ is the resistance of the external resistor (100Ω). The cross-sectional area, $A$, of the cell was measured with a travelling microscope to within ±0.0002cm. The measurements were repeated for a range of applied voltages (0–20 V) and a straight line plot of $V_i$ versus $V_r$ was obtained. Using a linear regression analysis a value for the ratio $V_i/V_r$ was calculated and substituted into [4.4].
At this point two disadvantages of the LZM became evident. The first was that the instrument does not have a means of thermostatting the cell. For this calibration, the LUT cell was mounted in a constant temperature water bath at 25 ± 0.1°C whereas it was possible to have the whole CRC LZM in a constant temperature room (25 ± 0.5°C). Secondly, the polarity of the electrodes could not be reversed which leads to ion migration and a resulting pH gradient in the cell. To prevent this pH effect the sample had to be changed after a maximum of five measurements. These two points were taken into account when making all microelectrophoresis measurements.

The next step was to determine $L_0$ for both the LUT and CRC LZM cells. The method used to determine the distance between the REPAP electrodes was followed (Section 4.5.2), the resistance of two solutions of known specific conductivity giving the "electrical" length between the electrodes.

The ratio of the potentials across the inner and outer electrodes of the LUT cell was then determined. The cell was placed in position on the microscope stage and the applied voltage, $V_o$, displayed by the LZM digital voltmeter was recorded. Simultaneously, $V_o$ was checked with a Solatron digital voltmeter and the voltage across the inner electrode, $V_i$, was measured with a high impedance electrometer. For potentials in the range 10-300V, good agreement was obtained between the LZM voltmeter and the
external test apparatus. Under 10V the LZM voltmeter did not give a stable reading and the Solatron had to be used. The ratio of $V_0/V_1$ with applied potential is shown in Figure 4.8. Initially the ratio increases before reaching a constant value in the range 15-300V, and measurements should only be made within this voltage range. The calibration details for the REPAP and both LZM cells are summarised in Table 4.1.

The hydrodynamic flow profile of the LZM cells was determined by following the same procedure used for the REPAP cell (Section 4.5.2), but instead of measuring the velocity of individual particles it was possible to use the rotating prism system to obtain mobility values. The result for an AT-rutile pigment is shown in Figure 4.9 and within experimental error the cell is suitable for use.

The final check on the instrument involved determining whether the digitally displayed mobility (zeta-potential/14.2) was comparable with the average mobility obtained by timing individual particles over a known distance. A recommended method (Goetz & Penniman 1975) was to suspend formaldehyde-fixed human erythrocytes in 0.15 mol dm$^3$ sodium chloride at pH 7.0. These cells obey the Smoluchowski equation as $K_a > 500$ but the relatively high electrolyte concentration produced gassing with the Pt-Mo electrolyte system.

To overcome this, the cell suspension was dialysed with decreasing concentrations of saline until eventually
Figure 4.8 A plot of the ratio between the voltages at the inner and outer electrodes against the voltage applied to the outer electrodes.
Figure 4.9 Cell parabola for the Laser Zee Meter.
the cells were suspended in a non-isotonic solution of 0.01 mol.dm\(^{-3}\) sodium chloride. The following results were obtained for the electrophoretic mobility, :

\[
\begin{align*}
v(t)_{\text{LUT}} &= -1.12 \pm 0.05 \quad \text{(by timing)} \\
v(\text{PR})_{\text{LUT}} &= -1.04 \pm 0.07 \quad \text{(by prism rotation)} \\
v(t)_{\text{CRC}} &= -1.29 \pm 0.06 \\
v(\text{PR})_{\text{CRC}} &= -1.21 \pm 0.07
\end{align*}
\]

Kayem (1978) found that the LUT LZM gave a systematic error of 16%, however the instrument now appears to output mobilities that are about 7% too low. This is considered to be within the limits of accuracy that a measurement can be made with the LZM and therefore the digitally displayed zeta-potential was divided by 14.2 and recorded as mobility.

4.5.4 Measurement of Mobilities

The electrophoretic mobility \(v/m^2.s^{-1}.V^{-1}\), i.e. the particle velocity \(v_o/m^2.s^{-3}\) per unit potential gradient, \(X\), in the stationary level is given by:

\[
v = \frac{v_o}{X} = \frac{nD}{t} \frac{L}{V}
\]

[4.2]

where \(nD/m\) is the distance travelled (\(n\) is the number of graticule squares of side \(D/m\)) in time \(t/s\), and \(V\) is the voltage applied across the electrodes separated by a distance \(L/m\).

If reproducible results are to be obtained then care has to be taken with a number of stages in the measurement.
and therefore a standard procedure was followed:

(i) sufficient time was allowed for the sample to reach temperature equilibrium (20 °C), but as the effluent dispersions were living, and therefore likely to change on standing, this period was limited to five minutes.

(ii) The cell was rinsed twice with about 20 cm³ of the sample dispersion and then filled, taking care to exclude any air bubbles,

(iii) the microscope was focussed at the stationary level, with the final focussing adjustment being away from the cell,

(iv) a check was then made to ensure that the particles were not moving systematically within the cell,

(v) a voltage was applied (>15V) and adjusted to give a suitable excursion time of the particles (3-5s) across a given distance in the crosshatch graticule.

With the REPAP meter, a particle in focus was selected and the time for it to traverse a fixed distance on the graticule was measured. The procedure was then repeated with the polarity of electrodes reversed. To avoid the possibility of bias, the particle to be timed was selected while stationary. Depending on the homogeneity of the suspension, it was necessary to take between 20 and 60 separate timings, before calculating an average mobility value.

The LZM measurements are less time consuming, and as a result less precise. Although the display voltage is only
accurate to ± 1V, the actual applied voltage is fed to an integrated circuit that compares it with the speed of the prism. The zeta-potential output is electronically stable to 0.1mV.

However, the accuracy of this instrument ultimately depends on the skill of the operator in determining when the particle speed is matched by the prism rotation. This is not easy and considerable practice is required to reproduce a reading to within ± 2mV. Measurements have to be repeated at least five times, and as the polarity of the electrodes can not be reversed, the solution has to be changed after a maximum of 3 measurements. Therefore the time saving advantages of the LZM are not as great as they might first appear.

The potential across the inner electrodes was measured with a Keithley electrometer and the ratio $V_i/V_o$ was checked before every measurement.

Temperature regulation is an important factor as the temperature coefficient of particle mobilities is around 2% per °C. If the sample is not at the same temperature as the cell then convectional disturbances may occur, and therefore microelectrophoresis cells are best immersed in a some form of bath. Particular care has to be taken when using the LZM as there is no means of controlling the temperature of the sample once in the cell. To overcome this the prepared sample was thermostatted in a stirred beaker (1 dm³) at 20°C, and the instrument was housed in a cool room in
which the temperature could be regulated.

The chief sources of error, not already discussed, are due to the Brownian motion of the particles and the depth of focus of the observing microscope. These have been estimated to give errors of around 2% (Smith 1973). If present, motile organisms may cause errors and some workers (e.g., Bangham 1961) have found it necessary to make measurements at low temperatures to eliminate this effect.

4.4.5 Sample Preparation

The intention was to study the mobility of the particles as found in the treatment systems. Therefore great care had to be taken to avoid either the adsorption at the surface of material not usually present, or the removal of surface components. The samples should also be fresh as, especially with biological samples that grow rapidly, there may be changes in both the suspension medium and the type and surface structure of the population. Therefore, grab samples were taken and the practise of using 24 hour composite samples was avoided.

Most of the effluent samples were too concentrated and had to be diluted otherwise the possibility of particle-particle interaction could lead to erroneous results. To decrease the particle concentration the sample was mixed carefully and a portion removed and stored at 4 °C. The remainder was allowed to settle for approximately a minute and the supernatant then decanted. A series of three
increasing centrifugations at 4 °C were carried out on the supernatant (200; 400; 1,000 g). This was done to minimise the amount of cellular material released into solution. A portion of the original stored sample was then added to the supernatant to give a final concentration of about $10^6$ organisms/cm$^3$. Initially the optical density of the solution was measured, but with practice it became possible to estimate a suitable concentration by eye.

The dilute suspension was then placed in a water bath at 20 °C and allowed to reach thermal equilibrium while slowly being mixed. This solution was used in the microelectrophoresis measurements.

4.5.6 Mobility Studies on Effluents

The following microelectrophoretic studies were made:

(i) Determination of the natural variations in electrophoretic mobilities of effluents at different treatment locations.

(ii) Mobility histograms for the effluent microbial populations.

(iii) Mobility of microbial cells as a function of pH.

(iv) Mobility of microbial cells as a function of electrolyte concentration. The electrolytes investigated were aluminium sulphate, calcium chloride and the relatively inert sodium chloride. A single grab sample was used for each set of experiments so that the same particle population and ionic concentration was present under each condition.
4.6 SEDIMENTATION EXPERIMENTS

The method used here is similar to that employed by Michaels & Bolger (1962) and Carstensen & Su (1970a,b). Three diameters (20mm, 25mm, 30mm) of 100cm length precision bore glass tubing were jacketted in glass. Each end was stoppered with a neoprene bung. The temperature of the columns was kept constant by pumping water at 20± 0.1 °C through the jacket.

The general procedure was as follows. A fresh grab sample, sufficient to fill the column, was thermostatted at 20± 0.1 °C and allowed to reach thermal equilibrium. Keeping the sample completely mixed, the column was filled, turned end-over-end ten times and then mounted vertically and securely on a stand. The instant the tenth rotation of the column was completed an electronic stop-watch (±0.01s) was started.

The change in height of the settling material was measured by one of two methods. The first involved making accurate marks on the glass column, and noting the time that the sedimentation boundary passed each mark using the lap-counting facility on the stop-watch. The second method consisted of marking the sediment height on the column with a fine tipped waterproof pen and simultaneously recording the time. With both methods the sediment was observed along the edge of a right angled set-square to avoid parallax errors. The height marks were measured with a cathetometer accurate to 0.1mm although the final accuracy of the method
was to within ± 1mm.

When the fall in the sediment was less than 2mm in a 15 minute period, the experiment was ended and the data analysed using the computer programme SEDIMENT (Appendix III).

The following sedimentation studies were carried out on each of the effluent sources mentioned in Section 4.4, however the TSS concentration in the pilot and full-scale biological treatment plants of the Bastrop Mill were too low to give any meaningful results. The sedimentation rate was studied as a function of:

(i) pH (5 and 7),

(ii) electrolyte concentration. The electrolytes investigated were the same as those studied for mobility measurements: aluminium sulphate, calcium chloride and sodium chloride,

(iii) TSS concentration; and

(iv) settling tube diameter.

A single grab sample was used for each series of experiments to prevent variations in TSS, ionic concentration, and particle composition. A portion of each sedimentation sample was prepared as in Section 4.4.5 and the mobility measured with the LZM.

It proved most convenient to carry out these experiments when at a mill location, as there was then an unlimited supply of effluent. Sampling from the BSAS reactors had to be restricted, or the steady-state conditions were upset.
4.7 CONDUCTIVITY MEASUREMENTS

The conductivity of effluent samples was measured with a meter designed for measuring the conductivities of industrial processes (Yellow Springs Instrument Co. Inc., Ohio, USA). The accuracy of the instrument was to within ±2.5-3.0%, and it was calibrated directly with .01 and .001 Demal solutions of dry potassium chloride in tri-distilled water. The instrument was easily transported and ideally suited for on-site measurements at treatment plants.

4.8 pH MEASUREMENTS

A large selection of pH instruments were used during this investigation. All, except the pH controller for the bench-scale activated sludge unit, were calibrated every day with three buffer solutions at pH 4.01, 6.50 and 9.10. The controller was calibrated every two days as its accuracy was not essential.

4.9 MICROSCOPY

Optical microscopy was used on a routine basis to observe the micro-organisms in the treatment systems as it gave a good indication of how well an operation was functioning. Scanning electron microscopy was carried out according to the method of Bulman & Stretton (1974), in the hope of sizing and characterising the effluent particles. However little progress was made. Samples were taken to the Corporate Research Center but again little was achieved.
CHAPTER 5

RESULTS AND DISCUSSION
5.1 PHYSICO-CHEMICAL PROPERTIES OF THE DISPERSION MEDIA

The physical properties of pulp and paper mill effluents fluctuate continuously, and therefore an effort was made to determine the range of conditions that were likely to be found in biological treatment systems. These fluctuations also occur in the pilot plants as the influent to these systems arises from the mills. With the bench-scale biological reactors it was possible to ensure constant influent and operating conditions and so these systems were better characterised.

5.1.1 Particle Size

The impurities in the mixed liquor of aerated lagoons may vary in size by about six orders of magnitude, from a few Angstroms for soluble substances to a few hundred μm for suspended materials. We were specifically interested in the micro-organisms and smaller colloidal material. The techniques available for particle size analysis were electron microscopy and the Coulter counter. Both suffered from the disadvantage that the particles were not analysed in their natural state, and the Coulter counter was further limited to particle sizes above 1 μm with the model available.

A Coulter counter particle size distribution was available for the Androscoggin Mill ASB effluent and the Ticonderoga Mill (TI) final effluent suspended solids (Table 5.1). These results show that the size of the suspended
<table>
<thead>
<tr>
<th>Average particle size</th>
<th>Androscoggin lagoon effluent</th>
<th>Ticonderoga lagoon effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>µm</td>
<td>ave.% diff vol.</td>
<td>ave.% diff vol.</td>
</tr>
<tr>
<td>1.59</td>
<td>-</td>
<td>30.5</td>
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<td>2.00</td>
<td>4.6</td>
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</tr>
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<td>3.17</td>
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</tr>
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<td>4.00</td>
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</tr>
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</tr>
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<td>0.4</td>
<td>0.3</td>
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<td>32.0</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>40.3</td>
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<td>0.1</td>
</tr>
<tr>
<td>50.8</td>
<td>0.8</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.1 Coulter counter particle size distributions (Hung 1981).
material is from ten microns to below 2μm, and when bacteria are typically from 0.5 to 1.5μm in diameter and 1-2 μm in length the restrictions of using this technique in this study are obvious.

Electron microscopy (EM) was used to observe the suspended material and proved both difficult and time consuming (Section 4.9). An idea of the problems that one was faced with can be seen in the electron micrograph shown in Figure 5.1. A very heterogeneous population is present which is difficult to examine in its natural state. Using washing procedures and critical point drying it was possible to observe the insoluble particles but they were then unrepresentative of the natural population. However, EM did enable us to visualise what particle interactions were likely to occur in these systems.

5.1.2 The Debye-Hückel Parameter, K

The ionic strength affects the thickness of the double layer, 1/K, and therefore the potential energy of interaction between two particles (Section 2.2.4). The determination of K requires the exact concentration of each ionic species in the dispersion media. However this is not possible for the very complex and continuously fluctuating effluents entering a mill treatment system. Furthermore it is not expected that the system would reach equilibrium at any stage of the treatment process.

An attempt was made to rationalise the situation. What
Figure 5.1 Electron Micrograph of a sample of Ticonderoga ASB effluent showing the following possible components:

a) bacterial rod,  
b) mixed debris,  
c) wood fibre, and an  
d) inorganic particle, (possibly kaolin).  

(X 86,000)
was required was a range of \( K \) values that were typical of the systems that were studied. Therefore the assumption was made that the only ions present in the effluents were those from completely dissociated sodium sulphate. That sodium and sulphate ions are present in significant amounts is beyond doubt, but many other ions will also be present with added complications such as incomplete dissociation and ion pair formation.

The theoretical relationship between the equivalent conductance and the concentration of sodium sulphate can be determined using the Onsager Limiting Law (1926, 1927). The restrictions to using this Law have been well documented (see Robinson & Stokes 1959): (i) complete ionization is assumed, (ii) it is only valid for low concentrations (~0.001 mol dm\(^3\)), and (iii) the theory behind it is weak for unsymmetrical electrolytes. In testing this theory against experimental conductance measurements, Harned & Blake (1951) found that the Limiting Law underestimated the true conductance of sodium sulphate by ~0.5\% at 0.005 mol dm\(^3\). This would be expected to be more significant at higher concentrations.

The concentration of sodium in the TI aeration stabilisation basin (ASB) was found to be in the region of 0.014–0.02 mol dm\(^3\), which if assumed to represent the concentration of sodium sulphate, gives a Limiting Law specific conductance in the range 1.56–2.04 mho cm\(^{-1}\).

The conductivities of biological treatment systems were
measured at four locations and representative data for a week are shown in Figure 5.2. Bearing in mind the accuracy of measuring the conductivity of such systems, the variation at a particular location is small. The Louisiana pilot plant shows the greatest variability, as it is subjected to the same shock loadings as the main lagoon and yet does not have its buffering capacity.

The specific conductivities compare favourably with those obtained by the application of the Limiting Law, although it is realised that this is an empirical route and probably fortuitous.

Using this approach, the range of sodium sulphate concentrations of $7 \times 10^{-3}$ to $1 \times 10^{-2}$ mol dm$^3$ was obtained and used to calculate an order of magnitude range for the Debye-Hückel parameter. This gave a $K$ range of approximately $4 \times 10^5$ to $6 \times 10^5$ cm$^{-1}$ and therefore a double-layer thickness of between 2 and 1.6 nm. Not surprisingly, there are no estimates in the literature of $K$ for pulp paper mill effluents.

5.1.3 Particle Concentrations

A number of standard analytical tests are used in the wastewater treatment industry to estimate the concentration of dissolved and particulate matter in effluents (Section 4.2). The tests have been developed to be used on-site at treatment plants on a routine basis and do not usually involve expensive analytical techniques. As a result, the
Figure 5.2 Conductivity measurements on paper mill wastewater treatment systems. ◊ Louisiana facultative lagoon; ○ Louisiana pilot-plant; □ TI ASB; ● BSAS units.
accuracy and significance of these tests has to be borne in mind. Typical values for these analyses for the biological treatment systems we investigated are shown in Table 5.2.

Of particular relevance to both the flocculation and sedimentation studies is the relationship between the values obtained from wastewater treatment analyses and both the number concentration and volume fraction of the particles. However this relationship is not simple.

The Total Suspended Solids (TSS) concentration is the mass of solid retained by a filter paper after heating at 105-103°C for an hour. The experimental concentration in mg dm³ has been found to vary according to the size of filter paper, and is not a linear function of the absolute concentration of the sample. Also some of the smaller colloidal material passes through the filter and is recorded as Total Dissolved Solids (TDS). For a given sample the sum of the TSS and TDS approximately equals the value obtained for the Total Solids (TS). The TSS is, however, usually taken as a measure of the suspended material although it must be considered to be an underestimate.

The Total Volatile Suspended Solids (TVSS) concentration is the mass of suspended material (excluding the water) that is volatile when heated to 550°C. The mass is usually considered as a measure of the amount of biological solids in the effluent. The obvious approximation is that only the biological material is volatile at the test temperature.
### Table 5.2 Typical SS and TVSS concentrations found at International Paper Mill Treatment plants.

<table>
<thead>
<tr>
<th>Sampling Sites</th>
<th>TS mg dm$^3$</th>
<th>TSS mg dm$^3$</th>
<th>TVSS mg dm$^3$</th>
<th>TDS mg dm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bench-scale AS units</td>
<td></td>
<td>3000</td>
<td>2205</td>
<td></td>
</tr>
<tr>
<td>TI Pilot Plant</td>
<td></td>
<td>3095</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TI ASB *</td>
<td>4207</td>
<td>2848</td>
<td>1764</td>
<td>1397</td>
</tr>
<tr>
<td>TI ASB (July 1982)</td>
<td></td>
<td>776</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TI Secondary Effluent *</td>
<td>1753</td>
<td>1164</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TI Tertiary Effluent *</td>
<td>61</td>
<td>43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bastrop Pilot Plant Effluent</td>
<td></td>
<td>100-200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bastrop Lagoon Effluent</td>
<td>2475</td>
<td>124</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>Androscoggin ASB Effluent</td>
<td>1534</td>
<td>201</td>
<td>135</td>
<td></td>
</tr>
</tbody>
</table>

* La Voie et al. (1980) Appendix I.
Therefore these analyses only produce approximate weights for the fractions of dissolved, suspended and volatile material. To determine the number concentration and volume fraction of bacteria in the effluent streams, consideration has to be given to the relative densities of the different particle fractions. From the TSS and TVSS data for TI (Table 5.2), the fraction of the suspended material that is biological in origin can be estimated as being 62% w/w. If account is taken of the fact that ~75% of the weight of micro-organisms is due to intracellular water, then the mass fraction of the TSS due to the microbial cells is around 71% in the lagoons. The remaining 29% is made up of the non-combustible compounds such as titanium dioxide, calcium carbonate, and kaolin which have a relatively high density.

Considering the biological material to consist of spherical particles with diameters of 0.75\(\mu\)m, and densities the same as water, then the average number concentration and volume fraction in the TI ASB is about \(4 \times 10^{12}\) organisms/dm\(^3\) and 0.01 respectively. An estimate of the volume fraction of the total particle population is arrived at from considerations of the final sediment heights of the effluents (Section 5.6.1).

From these estimations it can be deduced that the solid phases of the biological treatment systems that were looked at in this study are relatively dilute and consist mainly of bacteria. In the higher growth rate systems such as the
activated sludge process the microbial solids will form a larger fraction of the solid phase. The implications of the TSS concentration on the flocculation and sedimentation of these dispersions will be discussed later in this Chapter.

5.1.4 Electrokinetic Properties

5.1.4.1 Natural Variation at Treatment Plants

The electrokinetic mobility, $v_e$, of the particulate matter in the Ticonderoga Mill (TI) effluent was measured at three stages of the treatment system using the Laser Zee Meter (LZM). Initially the pH and ionic properties of the samples were not adjusted so that an idea of the normal variations in the mobilities of a typical effluent plant could be determined. This study was carried out in September 1980 (Figure 5.3) and again in June 1982 (Figure 5.4), and the results are summarised in Table 5.3.

Typically, the average mobility of the TI ASB effluent is reduced by 3-10% by the addition of sulphuric acid. After alum and cationic polymer additions, the effluent leaving the tertiary clarifiers has an average mobility of between $-0.824$ and $-0.718 \times 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$ (a further 54-58% reduction).

Two major variables were those of ionic strength and pH. The former could not be controlled at the mill and pilot plant sites, but could in the bench-scale activated sludge units (BSAS). However, in continuing the
Figure 5.3 Variation in pH and Electrophoretic mobility at the three stages of treatment at Ticonderoga (1980).
Figure 5.4 Shows the variation of pH and electrophoretic mobility with time at the Ticonderoga wastewater treatment plant (1982).
<table>
<thead>
<tr>
<th></th>
<th>Mean electrophoretic mobilities of effluents, $u_e/10^3 m^2 s^{-1} V^{-1}$</th>
<th>Mean pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASB</td>
<td>-1.895</td>
<td>-2.269</td>
</tr>
<tr>
<td>Secondary</td>
<td>-1.834</td>
<td>-2.025</td>
</tr>
<tr>
<td>Tertiary</td>
<td>-0.824</td>
<td>-0.718</td>
</tr>
</tbody>
</table>

Table 5.3 Variation of the average electrophoretic mobility and pH of the particulate dispersions found at the TI Mill Effluent Treatment Plant, September 1980 and June 1982.
investigations of the properties of typical mill treatment plants, the mobilities of grab samples were measured over a range of pH values (5-9) on each of five consecutive days (Figure 5.5).

Irrespective of the probable differences in effluent composition between the samples, each pH mobility curve shows features that are characteristic of the mixed, amino-carboxyl surfaces (type II curve, Section 2.2.2) reported by Douglas & Shaw (1958) and James et al. (1965). At pH<6 the mobility decrease was said to be due to the protonation of some of the amino groups, the negative charge at intermediate pH due to the presence of both -NH₃⁺ and -COO⁻ groups, and generally a higher negative value at pH>8 due to -COO⁻ groups alone.

However, in these complex solutions there are a number of macromolecules originating at the mill or produced by the micro-organisms that could adsorb at the particle surfaces and account for this type of behaviour (Section 2.3.1). The lignins and celluloses are two examples. Nevertheless, the charge at the hydrodynamic radius of the particles and therefore the electrostatic stability of this system, are not greatly affected by natural variations in pH.

It is known that changes in the physical and chemical environment in a biological treatment system can alter the surface characteristics of the population. This may be due to (i) changes in the types of organisms present, and (ii) changes in the quantity, nature and arrangement of the
Figure 5.5 The effect of pH on the mobility of Ti ASB samples. Each symbol represents a single effluent sample. The curve is drawn through the mean mobility for a particular pH.
ionogenic groups within each species. Changes such as these were not detectable by microelectrophoresis. This is not indicating that fluctuations in the effluent properties do not cause changes in the bacterial population, but rather that the surfaces of different populations in a particular treatment system have similar characteristics. The adverse effect of a period of high pH was observed at TI, where the TSS concentration was reduced from an average of 2848 mg dm$^3$ to 776 mg dm$^3$.

The LZM enables one to rapidly measure the average mobility of the population, but it is interesting to consider the mobility distribution of a sample of biologically treated effluent. The REPAP meter was used to obtain mobility histograms for the Louisianna facultative lagoon effluent (Figure 5.6) and sludge (Figure 5.7), the Louisianna pilot-plant effluent (Figure 5.8), and the influent to the two systems (Figure 5.9). As a comparison a typical histogram from the BSAS operating under steady-state conditions is shown in Figure 5.10.

The pilot-plant and main lagoon at Louisianna were very alike in having mobility maxima of $-0.8$ to $-1.2 \times 10^{-10}$ m$^2$ s$^{-1}$ V$^{-1}$ and similar distributions of mobilities. When one considers the heterogeneity of these dispersions, the distribution is narrower than expected, which may suggest the adsorption of common material onto the surfaces of the particles. The mobility distribution is then a function of the surface coverage and polydispersity of the population.
Figure 5.6 Mobility histogram for the Louisianna lagoon effluent.

Figure 5.7 Mobility histogram for a sludge sample from the Louisianna lagoon.
Figure 5.8 Mobility histogram for a sample from the Louisiana pilot-plant lagoon.

Figure 5.9 Mobility histogram of the influent to the main lagoon and pilot-plant at Louisiana.
Figure 5.10 Mobility histogram for a sample from the bench-scale activated sludge unit operating under steady-state conditions.
Workers have found that the mobility of bacterial populations varies during periods of physical growth and acclimatisation (Moyer 1936; Plummer & James 1961). This is borne out by the work of Ellwood & Tempest (1972), who indicate how bacteria undergo substantial changes in structure and function in response to changes in the growth environment. However, when starting up the BSAS units, the histograms were relatively stable despite the fact that other indicators such as COD and TSS measurements showed that the growth of the population was not at a steady-state. This further adds to the case for the adsorption of a common material onto these surfaces.

Whereas the particles in the effluent from the lagoons are mainly of biological origin, those from the influent can have the variety suggested in Section 1.2. The mobility histogram of the influent shows a broader distribution and a higher mean mobility range of $-2.26$ to $-2.6 \times 10^{-8} \text{ m}^2 \text{s}^{-1} \text{V}^{-1}$, possibly demonstrating the contribution of the non-biological materials. The reason for this may simply be that the influent particles are diluted in the lagoon and not detected in the relatively small grab samples used in the experiments. There is also the possibility that once these particles are in the lagoon, their outer surfaces become indistinguishable from the resident population by the adsorption of a common substance.

Tipping & Cooke (1981) have found that the presence of as little as 0.1 mg dm$^3$ humic substances results in oxides
having a negative charge over most environmental pH values (i.e. 4-10), whereas in simple electrolytes iron oxides have isoelectric points in the range pH 6-9. Similarly, in the paper industry, the adsorption of cellulosic compounds has been suggested as the reason for the changes in the mobility of titanium dioxide (Jaycock & Pearson 1975) and calcium carbonate (Dunlop-Jones & Jaycock 1981) when in a paper furnish.

A sample from the BSAS running under steady-state conditions has a mobility distribution which is narrower and lower than the real or pilot-plant systems. Again the narrowness would not be expected for a mixed microbial population. It is very unlikely that the BSAS will have the same microbial population as the lagoons in the USA and the model influent will again be different, therefore comparisons are difficult. However, the BSAS proved a convenient model system over which some control could be exercised, and it provided a supply of effluent on which techniques and ideas could be developed in the United Kingdom.

The mobility histogram of a sample of sludge from the bottom of the Louisiana lagoon was, as expected, different from that for the suspended material in the lagoon effluent. In a facultative lagoon such as this, the oxygen concentration decreases with depth. Therefore the microbial population and solution properties can be expected to be different in the aerobic, facultative and anaerobic regions.
of the sludge.

The important points arising from this investigation were that (i) the mobility distributions were narrow for a heterogeneous population, and (ii) there is a variation in the average mobility at different treatment lagoons (TI > Louisianna > BSAS). The mobilities varied from $-0.4$ to $-2.0 \times 10^{-6}$ m² s⁻¹ V⁻¹. The reasons for these characteristics are not easy to investigate owing to the complexity of the dispersions and to the dynamic properties of microbial populations.

Boyle (1979) has attempted to characterise the microflora of the IP biological treatment systems, but the organisms did not readily grow on the selective media that are usually used for this type of investigation. Media were developed that more closely resembled the properties of paper mill effluent streams, but to date little progress has been made.

To determine whether the lignins or celluloses are adsorbed on the particle surfaces, it was suggested that a BSAS investigation be carried out by operating two reactors under identical conditions, one was to have black liquor in the feedstock and the other not. A comparison of the population mobilities indicating the effect of the presence of lignins and celluloses. However, the usefulness of such an experiment is questionable as the population of organisms is not likely to be the same in each reactor.
In examining bacterial cells, James (1982) used standard washing techniques to remove the adsorbed materials and leave the cell surfaces intact. In doing the same with samples of BSAS effluent, it was found that if the cells were washed by repeatingly resuspending the cells in a fresh saline solution, a slight broadening in the mobility distribution was observed. This needs further investigation, but the indications are that the broadening results from the removal of a surface adsorbant so revealing the underlying heterogeneous surfaces.

5.1.4.2 Effect of Aluminium Sulphate (Alum)

Alum has been widely used to coagulate industrial effluents, but examples of its application in the paper industry are rare, as other treatment methods have usually proved more cost effective. However, the more stringent pollution legislation and the efficiency of alum treatment have resulted in its use at the Ticonderoga Mill (TI). As mentioned in Chapter 1, any improvements in the alum coagulation stage could result in considerable savings in treatment costs at TI, which currently run at $2.12 million per year.

The aluminium sulphate used in the paper industry varies in its degree of hydration and is generally described as \( \text{Al}_2(\text{SO}_4)_3 \cdot (14-18)\text{H}_2\text{O} \). The formula of the analytical grade salt used in this study was given as \( \text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O} \) (BDH Chemicals Ltd., Poole).
The major effects of aluminium sulphate when added to an effluent stream are:

(i) to compress the double-layer surrounding the particles and so reduce the stability of the system, and

(ii) to alter the electrostatic properties of the components by the preferential adsorption of certain complex species formed by the hydrolysis of aluminium sulphate. This often leads to a reversal of charge.

The hydrolysis of aluminium sulphate has been extensively investigated but only certain pertinent aspects will be considered here. For a more detailed review, the reader should refer to the many papers published by Matijević and his colleagues (e.g., Matijević et al. 1961; Matijević & Stryker 1966).

Despite these and other studies, the composition of the hydrolysis products are still unknown. A large number of species, mainly due to the polymerisation of various hydrolysed ions, are possible. Among those reported are $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_6(\text{OH})_{18}^2$, $\text{Al}_7(\text{OH})_{17}^3$, $\text{Al}_8(\text{OH})_{20}^4$, $\text{Al}_{13}(\text{OH})_{32}^7$, $\text{Al}_{13}(\text{OH})_{34}^5$. Using thermodynamic data available from the literature, solubility diagrams have been constructed (Figure 5.11). However, there are a number of limitations to using this type of data.

Patterson & Tyree (1973) state that it is unlikely that any solution of an aluminium salt could reach equilibrium, particularly at pH>5. When aluminium sulphate is used and the pH is adjusted using sulphuric acid (as it is at TI)
Figure 5.11 Aluminium solubility diagram
(Pearson 1973)
then the effect of the sulphate ion has to be considered. Matijević & Stryker (1966) have shown that more aluminium sulphate is required to coagulate a silver iodide sol if additional sulphate ions are present.

Determining the aluminium species after adding aluminium sulphate to a paper mill effluent is therefore complicated by:

(i) non-equilibrium conditions. The time, mixing conditions and adjustment of the pH after addition will all affect this.

(ii) Variation in the concentration of colloidal material which affects the amount of adsorption, and

(iii) variation in other electrolytes that may take part in equilibrium reactions.

The implication of these points are that the effluents are unlikely to be at thermodynamic equilibrium and the control lies in standardising the kinetics of a fluctuating system.

To scratch the surface of this problem, the electrokinetic properties of the effluent from the TI ASB were determined after the addition of aluminium sulphate, while concurrently running "jar" tests to determine the critical coagulation concentration (CCC).

A series of experiments were carried out on portions of a single fresh grab sample so that the particle and ionic concentrations were the same for each series. No attempt was made to ensure that thermodynamic equilibrium was reached as living microbiological samples would change on
standing and not then be representative of the true system. However, a constant time (5 minutes) was kept between addition of the electrolyte and making the first microelectrophoresis measurement.

The effect of alum concentration \((0-10^{-3} \text{ mol dm}^3)\) on the mobility of effluent samples from the TI ASB is shown in Figure 5.12 for pH 5 and 7. The greatest reduction in mobility occurred at pH 5 where the positive aluminium hydroxypolymers are formed. Over the particle and aluminium concentrations studied here, charge reversal was not evident at pH 5.

5.1.4.3 Effect of Calcium Ions

A variety of hypotheses have been put forward to explain the ability of divalent cations to promote the adhesion and flocculation of essentially anionic biological cells. The consensus of opinion appears to be that two processes are possible: (i) the ions are specifically adsorbed, so reducing the electrostatic repulsion between two interacting surfaces, and (ii) the ions form a complex between the carboxyl groups on the surfaces of the cells and/or the anionic molecules in solution.

The first indication that this process could be exploited in the treatment of kraft mill effluents was seen in the treatment data for the Androscoggin Mill (Figure 5.13). The final TSS concentrations at Androscoggin were normally in the region of 70 mg dm\(^3\), but in the space of a
Figure 5.12 The effect of aluminium sulphate on the mobility of a TI ASB effluent sample at pH 5 and 7.
Figure 5.13 Androscoggin Mill wastewater treatment data showing the reduction in final TSS concentration after pH adjustment with calcium hydroxide (March-April 1981).
day this was reduced to ~25 mg dm$^3$. The improvement in the final TSS concentration coincided with calcium hydroxide having to be used to adjust the pH of the effluent because the sodium hydroxide stocks were depleted. The pH and other characteristics of the influent and treatment system appeared to be normal over this period.

With the recent surge of interest in alkaline papermaking, there is the probability that there will be more calcium ions in paper mill effluents, which could be taken advantage of. For these reasons the effect of calcium ions on the flocculation of these systems was investigated.

Since the hydrolysis of calcium is only extensive above pH 11 (Sillen & Martell 1964), the cation will be predominantly in the form of Ca$^{2+}$ ions. The mobility of the TI ASB effluent as a function of calcium concentration is shown in Figure 5.14. The CCC was determined using "jar" tests. The effect of reducing the pH from 7 to 5 did not have much effect on the mobility, the slight reduction probably representing the decreased ionisation of the anionic surface groups.

The most striking difference between this and the alum coagulation experiments described in the previous section, was in the appearance of the supernatant in the "jar" tests. Whereas alum coagulation removed both the solids and the coloured material from solution when near the CCC, the calcium supernatant was still very brown in colour.
Figure 5.14 The effect of calcium ions on the electrophoretic mobility of a TI ASB effluent sample at pH 5 and 7.
at the CCC. On measuring the mobility of the sediment and supernatant populations, they were found to be significantly different, especially at low calcium concentrations, and the results are shown in Figure 5.15.

There appears to be some ambiguity between these findings and those at the beginning of the Chapter. The previous suggestion was that although the particle population was heterogeneous, the surfaces were relatively homogeneous. Yet the above result suggests the selective adsorption of calcium ions by the sedimented particles. An attempt was made to differentiate between the sedimented and suspended populations using optical and electron microscopy, but without success.

From the colour of the supernatant alone, it is possible that the mobility measurements were being made on colloidal lignin that was not visible at low cation concentrations. Lindström (1979) studied the effects of simple and complex electrolytes on the stability of lignins, and found that they were easily destabilised. This did not appear to be the case when the lignin was in the presence of microbial cells. However, increasing the calcium ion concentration to $10^{-2}$ mol dm$^3$ removed a significant amount of the colour from the supernatant. Therefore it does appear that the calcium ions are preferentially adsorbed onto microbial surfaces, but adsorption isotherms are needed before this could be stated with any conviction.
Figure 5.15 Electrophoretic mobility versus calcium ion concentration for the supernatant (o) and sediment (•) particle populations.
The important implication of this suggestion is that, although calcium ions may be efficient at removing the suspended solids, they may not remove the coloured materials. This is particularly relevant if the regulations on colour removal become more stringent, although a long-sighted approach to this problem seems the most sensible. It is a pity that the data shown in Figure 5.13 did not include the figures for colour removal over the time when the drop in TSS was observed.

5.2 THE CONVERSION OF MOBILITY TO ZETA-POTENTIAL

The method employed by O'Brien & White (1981) to display the mobility, \( \nu_e \), as a function of zeta-potential, \( \zeta \), and \( \kappa a \) is used here. The dimensionless mobility:

\[
E = \frac{\sigma M e \nu_e}{kT}, \tag{5.1}
\]

is plotted as a function of the dimensionless zeta-potential:

\[
y = \frac{e\zeta}{kT}, \tag{5.2}
\]

for the \( a \) values found during this investigation (Section 5.1.2), and the curves are shown in Figure 5.16. As \( \kappa a \) is increased, \( E(y) \) curves tend to the Smoluchowski form:

\[
E = 3y/2, \tag{5.3}
\]

but unlike curves for small \( \kappa a \) which reduce to the Hückel equation, there is no regime where all the curves reduce to
Figure 5.16 A plot of the dimensionless mobility, $E$, against the dimensionless zeta-potential, $y$. (1) Smoluchowski equation; (2-3) $ka$ range of 100-600 found at mill treatment plants using the O'Brien and White equations; and (4) these equations at low $ka$ \textit{viz.} 28.
the Smoluchowski form and become independent of $\kappa a$.

Taking the lowest estimate for $\kappa$, a particle radius of 0.5 $\mu$m and a relatively high electrophoretic mobility of $-2.0 \times 10^{-8}$ m$^2$ s$^{-1}$ V$^{-1}$, the error in using the Smoluchowski equation is of the order of 3%. Therefore in most instances the limiting equation is adequate.

5.3 POTENTIAL ENERGY OF INTERACTION

Much theoretical work has been done on the application of fundamental aspects of colloid chemistry to systems of interest in cell biology. Extensions have been made to the Lifshitz (1955,1956) theory that, in principal at least, allow the computations of free energies between particles of defined geometries.

Although these studies have proved informative, the application of this complex theory to a poorly defined mixed microbial population was not thought justified. Instead, the microscopic approach and the simple model cell described in Section 2.2.1.5 were used. Estimates are given for the magnitude of the interparticle forces in biological treatment systems, and the conditions under which flocculation is predicted by DLVO theory.

The computer programme DLVO (Appendix II) includes equations to calculate $V_T$ at constant surface charge or at constant surface potential. In calculating the attractive energy, the retarded Vincent (1973) or the more rigorous
Clayfield et al. (1971) equations were preferred.

It was found that for particle sizes of 0.5-2.0 μm, there was no significant difference between the Vincent and the Clayfield et al. equations, even for the largest particle size when the Vincent equations are most likely to fail. The constant charge equation always predicts a higher potential energy $\mu m$ than the constant potential equation, and the maxima usually occurs nearer to the surface, where these calculations are questionable.

As a first approximation the most favourable flocculation conditions were chosen, and the range of Hamaker constants for biological cells agreed on by Parsegian & Gingell (1973) and Pethica (1980) were used. Even for the lowest mobilities recorded in the TI ASB, the system can be considered stable as $V > 200kT$. However, the Louisiana pilot-plant and main lagoon had maxima of the order of $2-50kT$ for particle radii of $0.25-1.0 \mu m$ at constant potential. The surface potential of these systems has to be $<10mV$ before an appreciable barrier to flocculation is formed.

The effect of the range of potentials found in the treatment systems on the stability ratio is shown for particle radii of 0.25 and 1.0 μm (Figure 5.17). Although this plot is useful for showing how stable these systems are, it gives no idea of the time scale over which the flocculation process is occurring.
Figure 5.17 The relationship between the stability ratio and the surface potential for two particle radii.
1) $a=10\,000$ Å; 2) $a=2\,500$ Å.
It is possible to calculate the stability half-life of a particular dispersion by multiplying equation [2.45] by the stability ratio. If it is assumed that the particle concentration lies between the underestimate of $4 \times 10^9$ particles per litre (Section 5.1.3) and an overestimate of $1.6 \times 10^9$ ($\sim 0.04 \varphi$), then the theoretical relationship between log $W$ and log $t_\frac{1}{2}$ is that given in Figure 5.18. This graph is for a temperature of 20°C, but the effect of increasing the temperature by ten degrees (typical of the TI ASB) has only a marginal effect ($\sim 3\%$) on the half-life.

Looking at figure 5.17 again it can be seen that for a surface potential of 10 mV the time for the particle number to be reduced by half is 3.5-78 minutes. The particle concentrations used in this calculation were arrived at from the data for the TI treatment system. However, at the mill sites, low potentials were only found at Louisiana where the TSS concentration and therefore particle concentrations were very low. It therefore seems reasonable to say that the rate of diffusion controlled flocculation in these systems is slow.

There are other points to consider though. The flocculation is not entirely diffusion controlled, and consideration has to be given to the hydrodynamic forces in the system. But as was outlined in section 2.4, a lot remains to be done before the theoretical approaches to the problem can be applied to coarse suspensions such as these.
Figure 5.18 Theoretical relationship between the stability ratio and the stability half-life for two particle concentrations
1) $1.6 \times 10^{10}$ particles/cm$^3$; 2) $4 \times 10^{9}$ particles/cm$^3$. 
For practical systems, DLVO theory is open to question when the particle concentration is high. Particle-particle interaction might not begin at infinite distance of separation, as one particle may, on average, be sufficiently close to another to reduce the effective energy barrier which must be overcome for the particles to come into contact. There are, in addition, short-range forces which limit the DLVO theory to separations greater than 3nm.

Of particular interest in this work are the effects of adsorbed layers on the stability of the effluents. Calculations were made using the Vold (1961) approach, however they can only be considered to give a qualitative representation of the effects, as the heterogeneous microorganisms are represented by approximate Hamaker constants.

If the particle core is considered to be water, with a coating of galactose on the surface, then the effect of increasing the thickness of the sugar layer is to increase the stability of the system (decrease the attractive term). However as Table 5.4 shows, the increase in stability is marginal and can not be thought of as being significant in the flocculation of these systems.

Osmond et al. (1973) have looked at the consequences of varying the relative magnitudes of the Hamaker constants of the particles, adsorbed layers and medium on the interaction energy. They found that the net result of adding adsorbed layers to particles results in a net increase or decrease depending on two effects.
Firstly, the simple increase in core spacing that results from the addition of the adsorbed layer. This effect will be constant for a given geometry, and always leads to a decrease in the attractive term.

The second effect results from changing the Hamaker constant of the adsorbed layer from that of the medium to that of the adsorbed material (the addition of an adsorbed layer at constant centre rather than outer surface). Unlike the core spacing effect, this effect itself usually leads to an increase in the attractive term. However, over a very limited range and combination of Hamaker constants the so-called "Vold effect" may result when a further decrease in the attraction occurs. Therefore if using the range of sizes of bacteria with different thicknesses of adsorbed materials, the net effect of the layers depends on which of the above mechanisms are dominant.

On further examination of Table 5.4, it can be seen that for the particular Hamaker constants chosen to represent the microbial solids there is a "Vold effect", but it is hardly significant and results from the fact that the particles and the medium consist of water.

It may be that this is too much of a simplification and therefore the effect of varying the Hamaker constant of the particle from that of water only, to that of protein only, was examined. Calculations were made for the range of surface potentials that were found in the biological treatment systems and represented in terms of the stability
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<td>0.3</td>
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<td>100</td>
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</tr>
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<td>500</td>
<td>0.5</td>
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<tr>
<td>10000</td>
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<td>50</td>
<td>577</td>
<td>9950</td>
<td>-32.2</td>
<td>50</td>
<td>574</td>
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<tr>
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<td>-32.2</td>
<td>100</td>
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<td>9900</td>
<td>-32.2</td>
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<td>573</td>
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<tr>
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</tr>
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<td>100</td>
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</tr>
<tr>
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<td>-5.7</td>
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<td>0.2</td>
<td>9500</td>
<td>-5.7</td>
<td>500</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 5.4 Calculation of the total energy of interaction of equal spheres with various thicknesses of adsorbed carbohydrate ($K=5.65\times10^5$ cm$^{-1}$).
ratio (Figure 5.19). Again these variations show little
effect on the stability of the system, with the dispersion
being slightly more stable with a protein core.

If the carbohydrate layer is considered to surround a
filler particle such as titanium dioxide, or calcium
carbonate, then the results are similar to the above showing
little effect on the total energy of interaction.

It is not possible at present to take a more
quantitative approach. The difficulties lie, not only in
the undefined nature of the particles, but in their
heterogeneous composition which is not static. However, the
following conclusions can be drawn from this exercise: (i) a
surface potential of under 10mV is required for flocculation
to be possible according to the DLVO theory, (ii) varying
the Hamaker constants for typical cell constituents has very
little effect on the particle stability, (iii) it does not
appear that the adsorption of a substance on the surface
will have much effect on the stability. The effect of
adsorbed lignin was not considered as no Hamaker constants
were available, but it is not thought that the result would
be very different from that of having a layer of
carbohydrate at the surface.

The effect of adding calcium chloride or aluminium
sulphate to the system, appears to affect the surface
potential as well as the thickness of the double layer, and
both result in a decrease in the interaction energy.
Figure 5.19 The effect of varying the composition of the particle core on the stability ratio for the range of potentials found in paper mill effluent streams. 1) $A = 54.5 \times 10^{-21} \text{ J}$; 2) $A = 75 \times 10^{-21} \text{ J}$; 3) $A = 102.8 \times 10^{-21} \text{J}$.
5.4 SEDIMENTATION ANALYSIS

The computer programme SEDIMENT (Appendix III) was written to enable the rapid analysis of sedimentation data. It is coded in Prime FORTRAN66 to be used at a high resolution graphics terminal, and relies on the GINO graphics software (Computer Aided Design Centre, Cambridge) to produce the graphs. The time required to perform an entire analysis is of the order of five minutes for an experienced user.

The computer model is based on the theory of Carstensen & Su (1970a,b) which was summarised in Section 3.4. The analysis is carried out in three stages. Firstly, the critical time, $t_c$, is identified (Subroutine CRITIM). Then the data is analysed in turn for the regions before (Subroutine GFMMB) and after (Subroutine CARSU) $t_c$. The approach used and the behaviour of the analysis over each of these regions will be discussed, with reference to Figure 5.20.

5.4.1 Critical Time

The critical time is determined from a solution to the pair of simultaneous linear equations fitted by a least-squares technique to the points either side of the break in the sedimentation curve that occurs in the region BC (Figure 5.21). The solution is the point $t_c, H_c$. The accuracy of these values is improved by increasing the frequency with which the data is collected when nearing $t_c$, and their
Figure 5.20  Diagram of the sedimentation curve predicted by the Carstensen & Su (1970a,b) model.
Figure 5.21 Determination of the critical time and critical height.
reproducibility is to within 5%.

5.4.2 Short Time Data

The analysis of short time data involves fitting the following equation to the region AB:

\[
\ln\left[\frac{H-H_0 \exp(-kt)}{1- \exp(-kt)}\right] = -\omega t + \ln C, \quad [3.22]
\]

for a value of \(k\) that gives a straight line. Initially \(k\) is estimated and then, using a half-step iteration, the value giving the lowest residual sum of squares is found. The effect of varying \(k\) on the linearity of [3.22] is shown in Figure 5.22. The differences become indistinguishable by eye when nearing the correct value. At large \(k\), [3.22] approximates to a simple exponential of the form:

\[
\ln(H) = -\omega t + \ln(C), \quad [5.4]
\]

and the computer model fails.

Having determined \(k\), \(\omega\) and \(C\), a theoretical curve can be drawn through the data (Figure 5.23). Certain values of \(k\) show an artificial maximum in this curve at short times, but heights greater than \(H_0\) can have no physical meaning. This characteristic of the model was not commented on by Carstensen & Su, presumably because the \(k\) values for the systems that they studied did not produce a maximum.

The analysis of data from biological treatment systems showed a number of notable characteristics of the model. In
Figure 5.22  Short time analysis of an ideal set of data with a k value of 0.35 min⁻¹. The effect of high and low k values on the linearity of the fit is shown.
Figure 5.23 Theoretical curve drawn through a set of experimental short-time data points.

- \( k = 0.368 \text{min}^{-1} \)
- \( \Omega = 1.181 \text{min}^{-1} \)
- \( \ln(C) = 4.65 \)
- Ave. Error in \( H = 0.32 \text{cm} \)
- Time origin = 0.
most cases the experimental data was not found to follow the simple exponential relationship predicted by Michaels & Bolger (1962) for the early stages of sedimentation. Two competing mechanisms are thought to be occurring within this region. The first is due to the residual turbulence that is present after the start of the experiment. The second arises from the rate of floc formation, during and after this initial turbulence. Both can be considered to affect the apparent time at which the column starts to sediment. They are particularly important for most of the systems studied here, as the initial region occurs over a short length of time (~7-15 minutes).

Turbulence in the column will prevent the onset of sedimentation, effectively resulting in a positive shift in the apparent time origin. Likewise, the rate of flocculation can be postulated to cause a positive shift in the apparent time origin, as a period of time is required for the sedimenting plug to form. However, if the sample is not completely mixed, a negative shift in the time origin could be envisaged as initially the larger flocs will settle out.

In order that these possibilities could be investigated, a method of changing the time origin was included in the computer analysis. Figure 5.24 shows the effect that an increase and a decrease in the time origin has on the analysis of an ideal set of data points, with a critical time of 7.5 minutes. As a comparison, Figure 5.25 shows an
Figure 5.24 A graph showing the effect of changing the time origin on the analysis of an ideal set of data points. The middle plot has a time origin of zero.
Figure 5.25 An example of a set of experimental data that is best analysed after a change in the time origin.
experimental set of data that is best fitted by a shift in the time origin.

In analysing the short time data ($<t_o>$) from biological treatment systems it is usual to find a good fit to $[3.22]$ in the initial stages. This is demonstrated in Figure 5.26 where points 2-16 have been analysed. Figure 5.27 shows the effect of increasing and decreasing k on the resulting theoretical fits to this data.

The point to note is that the true rate of sedimentation is faster than the model predicts for this initial region. Increasing k produces a better fit at longer times but results in a poorer fit to the initial data. This characteristic can be further demonstrated by selecting different sections of the curve to analyse (Figure 5.28). A good linear fit can be obtained for points 16-24 of this data, but a very large unrealistic maximum is obtained in the curve. This is still the case for the range 5-24.

This analysis therefore gives values for the exponential rate constants: (i) for the decrease in height of the constant-density plug, k, and (ii) for the compaction of the bed forming at the base of the vessel. The significance of these values will be seen when the effects of changes in the physical and chemical properties of the sediment are discussed.
Figure 5.26 The short-time analysis of data for the sedimentation of a biological effluent, showing the linearity that can be obtained for the initial data points.
Figure 5.27 The effect of increasing and decreasing $k$ on the theoretical curves obtained from the analysis. The best fit for this set of data is when $k = 0.368$. 
Figure 5.28 The effect of analysing different portions of the short-time data on the final analysis curves.
5.4.3 Long Time Data

Two processes are believed to occur in the compaction of the sediment: (i) the flocs rearrange to give a more compact bed, and (ii) the individual flocs then collapse, with the latter mechanism dominating at long times. The analysis of sedimentation data after the critical time is done in two parts.

First, an estimate of the $A e^{-\omega_2 T}$ exponential in [3.32] is obtained by applying the linear equation:

$$\ln(H-H_u) = -\omega_2 T + \ln A_2$$

[3.32]

to a range of terminal data points. Using a half-step iterative technique, the value of $H_u$ is found that gives the lowest residual sum of squared errors. The analysis is repeated for different point ranges.

Decreasing the terminal range of points used in the analysis usually produces an improvement in the fit of [3.33], showing that this exponential (the collapsing mechanism) dominates at longer times. If there are enough data points, a range is reached which, if reduced, does not improve the analysis. On the other hand, if there are not enough long-time points the analysis fails, giving a value of $H_u < 0$. However extensive data is not required as the analysis provides an estimate $H_u$ well before its actual occurrence and estimated values are always to within $0.55$mm (Carstensen & Su 1970b).
With the estimates for $A_2$ and $\omega_2$ the linear equation

$$\ln((H-H_u)-A_2e^{-\omega_2T}) = -\omega_1T + \ln A_2,$$  \hspace{1cm} (3.26)

is fitted to a range of points after the critical time, where the rearrangement of the flocs is the dominant process. The statistically best fit is achieved by iterating on $A_2$. Again it is necessary to adjust the range of points used in this analysis. Selecting a range that is too close to the critical time gives a poor fit as the initial sedimentation processes are still present. Likewise, selecting a range close to, or significantly overlapping with the previous analysis gives a bad fit.

The computer model allows for the adjustment of the origin, which is effectively an adjustment in the critical time. Adjusting $t_c$ by a minute either side of the true critical time has no effect on the long-time analysis.

The outcome of the analysis is that values are assigned to the parameters $A_1$, $\omega_1$, $A_2$, $\omega_2$ and $H_u$. If the Carstensen & Su model is strictly obeyed by the sedimenting systems found in this work, then the following can be expected:

(i) increasing the concentration of the suspension will decrease or mask the $A_1$ term and increase $H_u$. At a critical concentration, the initial constant-density plug phase will disappear and then at a higher concentration the $A_1$ exponential will disappear.

(ii) The exponential compaction constant for the rearrangement mechanism, $\omega_1$, is inversely proportional to
The concentration of the sediment and proportional to the radius of the sedimentation column and the viscosity of the medium.

(iii) The exponential compaction constant for the collapse of the flocs, \( \omega_2 \), is inversely proportional to the viscosity and radius of the tube. It is also proportional to \( \theta \), which is a general term accounting for the interparticle forces. Therefore the effects of changes in the ionic environment on \( \omega_2 \) should give an insight into the flocculation mechanisms.

The final height of the sediment may be affected by further processes that are not accounted for in the model. This is particularly the case with living biological samples where metabolism continues throughout the experiment.

5.5 PHYSICAL FACTORS AFFECTING SEDIMENTATION

A number of physical factors will directly and indirectly influence the sedimentation rate of the suspended material in a biological treatment system. The aim was to determine how well effluent systems adhered to the Carstensen & Su (1970a,b) model and to gain a qualitative and quantitative insight into their effects on the sedimenting system.
5.5.1 Effect of Total Suspended Solids Concentration

The first investigation involved increasing the concentration of the initial dispersion. A single grab sample from the TI pilot plant was centrifuged and a range of suspension concentrations were made by resuspending varying amounts of the solid material (500-5 887 mg dm\(^3\)) in the supernatant (Figure 5.29). These concentrations covered the range likely to be found at any of the International Paper Company treatment systems, as well as those found in activated sludge systems.

For TSS concentrations under 2 000 mg dm\(^3\) the suspension did not form a porous bed in the initial sedimentation stage, but the flocs settled individually at rates that were determined by their sizes. Therefore it was not possible to use the Carstensen & Su model to investigate the natural state of sedimentation at sites where the TSS concentration was under 2 000 mg dm\(^3\) (see Table 5.2).

This technique was particularly useful for studying the activated sludge process and those lagoons, such as the TI ASB, where the TSS concentrations are relatively high. On occasions when the microflora of the TI ASB had been subjected to adverse conditions, such as periods of high pH, it was possible for the TSS concentration to be under 1 000 mg dm\(^3\) (June 1982).

The data in Figure 5.29 were analysed with SEDIMENT and the results are shown in Table 5.5.
Figure 5.29 Results for the sedimentation of different TSS concentrations of TI pilot-plant effluent in a 25mm column.
Table 5.5 Results of the analysis of sedimentation data at various TSS concentrations.

<table>
<thead>
<tr>
<th>TSS  (mg cm$^{-3}$)</th>
<th>$k$ $\text{min}^{-1}$</th>
<th>$\omega$ $\text{min}^{-1}$</th>
<th>$\omega_1$ $\text{min}^{-1}$</th>
<th>$\omega_2$ $\text{min}^{-1}$</th>
<th>$t_c$ $\text{min}^{-1}$</th>
<th>$H_e$ $\text{cm}$</th>
<th>$H_u$ $\text{cm}$</th>
<th>$\theta_{hcp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2193</td>
<td>0.039</td>
<td>0.246</td>
<td>0.159</td>
<td>0.0295</td>
<td>6.5</td>
<td>16.7</td>
<td>4.8</td>
<td>0.04</td>
</tr>
<tr>
<td>3127</td>
<td>0.039</td>
<td>0.222</td>
<td>0.179</td>
<td>0.0293</td>
<td>7.4</td>
<td>25.5</td>
<td>7.8</td>
<td>0.06</td>
</tr>
<tr>
<td>4013</td>
<td>0.039</td>
<td>0.136</td>
<td>0.173</td>
<td>0.0304</td>
<td>11.2</td>
<td>34.2</td>
<td>10.6</td>
<td>0.09</td>
</tr>
<tr>
<td>5887</td>
<td>0.483</td>
<td>0.028</td>
<td>0.023</td>
<td>0.0307</td>
<td>17.3</td>
<td>78.1</td>
<td>14.4</td>
<td>0.11</td>
</tr>
</tbody>
</table>
As predicted by the model, increasing the TSS concentration affects both the initial and final stages of the sedimentation process. The critical height increased and the contribution of the the rearrangement constant, $\omega_1$, decreased. For these relatively dilute suspensions, the initial phase did not disappear, but if a sample of sludge was taken then the initial phase was not detectable. Figure 5.30 shows a single exponential fit to all the data for a sedimenting sludge taken from the bottom of the Louisiana lagoon.

Increasing the TSS concentration has no effect on the sedimentation constant, $k$, over the range 2 000-4 000 mg dm$^3$. Above this range there is a decrease in the rate up until the stage where the initial phase disappears, reflecting the increased resistance to upward flow of the liquid as the concentration is increased. The difficulty in interpreting data for $k$ will be discussed later.

The compaction constant, $\omega$, in the initial stage, decreases with an increase in the initial volume fraction of solid material. A possible explanation of this behaviour could be that this constant has a component that at low concentrations is related to $\omega_1$ in the final sedimentation phase (i.e., the floc rearrangement term). As the concentration is increased, $\omega_1$ should be masked and the smaller start to dominate. In physical terms there is a transition from a floc rearrangement process to a floc collapsing mechanism at higher concentrations. Carstensen & Su have
Figure 5.30 The sedimentation of a sludge sample from the Louisianna main lagoon. The curve represents a single exponential analysis of all the data points.
found good agreement between \( \omega \) and \( \omega_1 \) for the systems they studied, but as will be seen later the validity of this comparison is questionable owing to the inaccuracies in \( \omega_1 \).

For the data after the critical time it was found that the floc rearrangement term, \( \omega_1 \), is constant at low concentrations but was reduced at the highest TSS concentration studied. The disappearance of this term was particularly well illustrated in Figure 5.30 where a single exponential can be made to fit all the data. However, as can be seen from the variation in the data, the absolute values of \( \omega_1 \) have to be treated with some caution. Carstensen & Su found that the coefficient of variation of this parameter was of the order of \( \pm 5\% \). On the other hand \( \omega_2 \) was found to be quite reproducible (\( \pm 1\% \)).

According to equation [3.28], \( \omega_2 \) should be inversely proportional to the mass of the rearranging bed. Perhaps a reason for there being no appreciable differences in the data is that the relative differences in the weights of the beds are negligible in the case of low density biological solids. The compaction rate constant \( \omega_2 \) should be proportional to \( \theta \), which is in turn related to the energy of interaction between the particles. As would be expected for this series of experiments, there is little appreciable difference between the values.

A useful feature of this experiment was the linearity that was obtained for the plot of \( H_u \) against TSS. Although expected, this gave credence to the final height analysis.
Furthermore, by assuming a hexagonal close packed array of the solids in the final sediment bed, it is possible to estimate the range of volume fractions that we are dealing with. Hexagonally close packed spheres occupy 74.0% of the total volume and therefore from the \( H_v \) values the TSS concentration range of 2193-5887 can be calculated as representing a volume fraction range of approximately 0.04-0.11. These values are an overestimate as close packing is unlikely.

### 5.5.2 Effect of Tube Diameter

Ideally a tube of infinite radius, or one with a size comparable to a sedimentation clarifier, is required for measuring sedimentation rates. But because of practical limitations a suitable diameter tube had to be chosen. A factor that had to be borne in mind was that the bench-scale reactors were limited to ~2dm³ of sample a day, although the majority of the experiments were performed on mill or pilot-plant effluents.

Three tube diameters were selected to compare the effect of tube diameter (20mm, 25mm, 30mm) on the parameters obtained from the sedimentation analysis of an identical sample. The results are summarised in Table 5.6.

For these three diameters the results from analyses are similar, with perhaps the data from the smallest tube showing a decreased sedimentation rate due to wall effects. For the expected primary particle sizes these tube radii are
similar to those used by other workers (Buscall et al. 1982; Carstensen & Su 1970a, b), but the effective increase in particle size that results from flocculation, will increase the effects of having a tube of finite radius.

Michaels & Bolger (1962), attempted to quantify the effect of tube diameter on the settling rate, but his empirical equation is not easily applicable to heterogeneous effluent dispersions.

### Table 5.6 Sedimentation analysis showing the effect of column radius.

<table>
<thead>
<tr>
<th>R (mm)</th>
<th>$r_0$ min$^{-1}$</th>
<th>k min$^{-1}$</th>
<th>$\omega_1$ min$^{-1}$</th>
<th>$\omega_2$ min$^{-1}$</th>
<th>H$_a$ cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5.8</td>
<td>0.21</td>
<td>.253</td>
<td>.10</td>
<td>8.3</td>
</tr>
<tr>
<td>25</td>
<td>5.6</td>
<td>0.43</td>
<td>.244</td>
<td>.116</td>
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</tr>
<tr>
<td>30</td>
<td>6.2</td>
<td>0.43</td>
<td>.182</td>
<td>.135</td>
<td>8.2</td>
</tr>
</tbody>
</table>

5.5.3 Other Contributing Factors

There are other factors that may affect the sedimentation rate but have not been investigated in this study. They are: (i) temperature, (ii) viscosity, and (iii) hydrodynamic shear forces. The first two are inversely related, and have been investigated by Carstensen & Su (1970a, b), Deane (1920) and Steinour (1944). However all the experiments in this study were carried out at one...
temperature (20 °C), and it was assumed that the variation in the character of the effluent did not produce any changes in the viscosity. These effects need investigating, and judging by the results of Carstensen & Su, their model would prove a useful tool.

5.6 CHEMICAL FACTORS AFFECTING SEDIMENTATION

The effects of aluminium sulphate, calcium chloride, and sodium chloride and changes in pH, on the sedimentation of effluents from biological treatment systems was investigated. The reasons for showing an interest in these particular compounds were outlined in Section 5.1.4.

Due to the large volumes of effluent that were required for a set of comparative experiments, the BSAS units were used to carry out the initial investigations and determine the feasibility of an approach. This series of results were all obtained from the TI activated sludge pilot-plant.

The results of the analysis of the sedimentation data using SEDIMENT (Appendix III) are shown in Tables 5.6-5.8. Before discussing these results it must be pointed out that in these experiments the effects are not always a function of the electrolyte alone. The chemical additions sometimes result in an increase in the TSS concentration either from the precipitation of a portion of the coagulant (e.g. aluminium hydroxide at high pH and concentration) or the flocculation of a component that was previously not detected as TSS. In addition, the TSS analysis itself may be
<table>
<thead>
<tr>
<th>NaCl mol dm$^3$</th>
<th>pH</th>
<th>k</th>
<th>$\omega$</th>
<th>$H_c$</th>
<th>$\omega_1$</th>
<th>$\omega_2$</th>
<th>$H_u$</th>
<th>TSS</th>
</tr>
</thead>
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<td>.225</td>
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<td>.243</td>
<td>.026</td>
<td>7.6</td>
<td>3033</td>
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<tr>
<td>----</td>
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<td>7.6</td>
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<td>.211</td>
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<td>.131</td>
<td>.029</td>
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<td>.211</td>
<td>26.2</td>
<td>.127</td>
<td>.029</td>
<td>8.0</td>
<td>3340</td>
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<tr>
<td>$10^{-1}$</td>
<td>5.0</td>
<td>.372</td>
<td>.209</td>
<td>26.0</td>
<td>.129</td>
<td>.027</td>
<td>7.7</td>
<td>3590</td>
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Table 5.6 Results of the sedimentation analysis of the data for sodium chloride addition.
<table>
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<th>CaCl₂ mol dm³</th>
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<th>k</th>
<th>ω</th>
<th>H_e</th>
<th>ω₁</th>
<th>ω₂</th>
<th>H_u</th>
<th>TSS</th>
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</thead>
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<tr>
<td>7.0</td>
<td>.710</td>
<td>.123</td>
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<td>.081</td>
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<td>.213</td>
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<td>26.7</td>
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<td>.039</td>
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<td>10⁻²</td>
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</tr>
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<td>.237</td>
<td>21.34</td>
<td>.243</td>
<td>.026</td>
<td>7.6</td>
<td>3033</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>.347</td>
<td>.213</td>
<td>22.24</td>
<td>.205</td>
<td>.028</td>
<td>7.6</td>
<td>2980</td>
<td></td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>5.0</td>
<td>.446</td>
<td>.030</td>
<td>22.14</td>
<td>.217</td>
<td>.029</td>
<td>8.1</td>
<td>2963</td>
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<tr>
<td>10⁻³</td>
<td>5.0</td>
<td>.411</td>
<td>.037</td>
<td>21.93</td>
<td>.324</td>
<td>.040</td>
<td>8.2</td>
<td>3047</td>
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Table 5.7 Analysis results for the effect of calcium ions on the sedimentation constants.
Table 5.8 Analysis results for the effect of aluminium sulphate addition on the sedimentation constants.

<table>
<thead>
<tr>
<th>$\text{Al}_2(\text{SO}_4)_3$</th>
<th>pH</th>
<th>$k$</th>
<th>$\omega$</th>
<th>$H_e$</th>
<th>$\omega_1$</th>
<th>$\omega_2$</th>
<th>$H_u$</th>
<th>TSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol dm$^3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>7.0</td>
<td>.330</td>
<td>.202</td>
<td>26.1</td>
<td>.130</td>
<td>.023</td>
<td>8.5</td>
<td>3260</td>
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<tr>
<td>$10^{-4}$</td>
<td>7.0</td>
<td>.334</td>
<td>.183</td>
<td>26.1</td>
<td>.122</td>
<td>.022</td>
<td>7.4</td>
<td>3250</td>
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<tr>
<td>$10^{-3}$</td>
<td>7.0</td>
<td>.14</td>
<td>.083</td>
<td>49.9</td>
<td>.146</td>
<td>.027</td>
<td>13.8</td>
<td>3430</td>
</tr>
<tr>
<td>----</td>
<td>5.0</td>
<td>1.25</td>
<td>.112</td>
<td>25.26</td>
<td>.102</td>
<td>.026</td>
<td>9.5</td>
<td>3300</td>
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<tr>
<td>$10^{-4}$</td>
<td>5.0</td>
<td>.384</td>
<td>.163</td>
<td>25.2</td>
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<td>.027</td>
<td>8.3</td>
<td>3361</td>
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<tr>
<td>$10^{-3}$</td>
<td>5.0</td>
<td>.188</td>
<td>.014</td>
<td>58.9</td>
<td>----</td>
<td>.027</td>
<td>19.2</td>
<td>3680</td>
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</tbody>
</table>
affected by the coagulant.

Each sedimentation parameter will be discussed in turn. Firstly, the constant for the initial rate of sedimentation of the constant-density plug, k, appears to give a variety of unrelated values. The probable mechanisms operating in this stage were discussed in Section 3.4, but in short they include: (i) the residual turbulence from the column rotation, (ii) the flocculation of the particles, and (iii) the rearrangement of the bed to form channels of lower resistance. An additional problem in analysing this system was that the initial stage was very short and therefore the errors are greater than for the slower sedimenting systems studied by, for example, Carstensen & Su (1970a,b) and Buscall et al. (1982).

The time origin was altered to see whether a systematic shift would produce a better fit to the data, however the time shift producing the best statistical fit appeared random. The conclusion that was reached was that these systems do not adhere to the Carstensen & Su model in the initial stages.

On searching the literature for theoretical treatments of flocculated suspensions there do not appear to be any solutions, apart from that of Carstensen & Su, that consider anything other than a linear relationship in the first stage. La Mer & Smellie (1956) noticed a non-linear behaviour for sedimenting phosphate slimes, but they only offered a solution for the linear case. A solution would
have to be empirical as it is not possible to unravel the processes that occur in the systems studied here.

The critical time gives a measure of the rate that the initial sediment is falling and this value has been used in the design of sedimentation clarifiers (Eckenfelder & Melbinger 1957). For the particular system studied here, the critical time is very short, occurring between 5 and 10 minutes. Longer times were found when aluminium sulphate was added, which may have been a reflection of the increase in TSS that results from the addition.

The long-time data was much more reproducible and gave more information on the flocculation mechanisms that were operating in biological effluent dispersions. The compaction constant for the collapse of the flocs, $\omega_2$, was not significantly affected by the addition of sodium chloride, the adjustment of pH, or the addition of aluminium sulphate.

In deriving the model it was shown that $\omega_2$ is proportional to $\theta$, a general term accounting for the interparticle forces. Both the addition of sodium chloride and the adjustment of pH have been shown to have little effect on the electrokinetic properties of the dispersion (Section 5.1.4), and therefore the term should not be greatly affected.

There are other possible mechanisms to be considered. If the particles are flocculated with polymer chains, then
the collapsing mechanism will depend on the structure (bridging) of the flocs and not necessarily on the interparticle forces described by the DLVO theory. This probably accounts for alum having no effect on this parameter. In this case the rate of collapse should give an indication of the floc strength, with a non-deformable floc giving a fit to a single exponential for the long-time data.

There was no appreciable difference between \( \omega_1 \) for the alum addition at pH 5 and 7. This was not expected as the coagulation mechanisms are different at these pH values. At pH 7, aluminium hydroxide is present, especially at the higher concentrations, which accounts for the increase in TSS, whereas at lower pH the polymeric hydrolysis products are present.

Calcium chloride results in a decrease in \( \omega_2 \), so indicating a different compaction process from the alum sludge. If the values for the ultimate height are considered, then this is further emphasised. The ultimate height of the calcium sediment increases gradually with calcium concentration, which suggests that some floc structure remains. The final sediment is closely packed, a factor that would be expected if cation bridging was occurring.

On the other hand, the alum sludge occupies a greater volume, which at pH 5, close to the minimum solubility point of aluminium hydroxide, is loosely formed. Aluminium hydroxide is certainly present in the sediment at this pH.
From these results it would appear that interparticle forces can not be accounted for by DLVO theory alone. If the calcium floc structure depended on a cation-carboxyl complex, then the effect of calcium addition would be expected to increase floc strength, as more cation-complex cross-links would be formed. However, calcium ions have been shown to decrease the mobility of the particles and therefore also the interparticle forces. This should result in a decrease in $\theta$ and therefore in $\omega_1$ with calcium concentration, but the opposite effect was found. The increase in $\omega_1$ can be accounted for by an increased floc strength.

This technique is therefore valuable in giving qualitative information about the sedimentation and flocculation processes. The model will need to be more rigorously tested before the analysis values can be taken as being quantitative. The possibility exists for using the technique in the design and operation of treatment systems.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS
The initial aims of the project were to investigate the flocculation and sedimentation of microbial cells in the treatment of kraft mill effluents. Therefore a review has been given of the theories and practical approaches to these processes, although examples of the application of theories from physical and colloid chemistry to heterodisperse effluents are rare.

To approach the problem, the physical and chemical characteristics of the particles and dispersion media had to be determined. However, this posed a number of problems as the influent to biological treatment systems is continuously varying, and in addition, the microbial cells vary in type and structure. Therefore a qualitative result had to be considered satisfactory in many instances.

What is badly needed is more information about the physico-chemical properties of the individual constituents in the paper mill effluent and their relationship to the microbial population. More defined model investigations on a continuous basis would help to isolate the interesting and useful characteristics.

An attempt was made to determine the particle size distribution of the treatment systems, but we were restricted to the electron microscope which proved both difficult and time consuming. Therefore we had to resort to using the typical particle size range of 0.5 μm to 2.0 μm for bacterial cells.
By making conductivity measurements on the effluents and assuming the conductivity to arise from completely dissociated sodium sulphate, a \( K \) range of \( 5 \times 10^5 - 4 \times 10^5 \) cm\(^{-1} \), was calculated theoretically. This value was, by chance, in agreement with the range that was obtained from a measure of the sodium in solution.

Armed with estimates for the Debye-Hückel parameter and the particle sizes, the operative \( K_a \) range of 100-600 was determined. This was needed in order to decide on which approach to use to convert electrophoretic mobilities to zeta-potentials. The O'Brien & White (1981) approach seemed the most suitable but even for the highest mobility value found in these systems, the error in making the conversion using the simpler Smoluchowski equation was only of the order of 4\%. \( K \) was also needed in the calculations using DLVO theory.

To produce a supply of typical kraft mill effluent in the United Kingdom, a bench-scale chemostat (BSAS) was designed and operated under steady-state conditions to mimic the Ticonderoga (TI) aeration stabilisation basin (ASB). The BSAS units proved particularly useful for determining the feasibility of an approach, although the results from them were not always found with the larger scale systems.

Electrophoretic mobilities of the population in the bench-scale unit and various pilot and full-scale lagoons were measured. The mobilities were found to be different between locations, but each population had a very narrow
distribution of mobilities for such a heterogeneous dispersion. The suggestion is that a material present in the effluent or produced by the microbial cells adsorbs on the population giving the particles similar surface characteristics. The variation with location may be due to a number of factors such as differences in the effluent composition, or a difference in the growth conditions in the lagoon.

The mobilities found at all the sites lay in the range -0.4 to -2.0 \times 10^{-8} \text{ m}^2\text{s}^{-1}\text{V}^{-1}. These values were used to calculate the potential energy of interaction of two particles in the system. To do this we needed to know the composition of the particles, but as mentioned earlier, this knowledge is not available at present. Nevertheless, order of magnitude calculations were made assuming the particles to be composed of water and protein with an adsorbed layer of carbohydrate on the surface. Calculations such as these should be repeated as more is learnt about the system, in which case it may be worthwhile applying the more rigorous Lifshitz (1955,1956) theory.

With the equations available in the computer programme DLVO (Appendix II) it was shown that if constant surface potential is assumed, then the TI ASB was stable over the whole mobility range, whereas the Louisiana lagoons and the BSAS particles were found to be less so. The constant charge approach always gave higher energy barriers to flocculation, and the true solution probably lies somewhere
between the two.

These calculations gave no idea of the time scale over which flocculation would occur, and therefore the stability ratio was calculated and related to the half-life of the systems. For diffusion controlled flocculation the prediction is that the process is very slow and almost certainly greater than 100 minutes. No estimate could be given of the effect that hydrodynamic shear forces could have on the flocculation rate, as solutions to the problem are only available for the binary collision of equal sized spheres.

The effect of aluminium sulphate on these systems gave an expected reduction in the mobility of the effluent dispersions, particularly at pH 5, where the polymeric hydrolysis products are present. No charge reversal was observed. This could have been because the particle concentrations of the initial dispersions were too high.

The effect of calcium ions was more interesting. The dispersions appeared to have two critical coagulation concentrations, initially the ions were adsorbed onto the original solid material, and at a second concentration the coloured material flocculated. This selective adsorption of calcium was borne out by mobility measurements where the mobility of the sediment was significantly lower than that of the supernatant. Adsorption isotherms are needed and here again, it will be necessary to look at a model system to start with (Tadros 1979).
The sedimentation model of Carstensen & Su (1970a,b) was developed and successfully transformed into a rapid and easily operated interactive computer programme (Appendix III). The model was tested on sedimentation data obtained from biological treatment systems and proved a useful investigative tool. This is not an ideal system on which to test a model and runs on defined model systems are needed.

Because of the rapidity of the initial sedimentation process for the systems studied, the short-time analysis could not be performed with any degree of accuracy and therefore it was not possible to see if the sedimentation of the effluents satisfied the model. However, the critical time and long-time analyses were suitable for describing the sedimentation of these systems. The long time data followed a combination of two exponential decays unless the dispersion concentration was very high.

The final height of the sediment was found to be a linear function of the total suspended solids concentration (TSS), a factor which was used to estimate that the TSS range of 2 000-5 000 mg dm$^3$ represented a volume fraction of 0.04-0.11. Therefore these dispersions are relatively dilute.

The effect of aluminium sulphate, calcium chloride and sodium chloride on the sedimentation behaviour was examined. The most useful parameter appeared to be the exponential constant that represented the collapse of the flocs. This constant was related to the interparticle forces between
the compacting flocs.

It was found that the addition of alum, or sodium chloride had little effect on this constant, whereas calcium ions produced a decrease in the constant. This constant is related to the total potential energy of interaction of the particles, and as all the above produce a decrease in energy the results may seem strange. Plausible explanations are:

(i) the effect of sodium chloride on the potential energy of interaction is small and therefore not detected, but this is surprising, (ii) the alum bridges the particles and the interparticle force is then related to the structure of the floc, and (iii) the calcium forms cation bridges between the flocs, which are increased in number on addition of the ion, so increasing the strength of the floc and therefore $\omega_2$.

In addition to being used as an investigative tool this sedimentation model could be used in the design and operation of treatment plants.

This work has given an idea of complexity of the problems facing physical and colloid chemists in this field. As emphasised earlier, the characteristics of the individual components need further investigation, and as the system becomes better characterised so theoretical approaches to the problem will become more useful.
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APPENDIX I: Flow diagram showing the Ticonderoga Mill sewer streams.
<table>
<thead>
<tr>
<th>LOCATION</th>
<th>FLOW, MM gal/day**</th>
<th>BOD₅</th>
<th>COD</th>
<th>pH</th>
<th>COLOR</th>
<th>Na</th>
<th>TS</th>
<th>TSS</th>
<th>TDS</th>
<th>TVSS</th>
<th>TOC</th>
</tr>
</thead>
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<tr>
<td>Paper Machines</td>
<td>4.72</td>
<td>3,122</td>
<td>28,491</td>
<td>7.40</td>
<td>888</td>
<td>6,085</td>
<td>42,048</td>
<td>21,193</td>
<td>21,443</td>
<td>13,249</td>
<td>6,307</td>
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<td>Pulp Mill General</td>
<td>0.88</td>
<td>1,805</td>
<td>11,125</td>
<td>9.90</td>
<td>9,261</td>
<td>2,879</td>
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<td>6,469</td>
<td>9,193</td>
<td>4,104</td>
<td>2,643</td>
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<td>Decker Overflow</td>
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<td>8,592</td>
<td>37,417</td>
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<td>50,040</td>
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<td>3,753</td>
<td>36,398</td>
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<td>4.44</td>
<td>7,076</td>
<td>32,859</td>
<td>2.33</td>
<td>27,113</td>
<td>13,348</td>
<td>104,256</td>
<td>2,917</td>
<td>99,178</td>
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<td>Bleach Plant Caustic</td>
<td>2.07</td>
<td>4,998</td>
<td>40,533</td>
<td>11.55</td>
<td>81,633</td>
<td>21,950</td>
<td>101,966</td>
<td>2,409</td>
<td>100,131</td>
<td>1,260</td>
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<td>5,187</td>
<td>39,238</td>
<td>10.17</td>
<td>14,389</td>
<td>4,578</td>
<td>82,091</td>
<td>56,810</td>
<td>25,320</td>
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<td>6.74</td>
<td>9,942</td>
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<td>1,868</td>
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<td>Caustic Plant</td>
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<td>Head Tank</td>
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<td>34,759</td>
<td>137,788</td>
<td>5.82</td>
<td>160,185</td>
<td>56,967</td>
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<td>26,569</td>
<td>206,751</td>
<td>13,501</td>
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<td>14,188</td>
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<td>60,173</td>
<td>537,415</td>
<td>363,803</td>
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<td>7,829</td>
<td>173,203</td>
<td>5,538</td>
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*The survey was conducted from September 12, 1979 through November 2, 1979. Most figures (excluding TOC) are daily composite sample averages compiled over 38 days.

**Millions of gallons per day.