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FOAM FLOTATION DESIGN PARAMETERS

NICHOLAS GROSE HENWOOD

This thesis is submitted to the Council for National Academic Awards in partial fulfilment of the requirements of the degree of Doctor of Philosophy

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LIST OF SYMBOLS

A	Air flowrate
B	Collision probability term
C	Concentration (general)
C_b	Bubble concentration
C_i	Initial concentration (general)
D	Coefficient of axial dispersion
F	Correlation parameter (mixing tests)
G	Correlation parameter (flotation tests)
H_0	Null hypothesis
H_1	Alternative hypothesis
K	Rate constant (general)
$M(k)$	Flotation rate distribution
N	Total number of stages
P	Probability of collection
P_a	Probability of adhesion
P_c	Probability of collision
P_e	Probability of continued adhesion during passage through flotation pool
P_f	Probability of survival in the froth
R	Retention time
S	Mass of surfactant concentrate added
T	Tracer concentration
T_i	Initial tracer concentration
V	Flotation cell volume
W	Surfactant inhibition function
X, X^1, Y, Z	Constants
$[X]$	Series of terms in multi-stage mixing equation
$[Y]$	Series of terms in multi-stage flotation equation
a	Plan area of flotation cell
b	Bubble surface area
c	Concentration of particles
c_i	Initial concentration of particles
d	Differential
d_i	Deviation parameter

e, exp	Exponential base
g	Gas pressure
h	Depth of flotation pool
k	Particle removal rate constant
m_0	Zero order surfactant removal rate constant
m_1	First order surfactant removal rate constant
n	Number of reaction stages
n_F	Number of degrees of freedom of parameter F
n_G	Number of degrees of freedom of parameter G
p	Post-collision collection probability term
r_b	Bubble radius
r_p	Particle radius
s	Free surfactant concentration
s_i	Initial free surfactant concentration
s_F	Standard deviation of parameter F
s_G	Standard deviation of parameter G
t	Time
	Statistical parameter in Student's t-distribution
u	Velocity of bubble
u_{pb}	Relative velocity of particles to bubbles
u_L	Liquid velocity
v	Water flowrate
w	Water pressure
x_1	Number of particles per unit mass of clay
x_2	Number of bubbles per unit volume of air
y	Distance from inlet of a tubular reactor
z	Head of water in flotation channel
α, β, γ, δ	Constants
∂	Partial differential
λ	Order of reaction
Ψ	Induction time
θ	Proportion of particles re-entering pool from froth
μ	Mean
ϕ	Temperature

π	3.14162.....
Ω	Conductivity
τ	Turbidity
!	Factorial
CTAB	Cetyltrimethylammonium bromide
NaLS	Sodium lauryl sulphate
LHS	Left hand side
RHS	Right hand side
ln	Naperian logarithm
log	Logarithm to base 10
$\int$	Integral

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DECLARATION

1. While registered as a candidate for the degree for which submission is made, the author has not been a registered candidate for any other award of the CNAA or of a University.

2. The candidate has completed four postgraduate courses:
   (i) Course leading to Part I of the Diploma of the Institute of Water Pollution Control.
   (ii) Course in computing methods.
   (iii) Course in statistical techniques.
   (iv) Course on the application of Laplace Transforms to problems in science and engineering.

3. The candidate has participated in the following colloquia:
   (i) Water Research Centre Conference on Flotation for Water and Waste Treatment; Felixstowe, June 1976.
   (ii) Joint I.Chem.E/BPBIF Symposium on Water and Effluent Treatment as it Affects the Paper Industry; Manchester, February 1980 (see Appendix 4).

ABSTRACT

Title: Foam Flotation Design Parameters

Author: Nicholas Grose Henwood

An investigation into the use of the foam flotation process for wastewater treatment is described, the main aim being to formulate a suitable method for the design and process optimisation of flotation units.

Preliminary trials were carried out on the purification of water abstracted from the River Trent, using a pilot plant loaned by the collaborating establishment. These trials established the major parameters of the foam flotation process to be influent feed rate, air flowrate, plant dimensions, surfactant concentration and foam removal method. A more detailed investigation into the effects of these parameters was carried out in two laboratory flotation units using a suspension of china clay in tapwater to represent the wastewater feed. In the final stages of the experimental programme laboratory flotation tests were carried out on a synthetic river water made from reconstituting river sediments with tapwater.

The results of the trials carried out showed foam flotation to be a viable method of wastewater treatment. Clarification by flotation was a rapid process and flotation units could be operated efficiently at low surfactant dose rates. In an optimised system floated particles could be collected as a sludge of high dry solids content.

A method for the rational design and operation of flotation units was formulated by adapting the established theories of mineral flotation kinetics. Generally a high degree of correlation was found between the theoretical relationships produced by this analysis and the results of the experimental programme.

CHAPTER 1

THE DEVELOPMENT OF FLOTATION METHODS FOR WATER AND WASTEWATER TREATMENT

1.1 INTRODUCTION

The primary treatment step in the purification of the majority of raw waters and waste liquors is the removal of suspended material, or turbidity. This consists of finely divided solids of geological, industrial or municipal origin; if a high quality finished water is to be obtained then turbidity must be eliminated.

In the wastewater treatment industry the most widely accepted method for removing suspended matter from its surrounding aqueous medium is sedimentation. For relatively large particle sizes the process relies primarily upon the existence of a significant difference between the densities of the solid and aqueous phases. Thus sedimentation is successful in removing the larger particle fractions found in raw waters, such as sands and silts. However, as the size of suspended particles approaches the colloidal range (eg clays and organic suspensions), Brownian motion and viscous drag around the particles combine to render the simple settlement process so slow as to be impractical as a treatment method. The traditional solution to this problem has been to promote flocculation in such suspensions until the size of the agglomerates produced is large enough for rapid sedimentation to take place. This may be effected physically by agitation and storage, or chemically by the addition of coagulating agents. Both alternatives imply an additional financial commitment to the process either by the necessity for larger treatment plants or by the use of costly chemicals.

In addition to the problem of particle size, certain types of suspended material in raw waters are of such low specific gravity that the necessary density difference does not exist and cannot therefore be exploited. One such example is that of the algal blooms which occur in waters rich in nutrients.

Flotation is a treatment method which holds considerable potential for the removal of slow settling suspensions since its effectiveness is not wholly dependent upon the

size and density of the particles. In addition the retention time required for satisfactory treatment by flotation is usually significantly shorter than that needed for sedimentation. This feature not only allows considerable savings to be made in terms of space and construction costs, but the added flexibility of the process enables it to deal more effectively with variable loadings. The two main disadvantages of the process are its relatively high energy requirement and the greater complexity of its operation. It is unlikely that flotation processes in any form will ever completely replace sedimentation as a primary treatment method; many commercial flotation units require sedimentation as a necessary preliminary step. However, in such cases the purpose of sedimentation is to provide a facility for the removal of very coarse particles and the size of the settlement unit is reduced to a fraction of its conventional requirements (1). Slow settling particles may then be removed by flotation and thus the combination of the two methods represents the efficient use of each step, leading to a greater degree of overall process optimisation.

1.2 MINERAL FLOTATION

The flotation of valuable ores from their associated gangue materials is a widely adopted and highly developed purification method in the mineral processing industry (2, 3). Flotation of minerals involves three main processes; bubble generation, capture of the valuable mineral particles by the bubbles and removal of the bubble-solid combinations from the flotation pool. Bubbles are usually produced by a dispersed air method, either by vigorous agitation of the pool using submerged impellers or by the diffusion of compressed gas through a porous frit. Particle capture is facilitated by the use of reagents known as collectors which render the surface of the particles hydrophobic. Selectivity of collection of one particle type from another is frequently aided by the use of modifiers, which may activate or depress collector action on particular particle surfaces. The resultant concentration

of floated particles at the surface of the flotation pool may be stabilised where necessary by frothing agents, and thus a mineral-rich concentrate may be obtained.

1.3 BUBBLE SEPARATION TECHNIQUES

A number of purification methods have been adopted from the original concepts of mineral flotation whose common characteristic is the use of adsorption on gas bubbles produced in a bulk liquid medium. This has resulted in their generic name of adsorptive bubble separation processes. The most widely accepted means of classifying this large array of different techniques was suggested by Karger et al (4) and is shown in Figure 1.

The first division made in this classification concerns the use of collectors for enriching the gas/water interfaces which results in the presence of a froth, or foam, phase. Processes which do not require such reagents are termed non-foaming adsorptive bubble separations and rely either on the formation of a concentration gradient along the path of the bubbles (bubble fractionation) or on the transference of adsorbed material into an immiscible organic layer on the surface of the flotation pool (solvent sublation). Foam separations, which require the use of a collector of some type can be subdivided further into foam fractionation, the removal of soluble surface active species into a foam phase by simple aeration and froth flotation, where the species to be separated is a particulate. Macro-flotation, which is similar to ore flotation, involves the removal of macroscopic material, while micro-flotation involves the separation of microscopic and colloidal material. The removal of insoluble precipitates by flotation when the precipitant is not the collecting agent is known as precipitate flotation and the removals of ionic and molecular species by chemical combination with collectors to form hydrophobic particulates are known as ion flotation and molecular flotation respectively. Adsorbing colloid flotation describes a process where soluble species are first adsorbed on to the surface of colloidal material specifi-

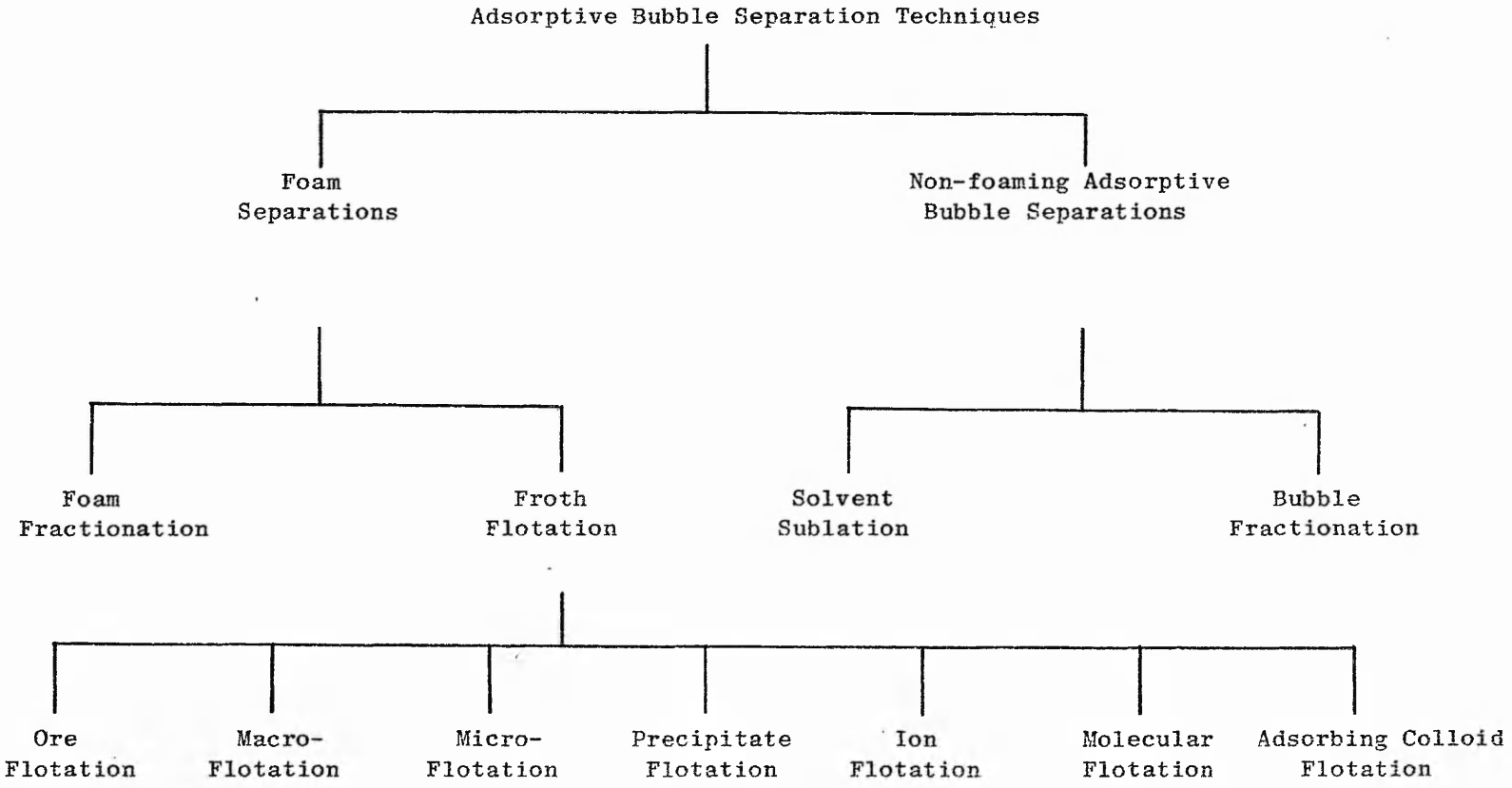


FIGURE 1: Classification of Adsorptive Bubble Separation Techniques

cally introduced for this purpose, after which the colloid-adsorbent combination is removed from the bulk solution by flotation.

1.4 THE USE OF ADSORPTIVE BUBBLE SEPARATIONS IN WASTEWATER TREATMENT

The extent to which the separation techniques described in the previous section, particularly those used in mineral processing, have been utilised by the wastewater treatment industry has been determined by the contrasting objectives of the two fields.

The common effect on the bulk solution of bubble separations is the selective removal of a particular species. This is especially noticeable in ore flotation, where selection is the major purpose of the treatment and is usually even more important than the rate at which the ore is processed. The primary objective of wastewater treatment, however, is the rapid removal of as comprehensive a range of pollutants as possible.

In ore flotation the value of the material being separated may make a process economically viable even if it necessitates the use of expensive reagents or if treatment times are long. The relatively low value which is generally attributed to the removal of pollutants demands that a wastewater treatment process must be inexpensive before it can be viable.

It would appear initially that the operation of both mineral and wastewater flotation plants is similar since it is usually desirable to run both as continuous processes. However, the operator of a mineral flotation plant has a higher degree of control over the process since although the exact constituents of the mineral/gangue mixture cannot be precisely predicted, the size and surface properties of the particles which are fed into the flotation unit can be controlled to some extent by the preliminary milling operations. In addition, the concentration of particles in the influent stream may be varied if desired since the particles are in a dry state at the beginning of the puri-

fication circuit. Operators of wastewater treatment plants are faced with the problem of an influent whose quality may fluctuate erratically and whose characteristics are largely unknown and uncontrollable.

Despite these general differences in aims and operation, some adsorptive bubble techniques, particularly foam separations, have been used extensively for the removal of pollutants.

Foam fractionation was the subject of considerable interest prior to the introduction of biodegradable detergents. At the time the effects on the receiving watercourses of "hard" or branched-chain detergents from sewage works effluents was considerable, since conventional biological treatment was ineffective in removing them. Aeration of the final effluent stream followed by removal of the resultant foam proved to be an inexpensive method capable of large-scale operation (5 - 8), with the added bonus that other pollutants were found to have been carried over with the foam. Other surface-active soluble pollutants, eg dyes (9), tannery wastes (10) and phenols from petrochemical wastes (11, 12 and 16) have been concentrated in a similar manner.

The use of ion and precipitate flotation has been reported for the treatment of various industrial waste streams, in particular for the removal of radioactive materials (13, 14) and for the reclamation of valuable metals from electroplating wash waters (15). Adsorbing colloid flotation has been utilised for the extraction of fission products using ferric hydroxide (17) and of the organic residues from acetylene manufacture using soot particles already present in the wastewater stream (18).

Of the various types of foam separations described in Section 1.3, microflotation, generally known simply as foam flotation, has been most widely used for wastewater treatment. The use of a flotation process for the removal of suspended impurities from river water was first suggested by Hopper (19), who hypothesised that negatively charged suspended and colloidal particles could be removed from

surface waters by dispersed air flotation using a cationic surfactant as the collector/frother. Preliminary experiments by Hopper and McCowen (20) and Moore and Bryant (21) showed turbidity removals of over 70% and bacterial removals of over 90% to be possible. The cationic surfactants used in these studies were of the quaternary ammonium type.

A more extensive study of water clarification by foam flotation was presented by Grieves in 1966 (22). This described investigations of the removal of a synthetic mixture of clays and sands by flotation with ethylhexadecyldimethylammonium bromide. The flotation process was considered to show promise for the clarification of low quality waters for supply to the armed forces or small municipalities. The residual surfactant concentration was claimed to be readily removed by adsorption on activated carbon. One potential disadvantage that was highlighted was the interference in removal caused by trivalent cations; this had been noted by the previously mentioned investigators. This effect was examined in greater depth, using ferric ions as an example, by Crandall and Grieves (23) who attributed the interference to competition between the particle surface and ferric hydroxide for surfactant. The transformation of the process from a batch to a continuous process was the subject of further studies by Grieves and Schwarz (24), who evaluated the effects of the basic process variables. These included air rate, temperature, retention time and surfactant dosage. It was found that higher surfactant concentrations were required with continuous operation to obtain comparable results with the previous batch experiments.

Grieves and Crandall (25) investigated uprating the process by using bentonite as a flotation aid, and later papers by Grieves et al (26, 27) extended the previous exploratory studies on synthetic waters to the purification by flotation of naturally occurring river waters.

The exclusion of micro-organisms by flotation has been the

subject of a number of separate studies. Early work by Dagnan and Dumontet (28) and Boyles and Lincoln (30) showed that bacterial spores and vegetative cells could be collected by foam separation. Levin and Barnes (29) concluded that algae could be harvested economically using flotation, and that it might have use as a sewage treatment process. Rubin and Cassell (31) found that E Coli could be floated but specified the use of low air rates for maximum efficiency of removal. Van Vuuren et al (32) and Cilie et al (33) developed a two-stage method for use in the reclamation of sewage effluents utilising nutrient stripping by algae followed by algal removal in a flotation unit. The early work of Moore and Bryant (21) examined virus removal by flotation, and this was investigated in greater depth by Guy et al (34), using quaternary ammonium salts. In addition to their surface active properties, these reagents were found to be toxic to the virus used in the study.
The use of foam flotation for the removal of sewage solids has not met with the same degree of success as the use of the process for purifying river water. In a study on the removal of solids from paper mill effluents and sewage wastes by foam flotation, Hansen and Gotaas (35) concluded that the process was economically unsuitable due to the low removal efficiencies and high collector consumptions encountered. Newe et al (36) experimented with 28 different detergents and reached the same conclusion. Van Vuuren et al (37) and Stander and Van Vuuren (40) found that sewage solids could be floated after coagulation with lime provided that the bubble size of the dispersed air phase was small. This was achieved by the introduction of air into the suction side of the centrifugal pump supplying the unit. D'Arcy (38) and Ashley (39) had previously found that a similar system gave good results for the treatment of industrial wastes. It thus became obvious that small bubble sizes and coagulation were essential for the successful flotation of sewage solids, and interest in these and similar techniques increased.

1.5 MICRO-BUBBLE METHODS

As interest grew in micro-bubble methods, the technology for the production of the necessary minute bubbles became correspondingly more sophisticated. In the early systems (37 - 40) micro-bubbles had been formed by dissolving excess air in the influent under the influence of pump suction, followed by the precipitation of this excess air when the influent entered the main tank and returned to atmospheric pressure. Thus rather than dispersion of air these processes featured dissolution and precipitation of air, and were consequently named dissolved air processes. Micro-bubbles had been created by a similar mechanism in the mineral processing industries by vacuum flotation (41). This involved subjecting the flotation pool to a partial vacuum which resulted in air precipitation.

Alternatives to the early systems gradually evolved as interest in dissolved air flotation increased. Commercial systems currently available rely on a variety of methods (42 - 44), the most common being the pressurisation of a portion of the effluent from the flotation unit followed by recycle and release into the pool via a special nozzle (45). Electroflotation provides a means of producing micro-bubbles by electrolysis of the aqueous medium. The fundamentals and scope of the process were reviewed by Kuhn (47) who concluded that it had a promising future in wastewater treatment, particularly for the thickening of surplus activated sludge.

The reasons for the success of dissolved air flotation over dispersed air methods for the flotation of sewage solids lies in the nature of the solids themselves. Kitchener (46) has pointed out that the lack of definite crystalline structure in such flocculent species precludes the achievement of a satisfactory contact angle between solid, liquid and gas phases. The dissolved air process is thus not considered to depend primarily on a surface process at an air/water interface. Its success is attributed to the entrapment of bubbles in the flocs formed by coagulation of the solids. Dispersed air bubbles would not be effective

in such a situation since the turbulence caused by the passage of the relatively larger bubbles through the pool would only serve to break up the delicate structure of any flocs formed. Since surface adsorption does not play a decisive role the use of surface active agents has been largely discontinued. The beneficial effects of poly-electrolytes are now thought to be due to their ability to strengthen the floc structure (48).

1.6 COMPARISON OF DISSOLVED AIR AND DISPERSED AIR FLOTATIONS FOR RIVER WATER TREATMENT

The success of dissolved air flotation in treating sewage and industrial wastes led to the introduction of the process for river water treatment. This was due mainly to the efforts of the Water Research Centre, who in 1969 initiated an extensive programme of research and development (49, 50, 51, 52). The large-scale system which evolved from this activity has been found to give satisfactory results when tested on a variety of natural waters (53). The rapid advance of the dissolved air process for river water treatment has resulted in a decline in the interest shown in the dispersed air process. One reason for this may be the basic chemical similarity of the coagulation/flotation process to the traditional coagulation/sedimentation method. Thus previous technology and knowledge could be utilized to the full and in some cases existing treatment plant would be suitable for conversion. The main technological claims to the superiority of the dissolved air process are the absence of a large volume of secondary effluent from the collapsed foam resulting in drier sludges, savings in reagent costs, and the absence of collector contamination of the effluent stream. Treatment times for the two methods are difficult to compare since they vary considerably depending on the precise nature of the river water undergoing treatment.

It could be argued that many of the technical disadvantages of the dispersed air process are due more to inefficient process control than to some fundamental weakness of the

method. If more efficient control of the process could be achieved, then the relative simplicity of construction and maintenance of dispersed air units might make them more attractive to the water treatment industry. In addition, the desirability of a quiescent pool for dissolved air flotation seriously limits the maximum values of air and water flowrates through a particular unit. Dispersed air systems are not dependant on an absence of turbulence for successful operation so could provide a greater degree of flexibility.

The arguments outlined above indicate that further investigations into the control of the dispersed air process might result in a river water treatment system of practical use. One application which would seem to utilise the advantages of the process over other flotation methods would be a small scale unit for mobile or emergency use.

CHAPTER 2

THE FORMULATION OF THE RESEARCH PROGRAMME

2.1 INTRODUCTION

This chapter will describe the initial development and planning of the research. This consisted of the definition of the problem areas to be investigated, the adoption of suitable methods of approach, and the formulation of an experimental programme.

2.2 DEFINITION OF THE PROBLEM AREAS

The objective of the programme of research described in this thesis was to investigate the parameters which govern the efficiency of dispersed air flotation when applied to wastewater purification. It was felt that a knowledge of the effects of these parameters would lead to a greater degree of process control and an increase in the viability of the process as a treatment method. In addition, such knowledge could be utilised in the design of large scale units and in the planning and evaluation of pilot plant investigations.

The parameters affecting the performance of a flotation system were divided for convenience into two broad groups:

a) Characteristics of the liquid undergoing treatment.

This group covered the properties of both the material to be removed and its surrounding liquid medium. Factors influencing the former included the physical state of the material (whether soluble, colloidal or particulate), the methods by which it could be rendered hydrophobic, and its size and concentration. The characteristics of the latter were those which might affect the surface activity of the material to be removed, eg the presence of dissolved substances which might inhibit or promote flotation.

b) Characteristics of the treatment system.

The main characteristics considered to be of importance are listed below:

Mode of operation; whether batch or continuous.

Tank size and geometry, and the configuration of any baffles.

Air rate and bubble size.

Feed rate of influent.
Type of surfactant used and its feed rate.
Method of removal of the resultant foam.

Whilst it was realised that the above classification did not constitute two completely exclusive divisions, it was felt that the major part of the research to be undertaken in this study should concentrate on the second group of parameters. The nature of the first group was such that in a practical wastewater treatment situation control of them would be extremely difficult, so that any optimisation of the process would have to be achieved by manipulation of the second group. This approach was reflected in the eventual choice of experimental system (see Section 3.3). The foundation of the research programme was a preliminary study of the treatment of River Trent Water (see Section 3.2) which had shown that a high percentage of suspended solids could be removed by dispersed air flotation using a cationic surfactant. The removal of clays was chosen as the basis of the main research since, in addition to its direct relevance to the water treatment field, such an approach was advantageous in that removal could be measured relatively easily (see Section 3.7.1). However, it was felt that the results and conclusions of such a study would be of use when considering the flotation of other wastewater pollutants.

2.3 METHOD OF EXPERIMENTAL APPROACH

Having established the basic field of study, it was necessary to assess the ways in which the significance of the process variables could be tested. Possible experimental approaches were classified into two general groups and examined for their suitability.

a) The use of a large-scale pilot plant was considered. It would be necessary for such a plant to be flexible enough in construction and operation for parameters to be varied singly or in groups. The effects of the parameters on the process could then be ascertained. Such an approach can be particularly useful in commercial development work,

since a large amount of practical information can be gathered on the applicability of a process to the treatment of a particular effluent. This provides the data necessary for the design of a full-scale plant. The disadvantages of this method in the case of this research programme were twofold. Firstly, experience with the Simon-Hartley pilot plant (see Section 3.2) indicated that the operation and modification of large scale plants demanded a high commitment of resources. Secondly, the size of such a plant would require a large supply of influent. This would have to be obtained from a river or sewage treatment works, introducing difficulties in the control and interpretation of experimental results.

b) A programme of laboratory based tests made in a small-scale unit was considered. However, previous experience with such systems had shown that whilst control of the process was greatly improved, it was likely that conditions in such a unit would not represent adequately those in a full-scale plant. In addition certain experimental operations, eg the withdrawal of samples or the addition of reagents, could significantly affect the performance of the unit.

A compromise between these two general approaches was finally adopted. Experimental flotation units were designed so that they were small enough to give the required degree of process control whilst being of large enough size to provide a reasonable representation of the operation at full scale.

2.4 METHOD OF THEORETICAL APPROACH

Within the confines of the general experimental approach it was necessary to evaluate a theoretical basis for the study.

One method used by previous workers in the field of wastewater flotation had been an analysis on empirical lines. Grieves and Bhattacharyya (54) suggested a model linking the removal of surface active species by flotation to the main process variables by means of the power relationship:

$$C_i - C = K \left[\frac{A}{v}\right]^{\alpha} \left[C_i\right]^{\beta} \left[\phi\right]^{\gamma} \left[r_b\right]^{\delta}$$

where C_i = Feed concentration

C = Bulk concentration in flotation cell

A = Gas flowrate

v = Liquid feed rate

ϕ = Temperature

r_b = Bubble radius

α, β, γ, δ, K = Constants

The numerical values of the various constants were calculated from experimental data by a computer-aided best fit procedure. Guy et al (34) used a similar method to predict the removal of viruses by flotation.

The disadvantage of the empirical approach is the difficulty of relating a set of empirical results obtained with a particular experimental apparatus to any other situation, particularly when scale-up is involved. In addition, relationships such as the above only describe the steady-state situation and cannot be used to evaluate plant performance under the rapidly varying feed conditions often found in wastewater treatment.

It was felt that whilst the empirical approach might be the only practical method of assessing the effects of the parameters listed in group a) of Section 2.2, it should be possible to analyse the effects of most of those in Group b) from a more fundamental standpoint. A review of mineral flotation research revealed that a considerable degree of success had been obtained using a method based on the well established theories of chemical reactor kinetics. It was felt that this approach had potential for the analysis of wastewater flotation despite the significant differences in the aims and operation of the process between the two fields (see Section 1.4).

2.4.1 Chemical Reactor Theory

This form of analysis, as its name implies, is used to predict the progress of chemical reactions with time in various types of reaction vessels. An early attempt at such analysis was made by Ham and Coe (55) in 1918. Other

initial developments were due to MacMullin and Weber (56) and Mickley, Sherwood and Reed (57). Subsequent progress has been extensive; Nagata (58) has given a comprehensive review of the field. A relatively simple approach was suggested since this was likely to be adequate to describe the flotation process.

2.4.1.1 Order of Reaction

The term "order" when applied to chemical reactions describes the way in which the amount of a certain constituent of the reaction varies with time as the chemical reaction proceeds. If a chemical substance is being converted to some other substance at a rate that is constant irrespective of the amount of substance present in the reactor, then the drop in concentration of the substance relative to time can be expressed in the following manner:

$$-\frac{dC}{dt} = K \qquad (I)$$

where -dC/dt represents the incremental drop in concentration, C, with time, t and K is the rate constant of the process. Equation (I) may be solved by separation of variables and integration between appropriate boundary conditions to give:

$$C = C_i - Kt \qquad (II)$$

where C_i is the initial concentration at time zero. This type of chemical reaction is known as a zero order process. The decrease in C relative to t is shown in Figure 2.a. In a first order reaction, the decrease in concentration of the substance at a particular time is proportional to the amount of that substance existing in the reactor at that time. Thus:

$$-\frac{dC}{dt} = KC \qquad (III)$$

using the same nomenclature. This may be solved in a similar way to equation (I), to give:

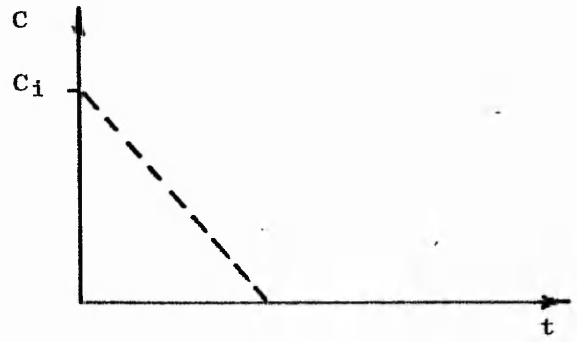
$$C = C_i \exp(-Kt) \qquad (IV)$$

This type of decrease is shown in Figure 2.b as an exponential decrease from the initial value C_i.

The above definition of the term "order" can be extended to

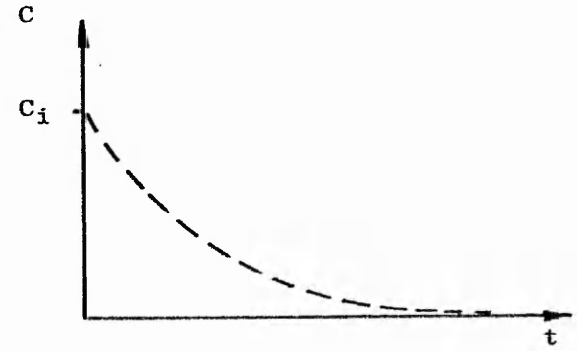
a. Zero-Order Reaction

$$-\frac{dC}{dt} = K$$



b. First-Order Reaction

$$-\frac{dC}{dt} = KC$$



c. λ-Order Reaction

$$-\frac{dC}{dt} = KC^{\lambda}$$

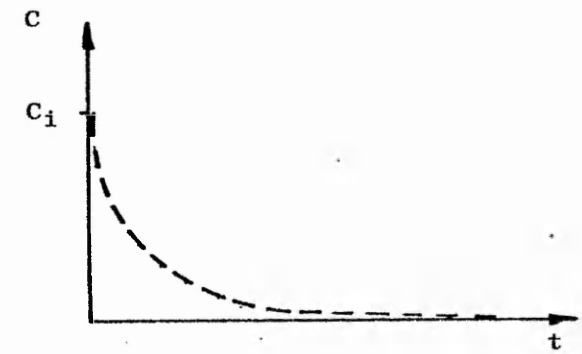


FIGURE 2: Chemical Reaction Kinetics

any value. Thus the differential equation describing a chemical reaction of any order, λ, has the general form:

$$-\frac{dC}{dt} = KC^{\lambda} \qquad (V)$$

In any case other than $\lambda = 1$, the solution of equation (V) may be expressed as:

$$\frac{1}{(1-\lambda)}\left[C^{1-\lambda} - C_i^{1-\lambda}\right] = -Kt \qquad (VI)$$

An example of this is shown in Figure 2.c for $\lambda = 2$, ie a second order reaction.

It should be stressed that although chemical reactions can occur which comply with these simple models, the situation may be complicated by other factors, eg the progress of another inhibiting chemical reaction simultaneously with the particular reaction being studied. The significance of the concept of reaction order with respect to flotation will be discussed further in Section 2.4.2.

2.4.1.2 Chemical Reactions in Continuously-Fed Reactors

The expressions for the variation of concentration with time developed in Section 2.4.1.1 are only adequate for describing the progress of a chemical reaction in a batch operated reactor, even if the chemical reaction follows a particular order expression without deviation. A batch operated reactor is one where a reaction is allowed to proceed to completion without any fresh input or output of substance. However, in most practical situations this kind of operation is inconvenient and it is usually desirable to run reactors in the continuous mode. Continuously operated reactors are subject to continuous or periodic addition of fresh materials at some point in the reactor combined with simultaneous extraction of reactor liquor at some other point. In such an operation, it is likely that the extracted liquor (or effluent) will contain unreacted components, and experience indicates that the effect on the progress of the reaction is to prevent the entire contents of the reactor from ever becoming completely reacted. If feed and extraction conditions remain constant then eventually the reactor reaches a steady state between this influent/effluent dis-

crepancy. The effect of the influent on the effluent is a function of the amount of mixing which occurs in the body of liquid in the reactor and on the relative locations of entry and exit points. Thus before the progress of a chemical reaction in a continuously operated reactor can be described mathematically, some kind of mixing model has to be formulated.

2.4.1.3 Mixing Models

Over the past four decades much interest has been shown in the creation of accurate and comprehensive models of mixing regimes. Reviews of the progress made in this field may be found in the work of Levenspiel (59), Nagata (58) and Oldshue (60).

Some mixing models can be extremely complicated, but it has been found that frequently only the simplest forms are necessary to describe the mixing in the vigorously aerated tanks found in conventional flotation circuits (61).

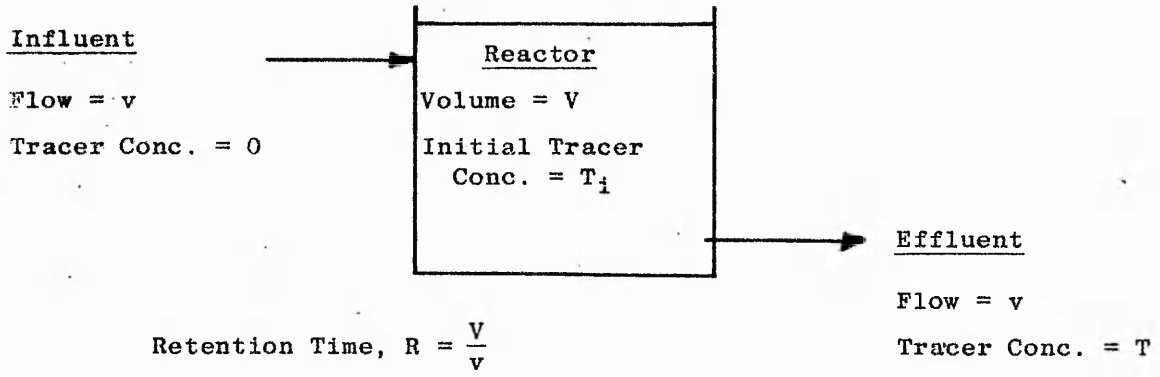
Mixing regimes are commonly investigated by the use of tracers: Figure 3 shows one method which will be considered in the present discussion. A continuously fed single-stage reactor of volume V is shown which has an influent/effluent system superimposed upon it, the flow of both streams being v. A quantity R, known as the retention time of the reactor, may be defined as:

$$R = \frac{V}{v} \qquad \text{(VII)}$$

The units of R are those of time since it is the ratio of a volume to a volume per unit time.

Initially the tracer concentration in the reactor is T_i, and as tracer-free influent is fed into the reactor the resultant variation in effluent tracer concentration with time characterises the type of mixing which prevails. Full details of such tracer response techniques are given in Section 3.7.3.

The most straightforward method of classifying the mixing regime prevalent in a chemical reactor is to define it in relation to two extreme conditions. These are described below:



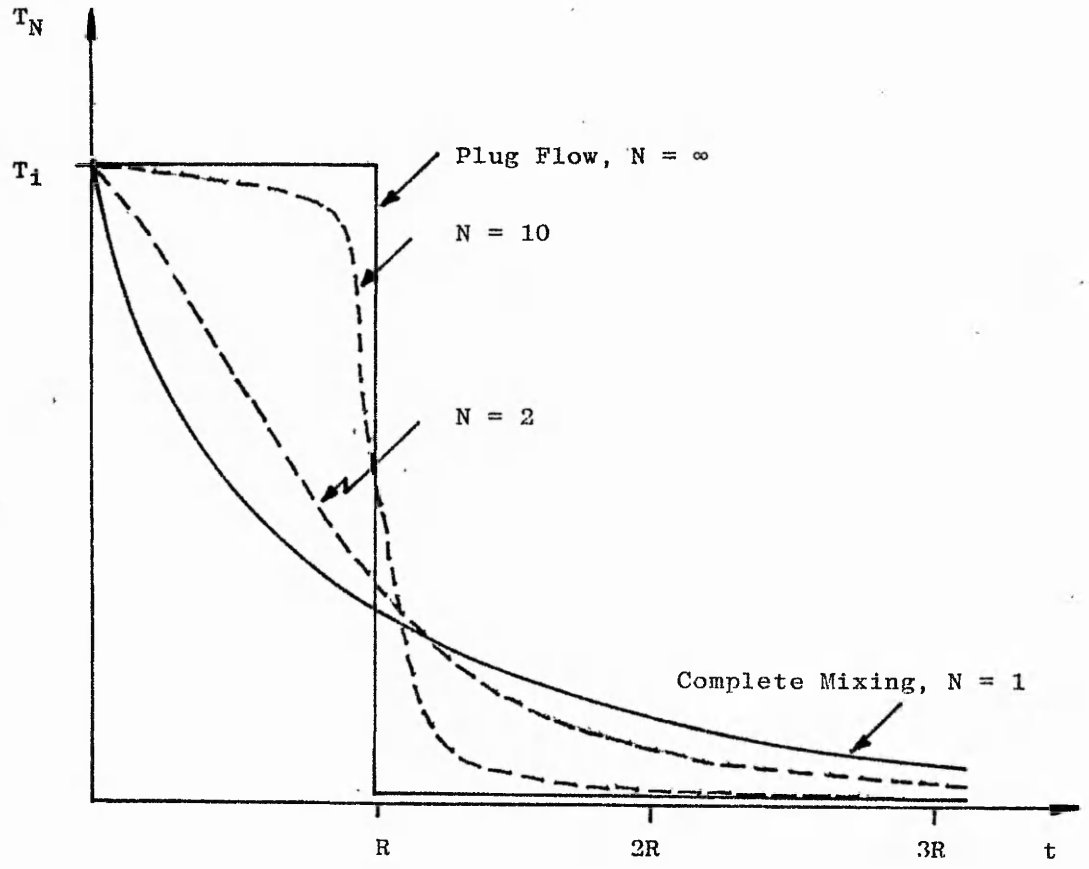


FIGURE 3: Mixing Models

a) Plug Flow

In this idealised regime there is no mixing between increments of volume in the reactor, and all increments of volume remain in the reactor for the same time period, the retention time R. Thus in a tracer test such as the one described above the effluent tracer concentration would remain at its initial value of T_i until the retention time, R, had elapsed. It would then drop instantaneously to zero, where it would remain for the duration of the test. This behaviour may be described mathematically by the expression:

$$T = T_i \quad 0 < t < R$$
$$T = 0 \quad R < t \qquad \text{(VIII)}$$

b) Complete Mixing

When a condition of complete mixing prevails, every increment of volume mixes simultaneously with every other and a completely homogeneous mix is obtained at all times. In a tracer test the variation of the effluent tracer concentration, T, may be derived by a consideration of the mass of tracer lost from the reactor in an increment of time dt. This will be:

mass of tracer lost = T v dt

The effect of this loss on the overall concentration in the reactor, - dT, is given by:

$$-dT = T \frac{v}{V} dt$$

$$\rightarrow -\frac{dT}{dt} = T \frac{v}{V} = \frac{T}{R} \qquad \text{(IX)}$$

Equation (IX) may be solved by separation of variables and insertion of appropriate boundary conditions:

$$T = T_i \exp\left[-\frac{t}{R}\right] \qquad \text{(X)}$$

These two extremes of mixing behaviour are illustrated in Figure 3. In the case of a single-stage flotation cell a mixing regime often prevails which conforms closely to complete mixing. Thus the mixing in a multi-stage flotation apparatus might be suitably described by a number of completely mixed vessels connected in series.

c) Multi-Stage Reactor

If the total volume of the reactor, V, is divided into N

completely mixed stages, each of volume V/N, the variation of tracer concentration with time for each stage is obtained by an extension of the previous analysis (see Appendix 1.1):

$$T_n = T_i \left[X\right] \exp \left[-\frac{Nt}{R}\right] \qquad \text{(XI)}$$

where T_n represents the tracer concentration in the effluent from the nth stage and where:

$$\left[X\right] = 1 + \frac{Nt}{R} + \frac{1}{2!}\left[\frac{Nt}{R}\right]^2 + \ldots + \frac{1}{(n-1)!}\left[\frac{Nt}{R}\right]^{n-1} \qquad \text{(XII)}$$

The series $\left[X\right]$ has n terms.

Figure 3 illustrates the relationship between T_N and t for a number of values of N. It will be seen that as N increases this relationship becomes nearer to that which would be expected for a condition of plug flow, ie:

as $N \to \infty$ $T_N \to 1$ $\quad 0 < t < R$

$T_N \to 0$ $\quad R < t$

The tracer response derived from a particular mixing regime will lie between the two extremes of complete mixing and plug flow, and one possible method of classifying it would be to calculate a hypothetical number of completely mixed stages which would yield a similar response. This approach will often provide a useful first approximation; additional flexibility may be obtained by the insertion of parallel connections or by the addition of areas where plug flow is assumed to take place.

d) Dispersion Model

This is a more sophisticated model which is used in the analysis of mixing in tubular reactors. The prevailing regime is assumed to be the product of turbulent dispersion in the direction of the flow through the unit. A consideration of the flow through an incremental volume situated at a distance y from the point of entry of the influent yields the differential equation (see Appendix 1.2):

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial y^2} - u_L \frac{\partial t}{\partial y} \qquad \text{(XIII)}$$

where u_L is the linear velocity of the liquid through the reactor and D is the coefficient of axial dispersion. The solution of equation (XIII) depends on the boundary conditions chosen.

The dispersion model is not usually applied to the solution of convential flotation systems since they do not employ tubular shaped tanks. However, Rice et al (62) have used it to successfully characterise the mixing in tall flotation columns.

2.4.1.4 Incorporation of Mixing Models into the General Theory

Having established a potential method for describing the mixing regime prevalent in a system, it is necessary to combine a suitable model with the relevant expression for chemical reaction order.

Figure 4 shows a schematic diagram of a single-stage reactor of volume V with a continuous feed of flow rate v and concentration C_i. The initial concentration of the liquid in the reactor is also C_i. Effluent is withdrawn at a constant rate v and has a concentration that can be represented by C at any time t. If first-order kinetics apply and a complete mixing regime prevails, then the change in C in incremental time dt can be represented by:

$$\frac{dC}{dt} = - KC + \frac{v}{V} C_i - \frac{v}{V} C$$

$$= - KC + \frac{C_i}{R} - \frac{C}{R} \qquad \text{(XIV)}$$

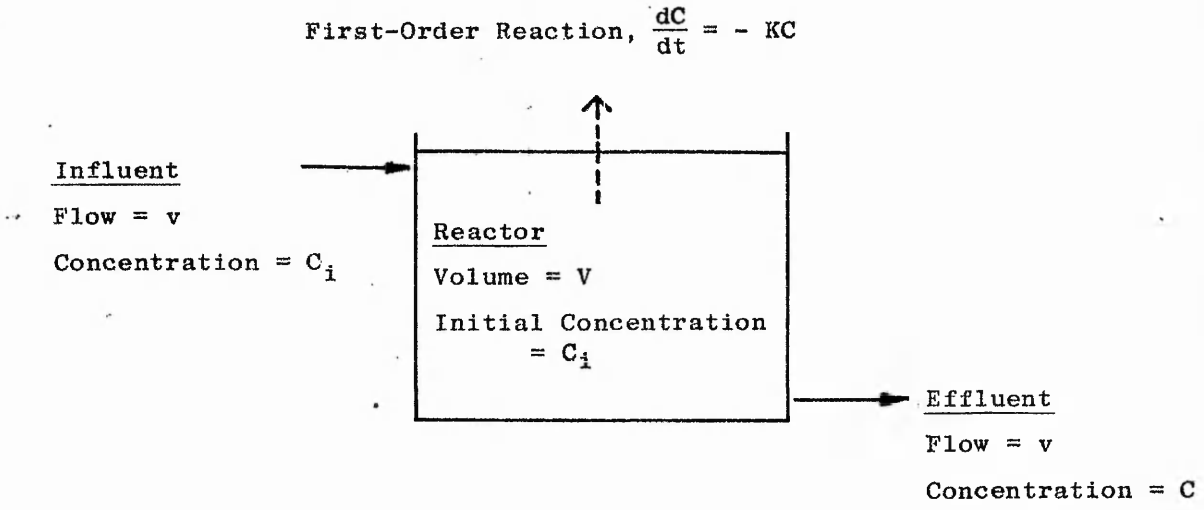
The first term on the right hand side of equation (XIV) represents the decrease in C due to the chemical reaction taking place, the second term represents the effect of the addition of influent, and the third term represents the effect of effluent withdrawal. Equation (XIV) can be solved using an integrating factor (see Appendix 1.3) to give:

$$\frac{C}{C_i} = \left\{\left[1 - \frac{1}{(RK + 1)}\right] \exp\left[- \frac{(RK + 1)t}{R}\right]\right\} + \left[\frac{1}{(RK + 1)}\right] \qquad \text{(XV)}$$

The variation of C/C_i with t is shown in Figure 4 for a typical example. At zero time the exponential term in equation (XV) tends to unity and thus the value of C/C_i at this point is also unity. As t increases from zero the exponential term gradually becomes smaller and the value of C/C_i tends to:

$$\text{as } t \to \infty, \ \frac{C}{C_i} \to \frac{1}{(RK + 1)} \qquad \text{(XVI)}$$

This value is constant and a steady state has been reached.



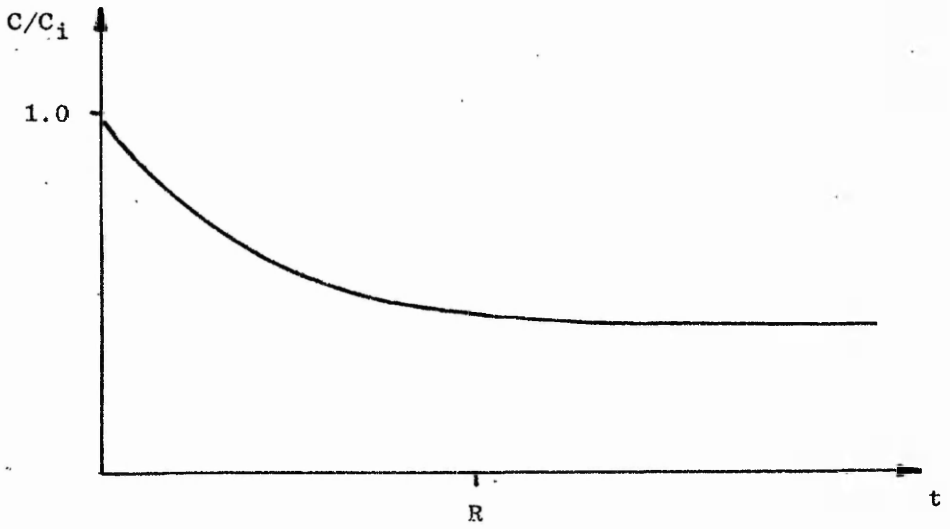


FIGURE 4: Kinetics of a First-Order, Single-Stage Reactor

However, this condition will only persist if the parameters R and K remain constant. If changes in operational parameters (eg v or V) or in chemical conditions (which will effect K) occur, a resumption of the transient state will result until another steady state is reached.

A similar approach can be adopted for more complex systems; one of particular interest in this research was a first-order reaction in a multi-stage mixing regime. Using the same nomenclature as above and including the same total reactor volume V, the following expression may be developed for the concentration of the effluent from the nth stage (see Appendix 1.4):

$$\frac{C_n}{C_i} = \left\{\left[Y\right] \exp\left[-\frac{(RK+N)t}{R}\right]\right\} + \left[\frac{N}{RK+N}\right]^n$$

$$\text{where } \left[Y\right] = \left[1 - \left(\frac{N}{RK+N}\right)^n\right] + \left[\frac{Nt}{R}\right]\left[1 - \left(\frac{N}{RK+N}\right)^{n-1}\right]$$

$$+ \ldots + \left[\frac{1}{(n-1)!}\left(\frac{Nt}{R}\right)^{n-1}\right]\left[1 - \frac{N}{(RK+N)}\right] \qquad \text{(XVIII)}$$

The series $\left[Y\right]$ has n terms, and attention is drawn to its similarity in construction to the series $\left[X\right]$ in equation (XII).

Typical curves for C_N/C_i vs. t for a series of values of N are shown in Figure 5. The lowest of the family of curves illustrated corresponds to a plug flow condition (see Appendix 1.5) and it will be seen that as N increases the relationship between C_N/C_i and t approaches this curve, ie

$$\text{as } N \to \infty \quad \frac{C_N}{C_i} \to \exp(-Kt) \qquad 0 < t < R$$

$$\frac{C_N}{C_i} \to \exp(-KR) \qquad R < t$$

The practical implication of this is that the nearer the mixing regime in a reactor can be made to plug flow, the lower will be the concentration in the effluent stream. This would suggest that a particular sized reactor may be made to function more efficiently by the insertion of suitable baffles.

2.4.2 Development of the Kinetics of Mineral Flotation

Panou (75) attributes the formulation of the first algebraic expression to describe the behaviour of a mineral flotation

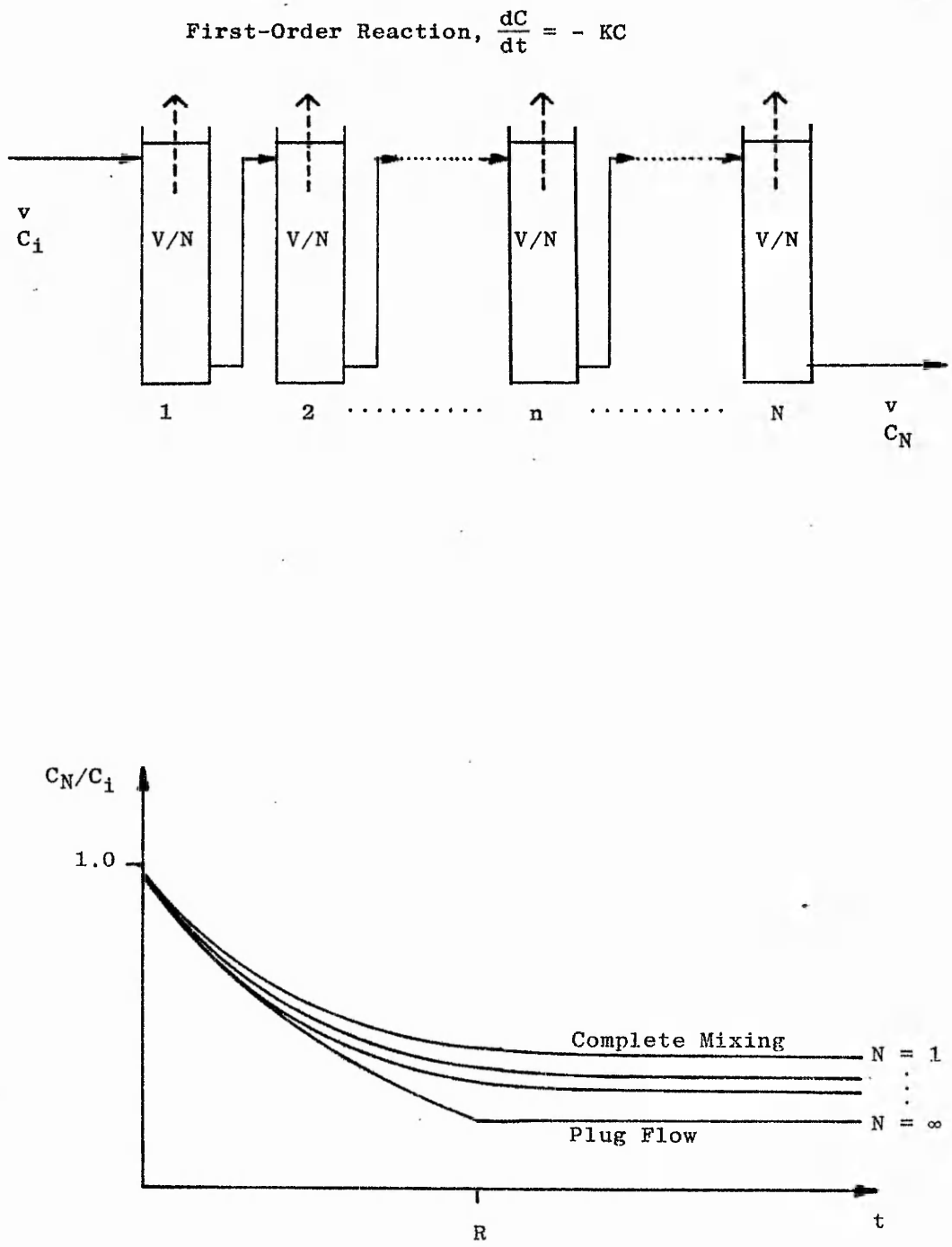


FIGURE 5: Kinetics of a First-Order, Multi-Stage Reactor

cell to Merlin and Gazo in 1928 (76). This was followed by contributions from Beloglazov (77), Garcia-Zuniga (78), and Gründer and Kadur (79).

The conclusion of these early workers was that the rate of flotation of particles at any time was proportional to the concentration of particles in the pulp at that time. This led to the suggestion that the flotation process was analogous to a first-order chemical reaction of the type described in equations (III) and (IV) in Section 2.4.1.1. The possibility of the existence of orders other than unity was examined by Arbiter (80), who reprocessed existing data and found that a second-order equation gave a closer correlation. However, his conclusions were criticised by Morris (81) and by Brown and Smith (82), who argued that either mathematical model was inaccurate at high rates of recovery.

Woodburn (83), in a recent review of models of the flotation process, has stated that this controversy over flotation rates served to illustrate the dangers of extending arguments by analogy. Thus it was realised that although the chemical kinetics analogy seemed appropriate for the analysis of flotation systems, it would need a more logical basis if its usefulness was to be fully exploited.

2.4.2.1 Probablistic Approach to Flotation Kinetics

The first attempt at a fundamental description of flotation is generally credited to Sutherland (84). He suggested a comprehensive expression to link the rate constant of a first-order removal process to particle properties and operating conditions:

$$k = \left[3 \pi r_p r_b u_{pb} C_b\right]\left[\operatorname{sech}^2\left\{\frac{3 u_{pb} \Psi}{4 r_b}\right\}\right]\theta$$

where: k = First-order rate constant for particle flotation

r_p = Particle radius

r_b = Bubble radius

u_{pb} = Relative velocity between particle and bubble

C_b = Bubble concentration (related to air rate, A)

Ψ = Induction time for particle/bubble adhesion

θ = Proportion of particles retained in the froth after successful collision and adhesion

The term in the first set of brackets represents the particle/bubble collision process, and was derived from an application of the standard treatment for streamlined flow around rigid spheres. The term in the second set of brackets is an attempt to describe the adhesion of a particle to a bubble after a successful collision. The third term recognises the possibility of floated particles being drawn back into the pulp from the froth. Sutherland's equation has been criticised on several counts, firstly because his treatment of the hydrodynamics of collision ignored inertial effects and secondly because many of the terms used were difficult or impossible to evaluate. However, it heralded the beginning of the probablistic approach to flotation kinetics, which is still the basis of most mathematical models of the process.

In 1956 Plaskin, Klassen and Berger (85) suggested a general description for flotation in which the rate of removal of particles from the cell was proportional to the product of the probability of a number of sub-processes occurring. Similar equations have appeared in later contributions by other workers (86, 87, 88) and have been summarised by Tomlinson and Fleming (89) as:

$$k = P = P_c \, P_a \, P_e \, P_f$$

Here P is the probability of successful flotation, which is comprised of the probability of collision between particle and bubble (P_c), the probability of adhesion of the particle to the bubble after collision (P_a), the probability that the particle will continue to be attached to the bubble during its passage through the pulp (P_e), and finally the probability that the floated particle will remain in the froth and eventually appear in the concentrate (P_f). The similarity of this approach to Sutherland's will be appreciated. The rate constant, k, was thus given a physical meaning rather than a purely empirical one, and much of the later research work in the field has been aimed at the evaluation of the constituent probabilities.

2.4.2.2 Probability of Collision

The assumption of first-order kinetics for flotation strongly suggests that the initial capture of particles by bubbles is based on a collision process. Other methods of capture were favoured by early investigators. For example Taggart (90) suggested that gas bubbles grew on the surface of a particle due to the precipitation of gas from a solution which had become supersaturated. It is now recognised (91) that whilst in conventional sub-aeration cells some localised gas precipitation does take place behind the blades of the rotating impellers, this is not the primary cause of particle capture. An exception is found to this in the vacuum flotation cell, which bears strong similarities to the dissolved air flotation process used in water treatment. Lin and Metzer (92) have investigated the kinetics of vacuum flotation and found that the order of removal can vary from 0.5 to unity depending on the pressure differential.

The mechanics of collision between particles and bubbles has recently been the subject of a number of important fundamental studies. These have used hydrodynamic theory developed for the study of raindrop coalescence (93) to develop a theory for particle/bubble collisions in froth flotation. Flint and Howarth (94) calculated grazing trajectories for particles in the path of a rising spherical bubble, and determined collision efficiencies in terms of an inertia parameter and a gravitational parameter. Two regions of particle/bubble behaviour were defined. For large particles the collision efficiency was found to depend mainly upon inertial forces, whereas for smaller particles the gravitational forces predominated. The existence of an optimum bubble size for the recovery of a particular size of particle was also demonstrated. Reay and Ratcliffe (95) extended this analysis to cover the range of particle sizes found in water and effluent treatment situations.

The probability of collision for particles greater than 3μm diameter was found to be given by:

$$P_c \propto \left\{\frac{r_p}{r_b}\right\}^{\varepsilon}$$

where ε varies from 1.9 to 2.1 depending on the density of the particle. Reay and Ratcliffe pointed out that since the volume swept out by a bubble is dependent on (r_b^2), then for the particle range considered the actual number of particles collected by a bubble is virtually independent of bubble size. In addition, coagulation in this range of particle sizes (ie an increase in r_p) would be beneficial.

Particles with diameters significantly lower than 3μm were considered to be collected mainly by a process of surface adsorption and the probability of collection (ie $P_c\ P_a$) was found to be given by:

$$P_c\ P_a \propto (r_p)^{-2/3}$$

Increase in particle size in this range would not therefore be beneficial.

The theoretical work of both Flint and Howarth and Reay and Ratcliffe was supplemented by preliminary experimental verification, and in a later investigation (96) Reay and Ratcliffe examined the collection of glass spheres and polystyrene particles. A study of fundamental importance to the use of collision theory in flotation has been conducted by Anfruns and Kitchener (63, 97) for quartz particles of both spherical and angular shape. The collection rates of single bubbles rising through a dilute suspension of particles were measured and compared with calculated collision rates. For angular particles these rates were very similar to each other, indicating that every particle colliding with a bubble was collected, ie:

$$P_a\ P_e\ P_f = 1$$

using the notation of Tomlinson and Fleming. In the case of spherical particles the collection rate was only a fraction of the calculated collision rate, indicating that the sub-processes following collision were less efficient. This behaviour was explained by a consideration of the mechanisms of particle/bubble adhesion.

2.4.2.3 Probability of Post-Collision Phenomena

The mechanisms affecting the sub-processes which occur after a collision between a particle and a bubble, in particular adhesion, have been reviewed by Laskowski (87) and by Blake (88). The probability of adhesion was considered by Sutherland to be dependant on the induction time, Ψ, ie the time during which a particle following a grazing trajectory came close to the bubble surface. Blake has estimated this time to be in the order of 10^{-2} sec. The processes involved in ahesion of the particle to the surface of the bubble must take place during this time or the collision will not result in capture. These processes consist of the thinning of the film separating the particle and the interface of the bubble followed by its rupture and the regression of water from the hydrophobic surface of the particle. Rupture is facilitated by sharp projections on the surface of the particle, a fact Anfruns and Kitchener used to explain their observations. Regression of the water film once rupture has occurred takes place very rapidly under the influence of the unbalanced surface forces present. This regression will continue until an equilibrium has been established.

In a recent investigation Rubenshtein and Filippov (98) attempted to determine the dependence of P_a and P_e on various conditions, including the concentration of collector in the pulp. The resulting formula, postulating an exponential relationship between P_a P_e and collector concentration, was confirmed experimentally using coal slimes and a variety of collectors.

The return of previously floated particles from froth to pulp was modelled by Arbiter and Harris (61), who assumed that the froth layer could be treated as perfectly mixed and that the re-entry of particles to the pulp was proportional to their concentration in the froth. This model was extended by Harris and Rimmer (99) and confirmed experimentally by Harris, Jowett and Ghosh (100). Bushell (101) postulated a proportional relationship between the rate of entry of particles to the froth and their rate of return to the pulp,

resulting in a modified rate constant for the overall process. Rubenshtein and Filippov (102) suggested a generalised equation which extended the concepts of Arbiter and Harris to include terms for the velocities of air and water phases and for spacial position within the flotation cell. The particular boundary conditions chosen for a solution of this model were those pertaining to a tubular reactor, and the resulting equations were solved using a numerical method.

2.4.2.4 Free and Inhibited Flotation

An important qualification was made to the chemical kinetics analogy in 1965 by Tomlinson and Fleming (89), who argued that first-order removal behaviour would only apply to flotation pulps containing an excess of air bubbles. Should this not be the case, the available bubble surfaces would become completely filled with collected particles and the rate of removal would be independent of pulp concentration. This would result in removal behaviour analogous to a zero-order reaction (see equations (I) and (II)).

Pogorely (103) also studied particle saturation of the available bubble surface in flotation, and suggested a simple exponential model to describe the mechanism of the bubble loading process. This has recently received experimental confirmation by King, Hatton and Hulbert (104) who have provided photographic evidence of the progress of bubble loading.

2.4.2.5 Variations of the Rate Constant with Particle Properties

The early investigations of the applicability of the chemical kinetics analogy to flotation showed that rate equations, whatever their order, could only be applied to one species of particles in a cell. The first experiments carried out on the relationship between k and particle properties centred mainly on particle size, and the various investigations reported have produced a variety of relationships. The apparent prediction of Sutherland's equation would be a linear dependence of k on particle size. Gaudin, Schuhmann

and Schlechten (105) found that the rate constant for galena was independent of particle size between 1 and 4μm and linearly dependent above 4μm. Morris (64), using various copper ores, identified a critical size in the region of 50μm above which k decreased linearly with particle diameter and below which a logarithmic relationship existed. DeBruyn and Modi (106) found not only a change of value for the rate constant over a range of particle sizes, but also a variation in the order of reaction. Bull (107) investigated the flotation of coal and quartz and found a linear relationship to apply within fairly narrow limits.

As a result of his investigations, Morris (64) postulated that not all the material in the pulp of a flotation cell would be floatable. The influence of this phenomenon was investigated by Jowett and Safvi (108) and also by Bushell (101), who modified the conventional first-order equation to suit the hypothesis. Bushell's conclusion was that the rate constant in his modified equation was independent of the particle size.

The idea of floatable and non-floatable species was modified in the work of Tomlinson and Fleming (89) to a classification of species as easily floated or poorly floated. They found k to be proportional to the square of particle diameter for easily floated particles and linearly dependent for poorly floated particles.

From the above description it will be apparent that the relationship between flotation rate constant and particle size may take various forms. This is due to the influence of other particle proportions (eg shape and surface activity), which must be included for a full description of the system under consideration. Therefore the predictions of flotation rate constants from a measurement of particle properties alone becomes prohibitively complicated, and in practice laboratory flotation tests are required to establish realistic values for k.

2.4.2.6 Flotation Rate Distributions

The variations of k with particle properties makes it most unlikely that a single value for k will characterise a

heterogeneous pulp of the kind found in commercial flotation cells. In an attempt to overcome this difficulty, Pogorely (109) suggested that a distribution of rate constants might be used to provide a more comprehensive model. Such a distribution could be described by a frequency function M(k), where M(k) dk represents the fraction of the total mass floated with a flotation rate constant between the limits k and k + dk. Thus the M(k) curve was a bounded function containing unit area, ie:

$$\int_0^\infty M(k)\, dk = 1$$

Imaizumi and Inoue (110) developed a graphical method for deriving such distributions from experimental data obtained in a series of batch tests. This was followed by the suggestion of Loveday (111) that the distribution of flotation rate constants within a flotation pulp might realistically be represented by continuous mathematical functions such as the gamma function. This was developed for both batch and continuous operation and experimentally verified by Woodburn and Loveday (112). King (113) has described the modifications made to the model by these investigators and others, culminating in an improved distributed parameter model (114). Similar models have been suggested by other workers. Harris and Chakravatti (115) included the transfer of froth particles back into the pulp, which the model of King et al (114) did not. Ball, Kapur and Fuerstenau (116) initially utilised a gamma function in their treatment but in later work (117) found a cubic polynomial to be more suitable since a numerical solution could be obtained with the assistance of an analogue computer. Kapur and Mehrotra (118) utilised the model of Harris and Chakravarti and suggested a solution by Laplace Transform. Bartlet and Mular (119), Panou (15) and Panu and Ene (120) have all formulated models of a similar type and Ek (121) has described their use for the evaluation of industrial flotation circuits. All these models assume conditions of free flotation.

Despite the apparent comprehensiveness of distributed rate models, they have not been widely adopted in commercial practice. Jowett (122), in a recent critique, stated that

such models had been extended and modified to a point where it had become difficult to assign any physical meaning to their constituent parts. He argued that there was a danger that they might become little more than empirical models containing an unnecessarily large number of curve-fitting parameters, whose practical application would involve an inordinate amount of computation.

2.4.2.7 Kinetic Approach to Continuous Flotation Systems

It will be seen from previous sections that the determination of a realistic value for the rate constant, k, for a particular flotation process can become extremely involved. However, if a rate constant can be determined and a representative mixing model can be obtained, it should be possible to predict the performance of a particular continuously operated flotation system.

Jowett (123) demonstrated that the mixing regime in a conventional sub-aeration flotation cell could be adequately described by the complete mixing model. Niemi (124) extended this analysis to a bank of cells in series, with the important proviso that the flow path of the particles through the system did not always follow that of the liquid. Jowett and Ghosh (125) used chemical reactor theory in their economic evaluation of the flotation process and showed that the profit from a given size of cell increased with the number of separate stages. This conclusion was also drawn by Golanov (126), who suggested the insertion of partitions along the path of the pulp to increase segregation. Loveday (111) demonstrated that this was also applicable to the case of heterogeneous pulps. One attempt to provide a better degree of segregation in the flotation cell was the introduction of the flotation column (127, 128), in which the pulp was passed down a tall tubular vessel and treated with a counter-current flow of air bubbles from a diffuser. Much of the turbulence created by the conventional air dispersion systems was eliminated and the process was claimed to be more efficient due to the creation of a concentration gradient

along the length of the column. Boutin and Wheeler (129) described a series of successful pilot trials with a 0.7m diameter column 8.5m high, and reported most of the initial operational problems to have been solved. An analysis of the kinetics of flotation columns was described by Rice et al (62), who used the turbulent diffusion model described in equation (XIII) combined with an assumption of first-order removal. Similar treatments have been reported by Bogdanov et al (86) and Sastry and Fuerstenau (130).

2.4.2.8 Alternatives to the Probablistic Approach

Woodburn (83) has classified mathematical models for flotation into two general groups; heuristic and phenomenological. The former encompasses the probablistic/ kinetic method and involves the postulation of a plausible model in order to produce a parameter (ie the flotation rate constant) which it is hoped will provide some insight into the mechanisms of the process. A phenomenological model does not require a prior conception of the process and is based on the correlation of direct observations. Because of its dependence on measurable quantities the phenomenological approach is considered more suitable for on-line control than for pilot investigations of a fundamental nature.

The deficiencies of heuristic models in the practical design of flotation equipment have been described by Flint (91). His alternative, "mechanistic", approach (131) is essentially phenomenological. The flotation cell is segmented into three phases (pulp, bubbles and froth) and observed rates of recovery are related to the various rates of material transfer between phases. Similar concepts have been utilised by Kapur and Mehrotra (132). Both models have as yet only been applied to the steady-state condition.

2.4.3 Application of Flotation Kinetics to Wastewater Treatment

Schroeder (133) has suggested that chemical reactor theory might be used for the design and evaluation of certain wastewater treatment systems. This would appear to be especially attractive in the case of wastewater flotation

since the use of the theory has been firmly established for mineral flotation. However, its potential does not seem to have been appreciated by the majority of workers in the wastewater flotation field. Exceptions may be found, most notably the analysis of particle/bubble collision phenomena in the lower size ranges by Reay and Ratcliffe. This has been followed recently by experimental investigations of the flotation behaviour of fine particles by Collins and Jameson (134) and of emulsified oil droplets by Angelidou et al (135). The analysis contained in the work of Grieves has mostly been based on empirically derived power relationships (see Section 2.4). However, a kinetic approach was adopted in work published by Grieves et al during the period 1968-70 (136, 137, 138). The significance of this work will be examined in Section 2.4.3.2.

One reason for this apparent lack of interest in flotation kinetics might be that the majority of work in the field of wastewater flotation has been concerned with the effects on the process of chemical variables. Certainly the potential of the kinetic approach for the design of wastewater flotation units and for the optimisation of their operation does not appear to have been the subject of extensive investigation. The majority of the work described in this thesis has been devoted to such an investigation.

2.4.3.1 Particle Removal

Preliminary tests on the treatment of river water using a 1,000 l pilot plant (see Section 3.2) indicated that provided feed conditions were kept constant, a removal curve of similar shape to that shown in Figure 4 was obtained. This indicated that the removal process could be described by an analogy with chemical kinetics. In order to avoid the complications created by a heterogeneous influent and also to ensure reproducibility of testing, synthetic materials were used in this study to represent the solid and aqueous phases present in river waters. The choice of the components of the synthetic mixtures created is discussed in Section 3.3. The assumed equation for the removal of particles from a

batch operated cell took the form:

$$\frac{dc}{dt} = - k\ c^{\lambda} \qquad \text{(XIX)}$$

where: c = concentration of particles

k = rate constant for particle flotation

λ = order of reaction

Initial investigations indicated a very strong correlation to the first-order model, ie $\lambda = 1$. The effects of many design and operational parameters such as tank geometry, air rate, foam removal and surfactant concentration could therefore be conveniently assessed by the value of the rate constant. In addition, the operation of flotation cells in the continuous mode could be predicted by incorporating a suitable mixing model, and the effects of variations in flow rate and residence time could be determined.

2.4.3.2 Surfactant Removal

Whilst the majority of the design and operational parameters could be preset or accurately controlled during testing, the maintenance of constant surfactant concentrations in the flotation cell posed a more difficult problem. In the continuous flotation experiments carried out in preliminary tests an arbitrarily set constant surfactant feed was maintained to the unit in a manner similar to that employed by Grieves and Schwarz (24). It was assumed that at some stage during a test steady-state conditions would be reached and the surfactant concentration would then be constant. However, this method was subject to two main disadvantages. Firstly, Grieves and Schwarz could not find a correlation between the surfactant doses required for batch and continuous tests. This was to be expected since the addition took place in a single initial dose in the former case and in a steady continuous dose in the latter. The pulsed addition of surfactant during batch tests was carried out by Grieves and Bhattacharyya (137) but did little to improve the precision of the technique. The second disadvantage of an arbitrarily set constant feed was that even if a correlation between batch and continuous experiments was not required, conditions of constant surfactant concentration in the cell could be

guaranteed only when a steady-state had been reached. Results obtained before steady-state might not have been able to be linked to the same surfactant concentration.

A possible solution to the problems outlined above came with the realisation that the surfactant concentration in a cell might be predicted and thus controlled by an application of chemical reactor theory similar to that used for particle removal. It was postulated that the following relationship applied for a batch operated flotation cell:

$$\frac{ds}{dt} = - m_\lambda \, s^\lambda \qquad \text{(XX)}$$

where: s = surfactant concentration

m_λ = λ- th order rate constant

A survey of the relevant literature provided details of the flotation characteristics of surfactants, in particular those of the quaternary ammonium compounds used in the present study. Grieves and his collaborators had themselves found the rate of removal of quaternary ammonium salts to be proportional to concentration (136, 137, 138), ie a first-order process. This was confirmed by Berezyuk et al (139). Therefore equation (XX) could be made more explicit:

$$\frac{ds}{dt} = - m_1 \, s \qquad \text{(XXI)}$$

Equation (XXI) describes the loss of surfactant from the cell, from which the amount of additional surfactant needed to maintain a steady concentration can be calculated. If S mass units of surfactant per unit time are added to a batch operated cell of volume V, equation (XXI) becomes:

$$\frac{ds}{dt} = - m_1 \, s + \frac{S}{V} \qquad \text{(XXII)}$$

For the maintenance of constant surfactant conditions ds/dt should be equal to zero. Therefore for a constant surfactant concentration of magnitude s:

$$S = V \, m_1 \, s \qquad \text{(XXIII)}$$

Thus if the flotation rate constant for the surfactant is known, conditions of constant surfactant concentration can be maintained. In practice this was effected by the addition of an equivalent volume of surfactant concentrate at discrete time intervals.

A similar analysis may be applied to the case of a continuous cell, resulting in:

$$S = V m_1 s + vs \qquad \text{(XXIV)}$$

Where v represents the flowrate through the cell. In practice the required dose was administered via the influent stream. Equations (XXIII) and (XXIV) were modified during the experimental programme as additional information on the kinetics of surfactant removal was obtained. However, the method was found to give a basis for the control of surfactant conditions, and was instrumental in the aquisition of accurate data.

2.5 EXPERIMENTAL PROGRAMME

The purpose of this section is to indicate the general scope of the experimental programme; details of individual tests have been tabulated in Appendix 2.

2.5.1 Group P Experiments

This preliminary group of experiments was designed to test the applicability of the flotation process to the treatment of river water. A pilot plant provided by the collaborating establishment was used to evaluate the effects on continuous flotation of feed concentration, flow rate through the unit, and surfactant dose.

2.5.2 Group A Experiments

The main purpose of these experiments was to ascertain the suitability of the chemical kinetic analogy as a model for the design of a flotation process for a synthetic river water. After initial equipment calibrations (A1, A5), tests were carried out to characterise the mixing regimes prevalent in the experimental flotation cell (A2 - A4). A series of batch runs was then undertaken in order to obtain data on the particle removal rate constants (k) at a variety of air rates (A6 - A14). During some of these runs (A6, A8, A10, A12, A14) the surfactant concentration in the cell was set at an initial value of 25 mg l^{-1} and then allowed to vary over the period of the test. In this way values of the surfactant removal constant (m_1) could be determined. These values were only approximates since at this stage the appropriate

analytical techniques had not been fully developed. The runs were then repeated (A7, A9, A11, A13) and a constant surfactant concentration in the cell was ensured by the addition of an amount of surfactant concentrate calculated from equation (XXIII). The nominal value of this constant surfactant concentration was 25 mg l^{-1}. The remaining tests in Group A were continuous runs with air and water rates chosen so that the results of batch and continuous experiments could be compared. A constant surfactant concentration was maintained by the method described in Section 2.4.3.2.

Samples from one test were subjected to a detailed particle distribution analysis (A31).

During the Group A experiments a nominal surfactant concentration of 25 mg l^{-1} was adopted.

2.5.3 Group B Experiments

This group of experiments were mostly batch tests designed to evaluate the influence of surfactant concentration on particle removal. Improved methods for measuring the concentration of surfactant in a sample were used (B33, B34), and the kinetics of surfactant removal were examined in greater detail (B2 - B6). Batch tests at a variety of different air rates and surfactant concentrations were then carried out (B7 - B32).

The depth of the flotation pool was reduced for the Group B experiments and the effects of this on the prevailing mixing regime were determined (B1).

2.5.4 Group C Experiments

The experiments in this group comprised a number of batch and continuous runs in a flotation unit of different design to the single-stage reactor used for the tests in Groups A and B. A variety of mixing regimes could be created in the unit by the insertion of suitable baffles. The applicability of multi-stage mixing models was tested (C1 - C4), followed by a series of batch (C5 - C8) and continuous (C9 - C16) experiments.

2.5.5 Group D Experiments

These experiments were carried out in the single-stage flotation unit and were conducted for a variety of purposes.

A series of batch runs (D1 - D4, D20 - D23, D35) was undertaken to examine the effects of different pool depths on the rate constants for particle and surfactant removal. Another set of batch tests (D9, D6, D8 - D20, D24 - D28) was carried out to investigate further the relationship between particle removal and surfactant concentration, prompted by the findings of the Group B experiments.

Test D29 was a continuous run in which the flow rate to the unit was varied over a range of values and the effects on the performance of the flotation unit determined. The creation of a multi-stage type mixing regime in the single-stage unit was attempted in tests D36 and D37. Finally, the applicability of the simple kinetic equations to the flotation of non-synthetic, hetrogeneous suspensions was examined (D7, D30 - D34).

CHAPTER 3

APPARATUS AND EXPERIMENTAL TECHNIQUES

3.1 INTRODUCTION

Four main operations were involved in the experimental programme: preliminary tests to assess the viability of flotation as a wastewater treatment method; the choice of a suitable experimental system; the design and construction of equipment; and the development of analytical methods.

3.2 PRELIMINARY TESTS USING THE SIMON-HARTLEY PILOT PLANT

As a precursor to the main experimental programme, a series of tests were carried out to investigate the practicability of the dispersed air flotation process. A pilot plant was utilised which had been loaned by the collaborating establishment and installed at the Colwick Advanced Water Treatment Unit (Severn-Trent Water Authority).

Figure 6 shows the layout of the system used in these tests. Water was extracted from the River Trent using a submersible pump (A) and stored in a holding tank (B). It was then delivered to the unit at the required flow via a centrifugal pump (C) and a rotameter (D). The flotation plant consisted of a steel tank (E) of approximately 1,000 l capacity supplied with inlet and outlet weirs and a provision for foam removal. The tank was divided into two sections connected in series, the first being 600 l in volume and the second 400 l. Air was fed into the unit from an air compressor (F) via rotameters (G) and a manifold (H) to diffusers (J). These measured 175 mm in diameter and were of the porous stone type commonly used in activated sludge units. Flotation was initiated by feeding surfactant concentrate into the inlet weir chamber from a supply (K) using a peristaltic pump (L) controlled by a rotameter (M). The final effluent stream (N) was discharged to a soakaway.

The results of the preliminary tests are reported in Section 4.2 and discussed in Section 4.7.5. The general conclusion was that the process could produce effluents of sufficiently low turbidity to have potential as a treatment method. However, a more fundamental study would require a greater degree of control over the quality of the influent than could be afforded by the existing

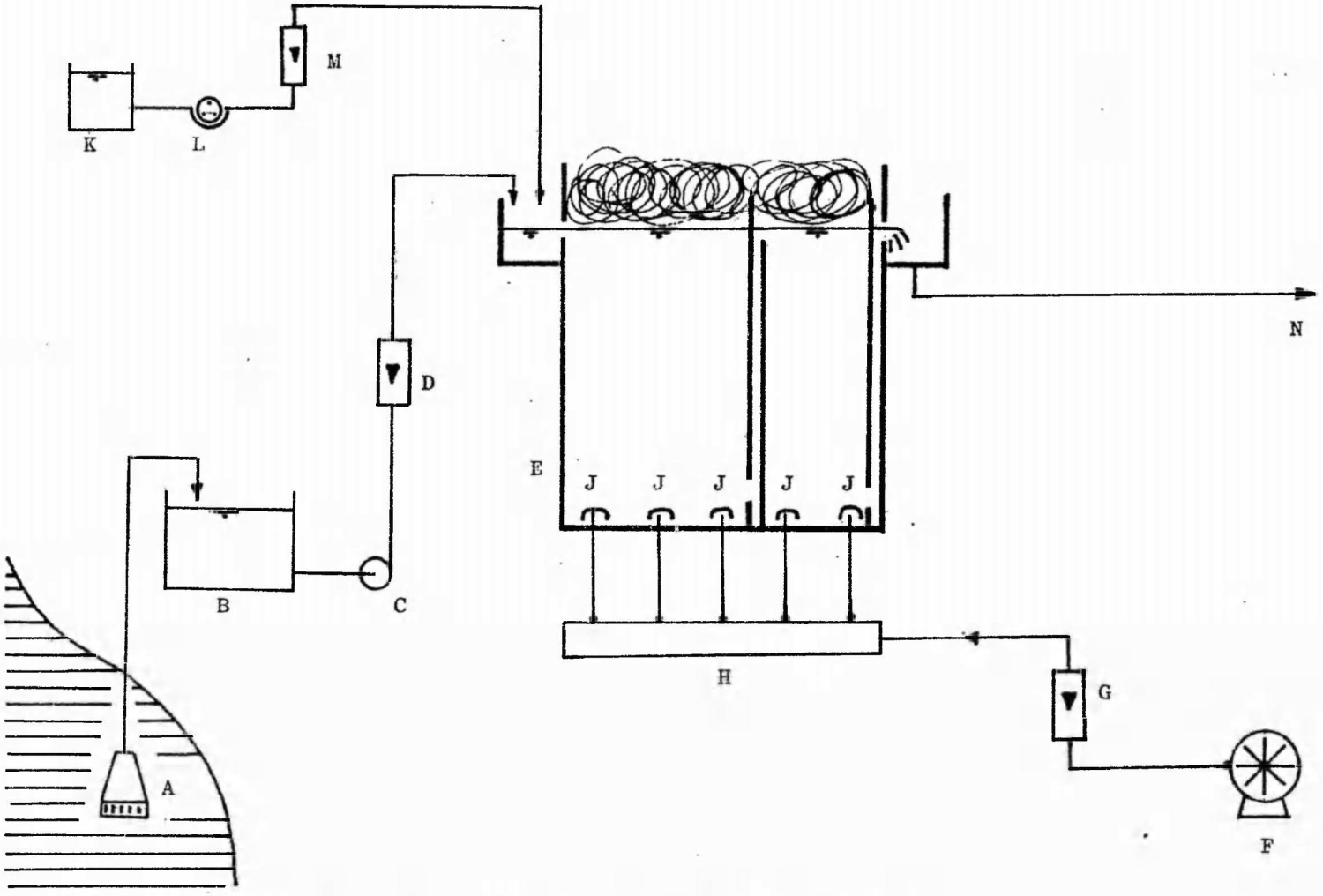


FIGURE 6: Experimental System used in Preliminary Tests

system. Consideration was therefore given to methods by which this could be achieved.

3.3 CONTROL OF INFLUENT CHARACTERISTICS

The preliminary tests had shown that variations in the character and concentration of the solids suspended in the influent were inevitable when a naturally occurring river water was used. An alternative supply was required if complete control of the process was to be provided. Such a supply would have to be produced by the combination of synthetic constituents, but would preferably retain the same general characteristics as a natural river water.

3.3.1 Solid Phase

A number of alternative materials were considered to represent the solid phase of a river water. Workers in the mineral flotation field (62, 63) had used quartz as a general representation of the particles in a flotation cell. Suspensions of accurate concentration could be produced by the addition of known masses of quartz powder to the aqueous medium. A degree of particle size control could be obtained by sieving. The disadvantage of using such material in this study was that the range of particle sizes available would have been representative only of the coarser fractions of a river water such as silts and sands rather than the colloidal clay fractions. It was the clay sized particles which were most suited to treatment by flotation since they were not readily removable by sedimentation.

The use of synthetic latices was considered since they were possible to produce at a size similar to that of naturally occurring river suspensions. These were used by Collins and Jameson (134). However, the characteristics of the surface of such particles would have borne little similarity to the surfaces of particles found in river waters and this possibility was considered to be unsatisfactory.

The eventual choice of synthetic particles represented a compromise between the conflicting needs for experimental control and for similarity to the practical problem. It was decided that some form of clay-like mineral should be

used which could be obtained as a dry powder and suspended in the aqueous medium immediately before use. In the final stages of the experimental programme such material was obtained from a sample of a natural mudbank by a process of drying and sieving. However, for most of the tests described in this thesis one further characteristic was required of the test material which could not be provided by such a procedure. This requirement was that a single rate constant could be applied with reasonable accuracy to the flotation of the material for any given set of experimental conditions. Morris (64) among others had demonstrated the marked effect on the rate constant of variations in particle diameter, so that this stipulation implied that the test material should be as near to mono-sized as possible. Such a characteristic was found to be difficult to attain for materials in the clay size range. However, consultation with a major supplier of clays to the ceramic and paper-making industries (65) revealed that a refined kaolinite was available which would adequately fulfil the requirement described above. This material was coded RLO 1724; it had been prepared by repeated gravity separations of the larger particle fractions found in a china clay slurry. This purified concentrate had then been dried and lightly ground to break up loose agglomerations. This procedure resulted in a particle size distribution of relatively narrow range (see Figure 25a). Accurate concentrations of such material could be obtained by the suspension of a weighed portion in the aqueous phase.

3.3.2 Aqueous Phase

The primary requirement for the aqueous phase was that its characteristics should not vary significantly over the period of the research. The small-scale tests of previous workers (22 to 25) had been conducted using distilled water. However, this was not considered practicable for experiments undertaken at the scale of the present study, and consequently tap water was used. The conductivity of

the tap water available in the laboratory was regularly checked and found to be of consistent quality. Its use as the aqueous phase in this research was therefore considered to be justified.

3.4 CHOICE OF SURFACTANT

The cationic surfactants used for the foam flotation of river suspensions in previous research work (see Section 1.4) had been mostly of the quaternary ammonium type. In the preliminary tests described in Section 3.2 a commercially available blend of a number of such compounds had been used. This was ARQUAD T50 (Armour-Hess) and contained 50% active quaternary ammonium chlorides combined with a number of other substances, predominant among which was a propanol frother (66). The disadvantage of using this particular reagent for experimental investigations was that the frother tended to evaporate while the surfactant was being weighed out, and solutions of accurate concentration were consequently difficult to prepare. This problem was not encountered when laboratory grade surfactants were used since volatile frothing agents were not included in their composition, and they were preferred for this reason. The compound chosen for use throughout the remainder of this research was cetyltrimethylammonium bromide (CTAB) which was available in powder form. Solutions of a particular concentration could be accurately prepared by dissolving a weighed mass of CTAB in a known volume of water.

3.5 FLOTATION UNITS

Having established a model system to represent the phases in a naturally occurring river water and having chosen a suitable surfactant, two flotation units were designed which would enable the objectives described in Section 2.5 to be achieved. The first unit was designed as a single-stage reactor so that the effects of the various process parameters could be studied under relatively simple mixing conditions. This apparatus has been referred to throughout this thesis as the flotation column since its principal

feature was a relatively large pool depth combined with a small plan area, resulting in a tall, narrow structure. In contrast the flotation channel had a shallower pool but an increased plan area. The channel was designed so that a number of different mixing regimes could be created and their effects on flotation efficiency examined.

3.5.1 Flotation Column

The design of the flotation column reflected the need for a flexible unit which could be run under a wide variety of experimental conditions.

Figure 7 shows the plant layout. The flotation column (A) was a tall watertight tank with facilities for the supply of air and surfactant and with provision for the passage through the unit of the process stream. A metered air supply was provided, originally from bottles of compressed air (B) with pressure control by a two-stage regulator (C). In the later stages of the experimental programme the air bottles were replaced by an air compressor (Q) with pressure regulation by means of a manostat (E). In all cases the air flow was measured by a rotameter (D). The compressed air stream was fed to a diffuser (F), resulting in a flow of bubbles in the flotation pool. The diffuser was a 175 mm porous dome identical to those used in the preliminary tests (see Section 3.2).

When continuous operation of the unit was required, influent was fed to the column from a stirred holding tank (G) via a centrifugal pump (H) and a rotameter (J). The water level in the column was maintained by adjustment of a valve (K) which matched influent and effluent flow rates. The effluent from the column was discharged to a drain (L); samples of this effluent could be taken at point (M) when required.

Batch operation of the column was achieved by the closure of valves (K) and (N) and the opening of valve (P). Re-circulation of the liquid in the column then took place and samples could again be extracted at (M).

In order to maintain constant surfactant concentrations in

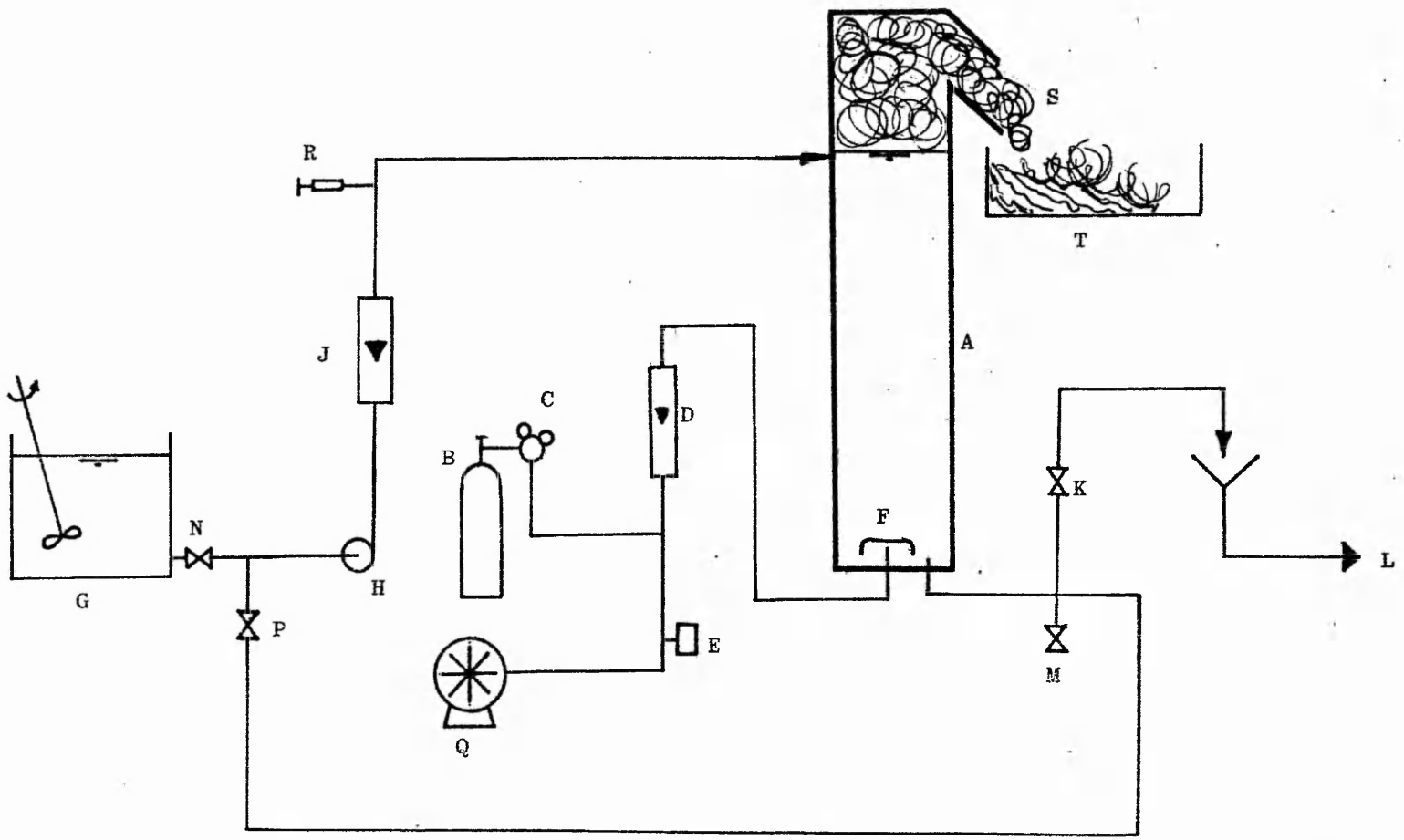


FIGURE 7: Experimental System used with the Flotation Column

the column the method outlined in Section 2.4.3.2 was adopted. Forbatch operation this required the addition of small volumes of surfactant to the flotation pool, and this was facilitated by injection at point (R). The dose of concentrate was then delivered to the pool by the action of the recirculating liquid stream. Surfactant concentration during continuous operation was controlled by adjustment of the concentration of the influent stored in the holding tank (G).

The foam created by the flotation process (S) was extruded through an opening at the top of the column and allowed to collapse into a tank (T).

The constructional details of the column are shown in Figures 8 and 9. The unit was fabricated from "Wisoform" resin impregnated laminate with a perspex front panel for observation of the pool. This panel was bolted to steel support angle fixed to the sides of the column, and a rubber gasket was sandwiched between perspex and steel to produce a watertight seal. The internal joints of the column were coated with waterproof paint for further protection against leakage.

A false floor was provided in order that the depth of the flotation pool could be varied without altering the distance from the top water level to the foam outlet. This ensured that the distance available in the column for drainage of the foam was the same for all tests and therefore eliminated this parameter as a variable of the process. The false floor was supported on a section of large diameter plastic pipe, the length of which could be varied to provide a range of pool depths. For convenience the air diffuser was fixed to this floor, and was surrounded by a concentric perforated pipe which acted as an effluent outlet. Influent was fed into the unit via a central pipe which protruded approximately 50 mm below top water level.

The flotation column was supported by a frame fabricated from welded steel hollow section. A sketch of this arrangement is shown in Figure 9b.

In plan the column floor measured 316 x 316 mm, giving an

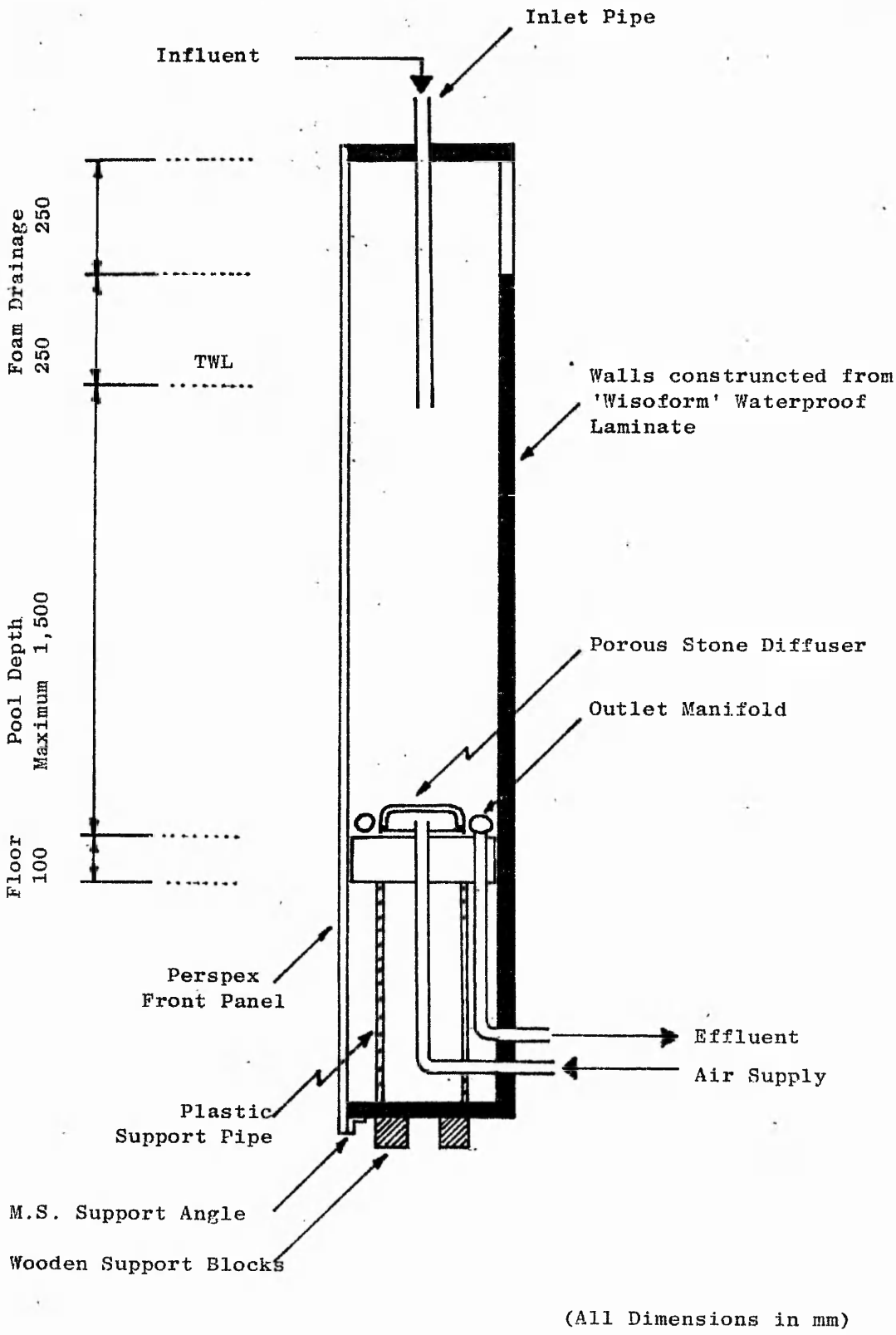
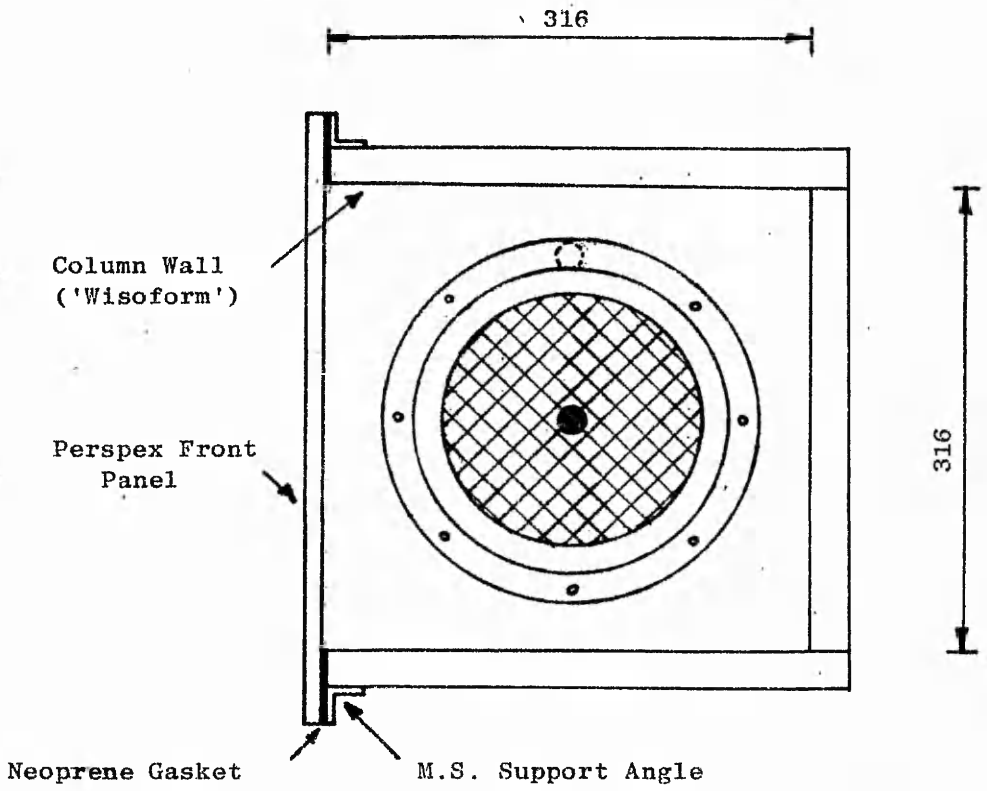
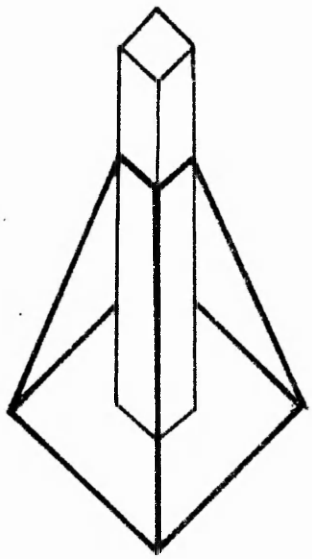


FIGURE 8: Constructional Details of Flotation Column (I)



(a)



Support Frame
Fabricated from Welded
M.S. Hollow Section

(b)

(All Dimensions in mm)

FIGURE 9: Constructional Details of Flotation Column (II)

area of approximately 0.1 m^2. Thus every 10 mm of column height was equivalent to a volume of 1 l, and since the maximum available pool depth was 1,500 mm, a maximum column volume of 150 l could be achieved.

The design of the flotation column provided sufficient flexibility for the major process parameters to be varied over a relatively wide range. The ranges available for specific parameters are given below:

Air Rate:	5 to 25 l min^{-1}
Water Rate:	2 to 8 l min^{-1}
Pool Depth:	500 to 1,500 mm
Column Volume:	50 to 150 l

Plates 1 and 2 show general views of the flotation column.

3.5.2 Flotation Channel

The main purpose of the channel flotation unit was to provide a vessel in which flotation could be studied under a variety of mixing conditions. Figure 10a shows the basic dimensions of the unit designed to provide this facility, which had a fixed pool depth of 500 mm and a plan area equivalent to six flotation columns. The arrangement chosen was to make the channel width identical to that of the column, ie 316 mm, and the length of the channel equal to six column widths, ie 1,897 mm. Six air diffusers were provided at spacings of 316 mm. By insertion of suitable baffles this unit could be operated either as a single-stage or multi-stage reactor (see Figure 10b), possible combinations being 1, 2, 3 or 6 stages. The foam drainage conditions were designed to be identical to those provided in the column unit.

The layout of the flotation channel and its ancilliary equipment is shown in Figure 11. The arrangements for the passage of influent and effluent were similar to those used for the column, comprising a stirred holding tank (G), centrifugal pump (H), rotameter (J), and adjustable outlet drain (K and L). Batch operation was provided by the closure of valves (K) and (N) and the opening of valve (P). A sample of the final effluent could be obtained from

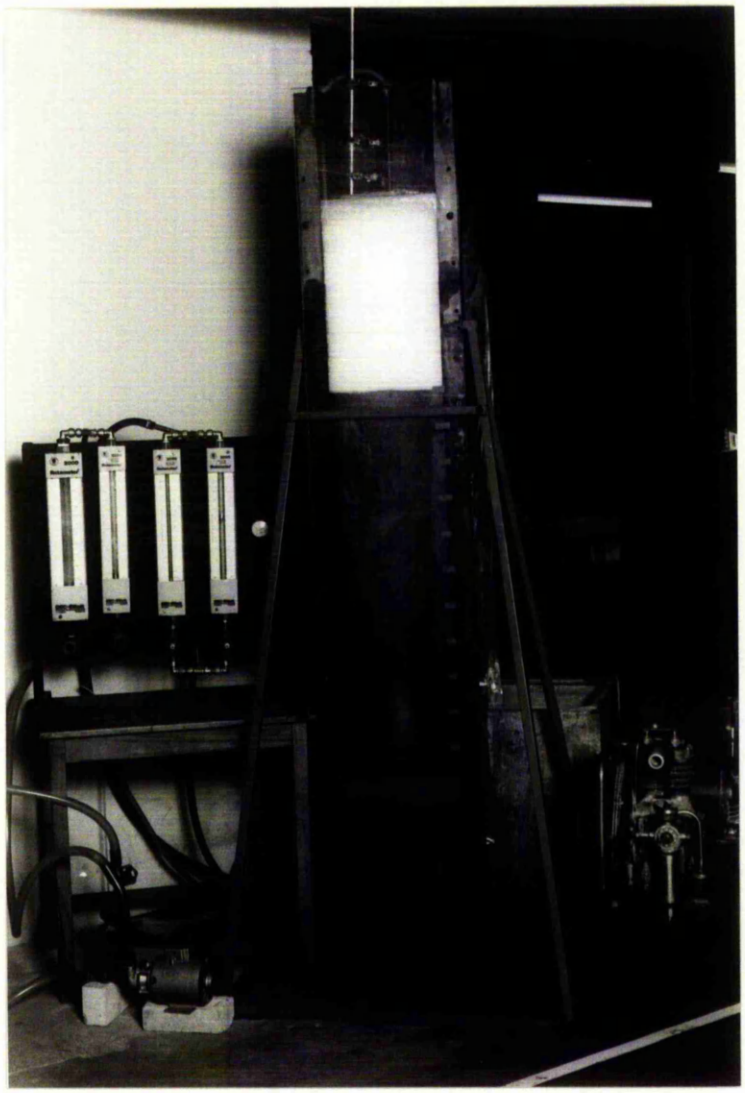


PLATE 1: Flotation Column (Front View)

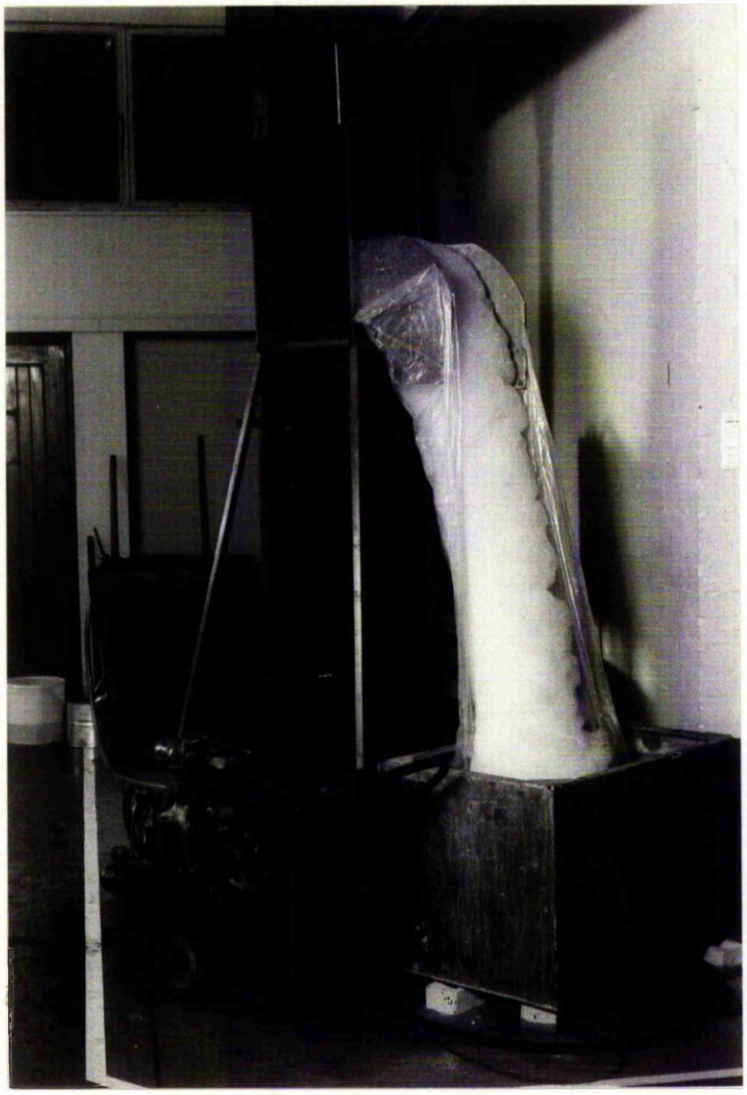
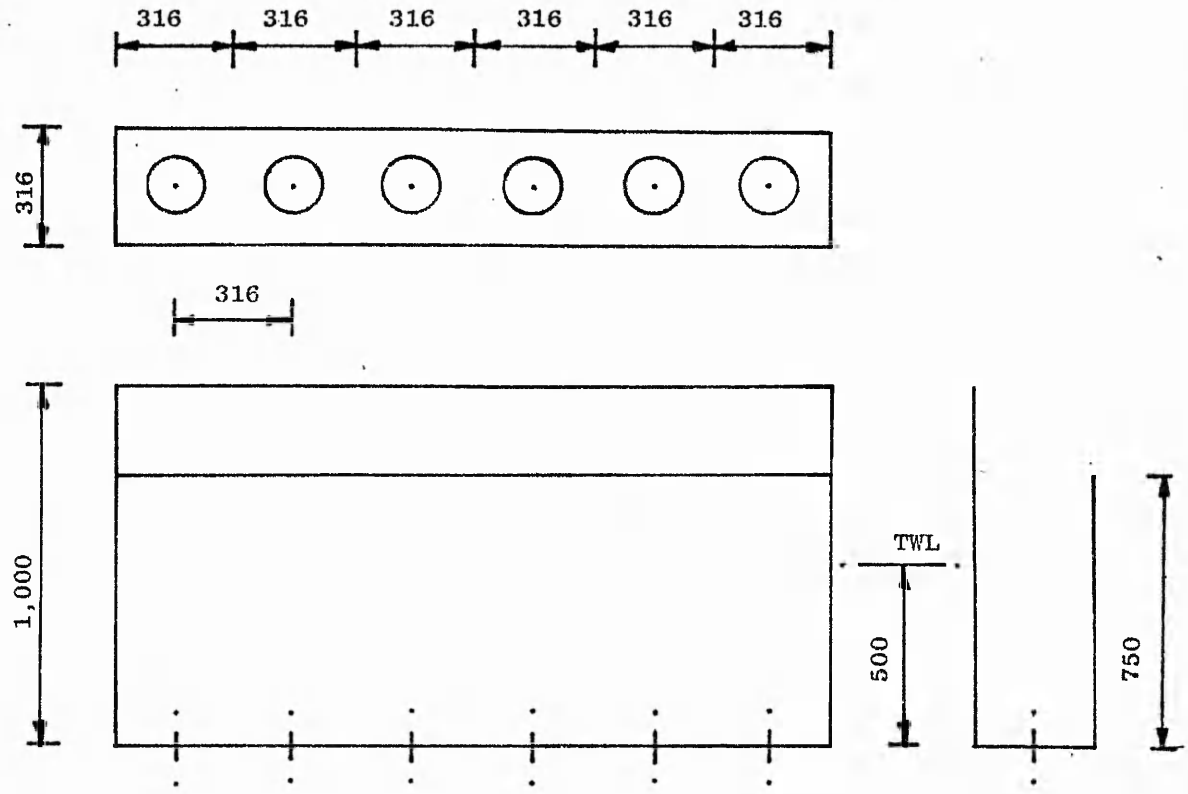


PLATE 2: Flotation Column (Rear View)



a. Basic Dimensions (All Dimensions in mm)

b. Possible Baffle Combinations

1 - Stage

2 - Stage

3 - Stage

6 - Stage

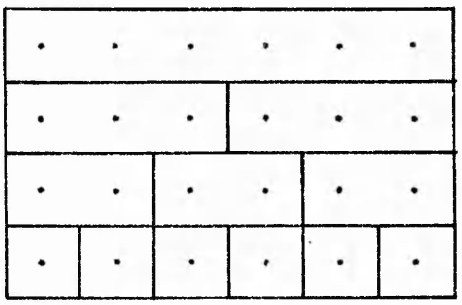


FIGURE 10: Design of Flotation Channel

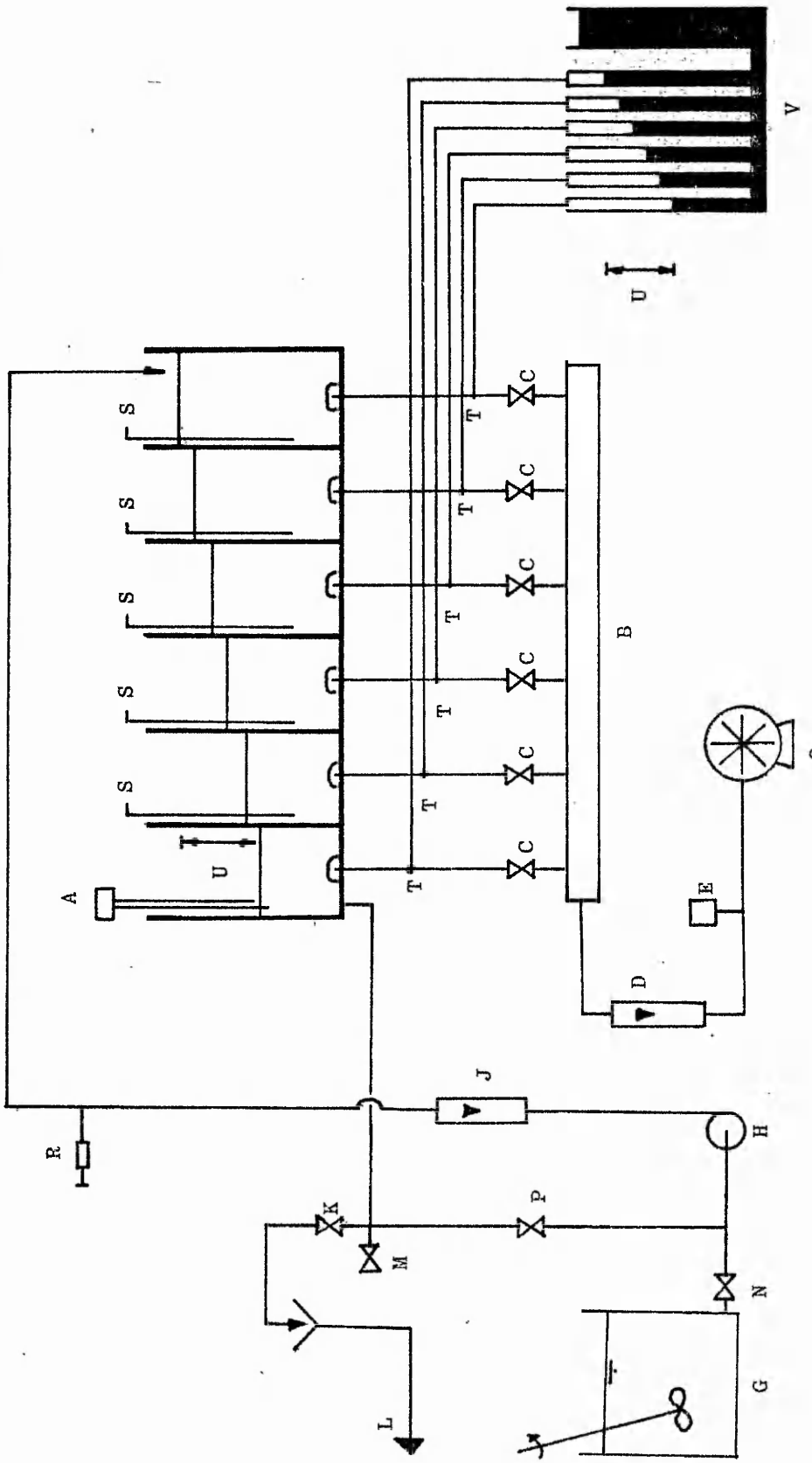


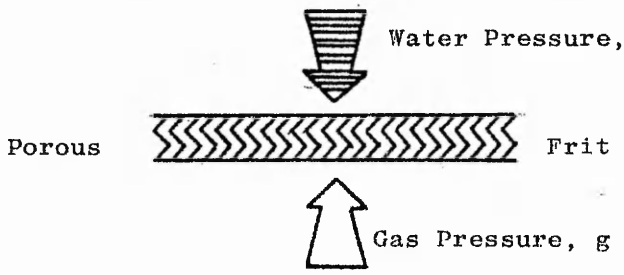
FIGURE 11: Experimental System used with the Flotation Channel

point (M), and samples of the contents of the other stages in the channel were extracted using sampling tubes (S). An injection point (R) facilitated the addition of surfactant concentrate to the pool during batch tests. An electronic depth indicator (A) assisted in the maintenance of a correct water level in the unit since the channel did not have transparent sides and the top surface of the liquid pool was obscured during flotation by the foam resulting from the process.

The air supply to the channel consisted of the same combination of compressor (Q), manostat (E) and rotameter (D) used for the flotation column, but some provision had to be made for splitting this air flow into six equal parts. A simple manifold was found to give a sufficiently accurate division of flows when the unit was operated as a single-stage reactor. However, when baffles were inserted for multi-stage operation, head losses occurred from one section to another resulting in slightly different pool depths in each stage. This caused differences in pressure due to the variation in water head above individual diffusers. The situation is shown in Figure 12.

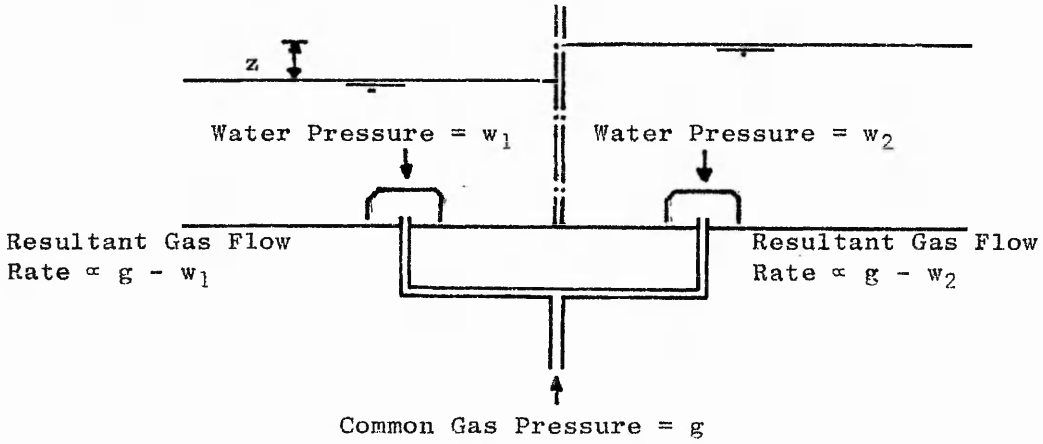
The operation of porous frit type air diffusers depends on a difference in pressure across the frit (see Figure 12a), ie: Pressure difference = g - w

where g and w are the air and water pressures respectively. If a flow of air is to take place then the quantity (g - w) must be positive. Differences in the value of w for each diffuser (see Figure 12b) cause variations in the value of (g - w), and thus differences in the air flow rate for each diffuser. However, if g can be adjusted individually for each diffuser so that the value of (g - w) is constant, then the air flow rate through each diffuser will be equal. This is demonstrated in Figure 12c. If the difference in water pressure between the two compartments is z mm of water, then equal air flows will result if the difference in gas pressure in each supply line (as measured by a water manometer) is also z mm of water.

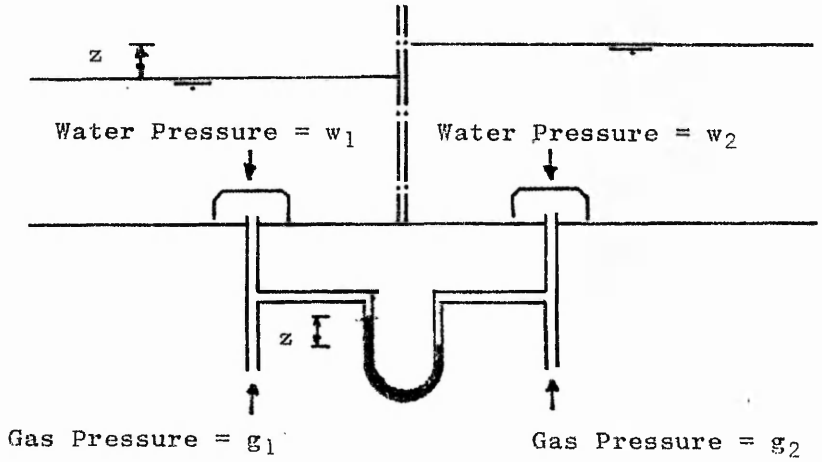


Resultant Gas Flow Rate $\propto$ (g - w)

a. Assumed Operation of Porous Frit Type Air Diffuser



b. Unequal Gas Flow Rates with Common Gas Pressure



Resultant Gas Flow $\propto$ $(g_1 - w_1) = (g_2 - w_2) = z$

c. Equal Gas Flow Rate with Individually Adjusted Gas Pressures

FIGURE 12: Equalisation of Gas Flow through Diffusers

Figure 11 shows how this concept was utilised in the operation of the flotation channel. The air flow from the compressor was divided into approximately equal flows by the manifold (B). Accurate equalisation was effected by the use of a globe valve (C) and a manometer tapping (T) inserted in each supply line. In Figure 11 the head loss between initial and final stages in the unit (U) is reflected on the manometer bank (V) by adjustment of the appropriate globe valves. Such a procedure resulted in an equal air flow through each diffuser, and similar adjustments were made for every other section of the unit. The air flow equalisation apparatus is also shown in Plate 3. The construction of the channel is detailed in Figure 13. The unit was fabricated from 20 swg sheet steel with welded joints. This structure was supported upon a wooden base which raised it sufficiently high for the air supply lines and effluent outlet to be connected. A general view of the channel is shown in Plate 4.

The steel tank was found to be insufficiently rigid for it to remain undeformed when filled with water. It was therefore clamped between two supporting walls made from standard formwork sections.

The design of the baffles which were to provide a variety of mixing regimes in the unit posed a number of problems. Previous experience had shown that the elimination of backmixing between two highly turbulent regions was only possible if the area allowed for the passage of water between them was kept to a minimum. Leakage around the sides of a baffle had been found to result in a considerable amount of backmixing and inefficient segregation. Therefore a primary requirement for any design was that the seal between the baffle and the sides of the tank should be watertight. However, the experimental programme made it desirable that baffles should also be easy to remove or insert. The obvious solution of welding steel baffles to the sides of the tank could not therefore be adopted. Figure 14 and Plate 5 show the eventual choice of baffle design, which provided a satisfactory solution to these requirements. The basic partition was made from marine

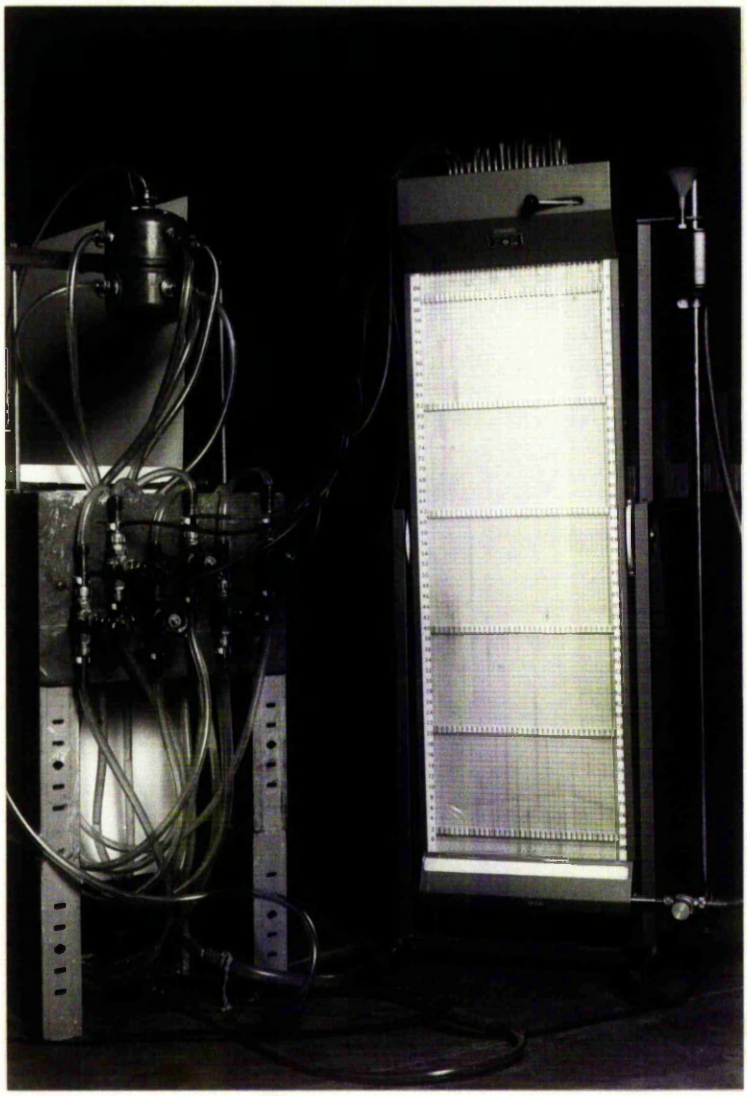


PLATE 3: Apparatus for Air Equalisation in Flotation Channel

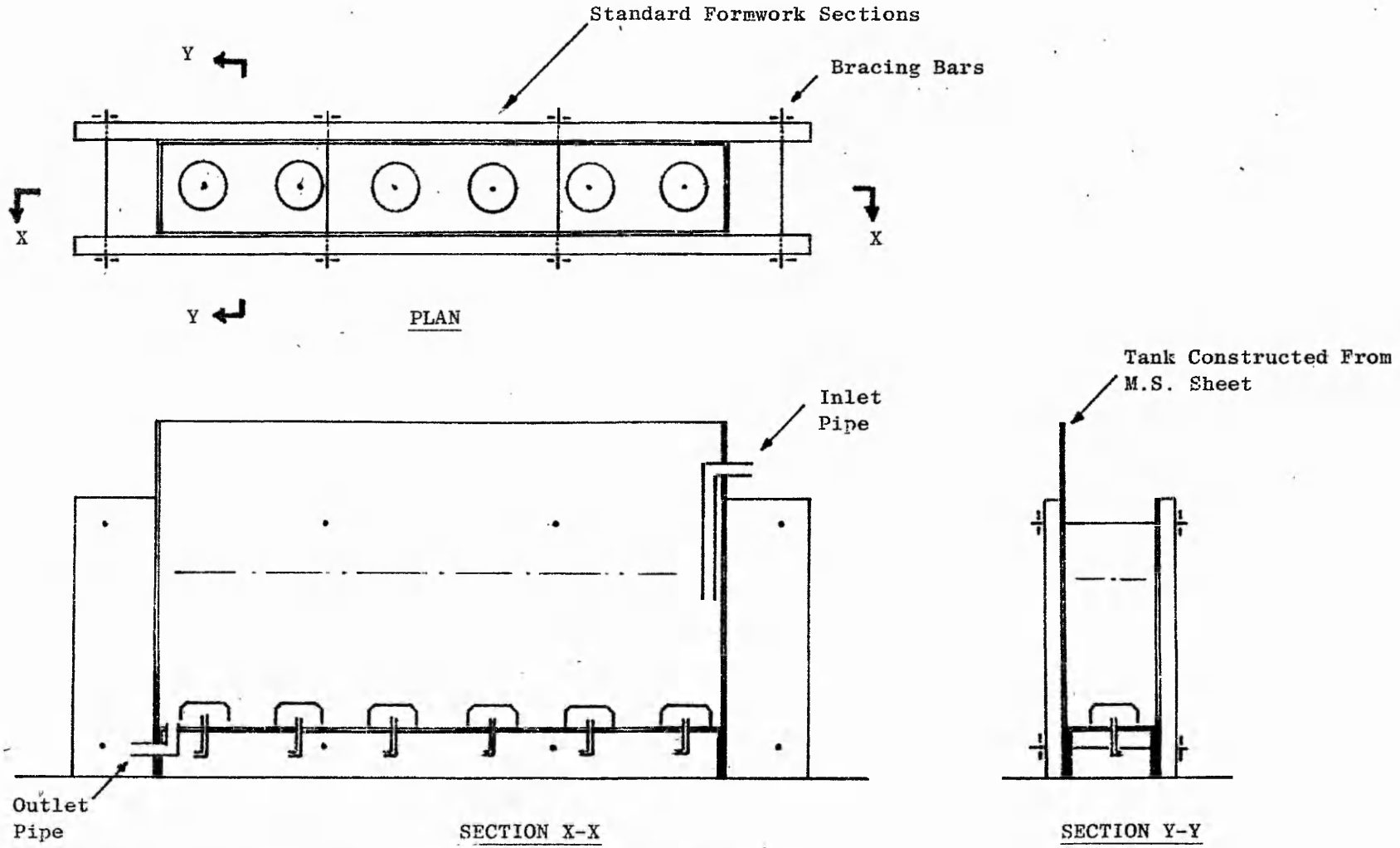


FIGURE 13: Constructional Details of Flotation Channel

PLATE 4: General View of Flotation Channel

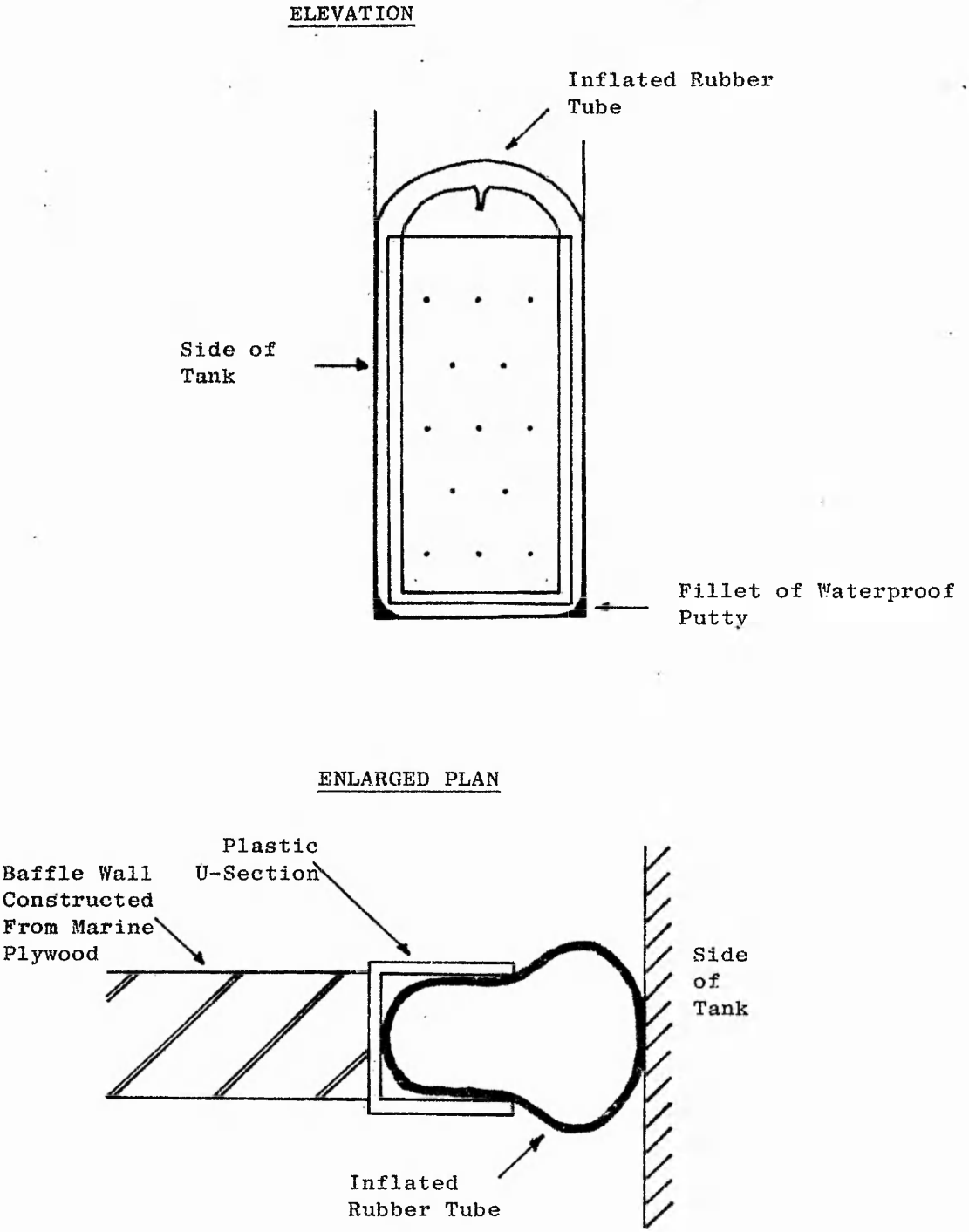


FIGURE 14: Baffle Design

PLATE 5: Baffle Plate for Flotation Channel

plywood drilled with a small number of holes for the passage of liquid. The gaps between the baffle and the sides of the tank were sealed by a rubber tube which could be inflated until they were completely filled. Slippage between the inflated tube and the baffle wall was prevented by a plastic U-section fixed to the edge of the baffle. This system provided a watertight seal except for two small triangular spaces at the bottom edges of the tank. These spaces were filled with fillets of waterproof putty. The main purpose of the experiments using the channel unit was the study of the effects of various mixing regimes. However, other process parameters could also be varied, and the extent of possible variations is listed below:

Air Rate: 30 to 50 l min^{-1}

Water Rate: 2 to 12 l min^{-1}

3.6 EXPERIMENTAL PROCEDURE

The details of the proposed research programme have been given in Section 2.5; it will be seen that a large number of flotation tests were planned using column and channel units in either batch or continuous modes. The subsections which follow outline the basic experimental procedure employed. Reference is made to the process flow diagrams (Figures 7 and 11).

3.6.1 Batch Flotation Tests

Before the start of a test the unit was partially filled with tapwater, and clay and surfactant concentrates were added to create the initial conditions of the test. Valves (K) and (N) were closed and valve (P) was opened, resulting in recirculation of the liquid pool. This was continued for a period of 30 minutes to achieve an absorption equilibrium between the surfactant and the clay.

A batch test was initiated by starting the air supply to the unit, whereupon flotation began. In the event of conditions of constant surfactant concentration being desired, surfactant concentrate was injected into the recycle stream at predetermined time intervals. Samples were taken when required and analysed for suspended solids and surfactant concentration.

The foam generated from the tests was allowed to collapse in the holding tank provided. Where necessary this collapse was hastened mechanically.
Batch tests were generally run until an approximately 90% turbidity drop was recorded, after which the unit was drained and cleaned.

3.6.2 Continuous Flotation Tests

The initial preparations for continuous flotation tests were similar to those for batch testing. Recirculation of the liquid pool was carried out for a preliminary period of 30 minutes and the contents of the holding tank (G) were stirred for the same period.
Continuous testing was commenced by closing valve (P), opening valves (K) and (N) and turning on the air supply to the unit. In the case of the flotation channel an initial adjustment to equalise air flows was also necessary. During continuous tests the water level in the unit being used was monitored (either visually or by the use of indicator (A)) and adjusted using valve (K).
Conditions of constant surfactant concentration were maintained by the initial adjustment of the concentration of the influent liquor in the holding tank (see Section 2.4.3.2). In one test (Test D29) the injection point (R) was also employed.
Samples of the effluent stream were taken at point (M), with additional sampling via extraction tubes (S) when the channel unit was being run on a multi-stage basis.
Tests were usually continued until an approximately steady-state situation was reached. This was indicated by three consecutive samples having the same suspended solids concentrations.

3.7 ANALYTICAL TECHNIQUES

It will be seen from Section 2.5 that methods were required for the determination of three main parameters. In order to assess the efficiency of the flotation process it was necessary to measure the concentration of suspended solids in the influent and effluent streams. A means of analysing

samples for their surfactant concentration was desirable so that accurate process control could be achieved. Finally, the determination of the mixing characteristics of the flotation units was required in order to compare experimental results with those predicted from the relevant theoretical models.

3.7.1 Measurement of Suspended Solids Concentration

The experimental programme involved the analysis of a large number of samples for suspended solids, and a method was needed which was both rapid and accurate. Three possibilities were considered; the standard method, the measurement of turbidity, and the use of the Coulter Counter.

3.7.1.1 Standard method

A detailed description of this method may be found in the standard texts on water analysis (67). A measured volume is filtered through a pre-dried and pre-weighed filter paper. The paper is then dried and weighed again, the suspended solids concentration being given by the difference between final and initial weights divided by the volume of sample.

The standard method was not found to be compatible with the practical requirements of the experimental programme for three main reasons. Firstly, the amount of time needed for analysis, even if vacuum filtration equipment were to be employed, was considered to be prohibitive in view of the large number of samples involved. Secondly, the results of such a measurement would not have been available until some time after an experiment had finished, and immediate process control would not therefore have been available. Finally, the extraction from the flotation cell of a number of samples of the volume required for accurate analysis (approximately 250 ml) would have significantly depleted the cell volume and could have led to experimental errors.

3.7.1.2 Turbidity Measurements

The turbidity of a liquid is an optical characteristic which gives a measure of the apparent loss of energy of a

beam of light as it passes through the liquid. McCluney (68) has attributed this energy loss to two fundamental processes; absorption and scattering. Absorption is the most significant factor when considering the radiometry of coloured solutions with little suspended material, and represents a transformation from light energy at a particular wavelength to light energy at a different wavelength or to some other form of energy altogether (eg heat or chemical change). The optical characteristics of suspensions of solid material in liquids are due mainly to light scattering, as the initially collimated beam of light undergoes successive reflections from the surfaces of the suspended particles. The magnitude of the energy loss caused by scattering is dependant, among other factors, on the concentration of particles suspended in the liquid. Turbidity can therefore be used as an indication of suspended solids concentration.

Instruments which measure absorption and scattering of light by liquids are known generally as turbidimeters, although a more precise term for an instrument which measures the latter phenomenon is a nephelometer. Turbidimeters have found wide acceptance throughout the field of water analysis since they are simple to operate and allow rapid determinations to be made. However, as the conclusions of a recent symposium on turbidity have shown (69), the exact significance of the parameter is often not fully understood. The relationship between turbidity and suspended solids concentration is unique for any particular set of conditions, and a turbidity reading may only be used for precise interpretation if all properties, other than solids concentration, remain constant.

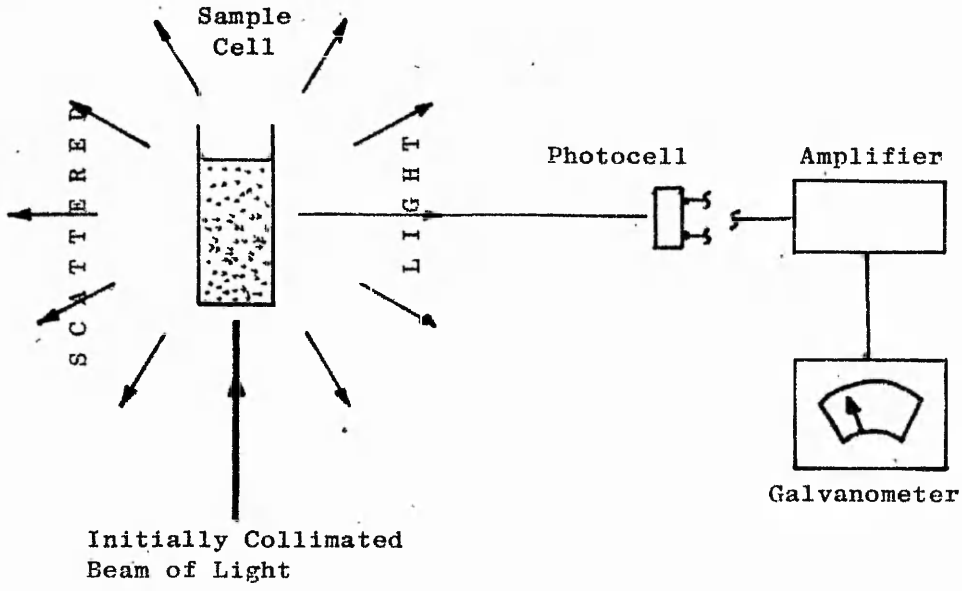
The use of turbidimetric methods, particularly nephelometry, in the present study appeared most desirable since large numbers of samples could be analysed rapidly, and the volume of sample required for each analysis was small. In addition, the use of a synthetic effluent of the type described in Section 3.3 avoided most of the restrictions usually placed on the correlation of turbidity readings

directly with suspended solids concentrations. This was because an aqueous phase of consistent characteristics was used and also because the suspended solid phase employed was nearly monosized and of constant composition. Thus it was considered that the three main factors causing variations in the relationship between turbidity and suspended solids concentration (liquid refractive index, particle size distribution and reflective properties of the particles) had been standardised for this experimental programme, and that turbidity could be used as an accurate indication of suspended solids concentration. Experience throughout the test programme confirmed this as a realistic assessment. The turbidimeter used in all the tests described in this thesis was the Hach 2100A; a direct-reading nephelometer capable of accurate determinations over a wide range of turbidities. The principle of its operation is shown in Figure 15a. A collimated beam of light is shone through a glass cell containing the sample and is scattered in all directions by the suspended particles present in the sample. The light scattered at right angles to the original path of the beam is allowed to fall on to a photocell, causing a flow of current which is amplified and displayed on a galvanometer. The instrument is calibrated against standard solutions to provide direct turbidity readings. These standards consist of suspensions of Formazin in distilled water, and the turbidity readings from the instrument are expressed in Formazin Turbidity Units (FTU).

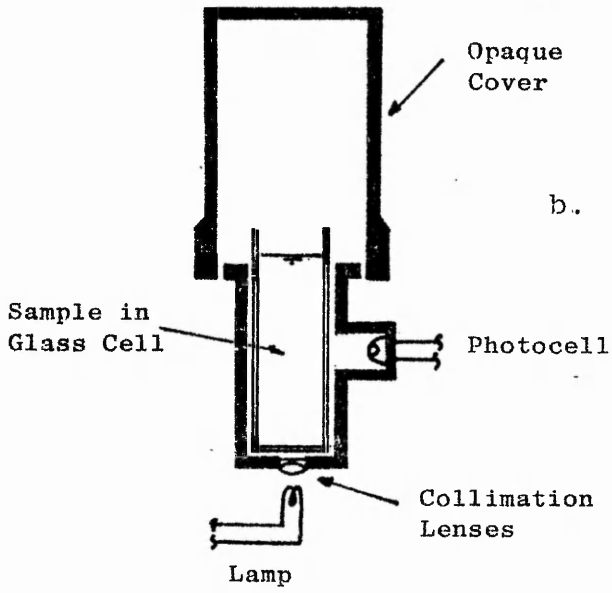
Figure 15b shows details of the illumination chamber of the instrument, which is made from non-reflective plastic. The glass sample cell, which contains 25 ml, is placed in this chamber and covered to eliminate stray light. A turbidity reading may then be obtained.

3.7.1.3 Analysis by Coulter Counter

The Coulter Counter is an instrument with a wide range of applications, including the field of water and wastewater analysis. It enables a size distribution of the particles



a. Principle of Operation



b. Details of Cell

FIGURE 15: Hach 2100A Turbidimeter

in a liquid to be obtained.

Figure 16 illustrates the principal components of the instrument. The sample to be analysed is diluted with an electrolyte (eg sodium chloride solution) and a glass tube, known as the orifice tube, is dipped into the resultant suspension. This tube contains a minute orifice through which a small portion of the suspension is drawn by the action of a mercury column. A platinum electrode is immersed in the liquid on either side of the orifice, and as individual particles move through the orifice the resistance between the electrodes alters momentarily. This produces a voltage pulse of short duration having a magnitude proportional to the particle size. The series of pulses resulting from the passage through the orifice of a number of particles is electronically scaled and counted. This may be transformed into a particle size distribution by a simple calculation. If the average density of the particles and the original dilution of sample in electrolyte are known, this distribution may be integrated to give a value for the suspended solids concentration.

It will be seen from the above description that a Coulter Counter analysis will provide considerably more information about a sample than either of the two methods described in previous sections. However, its use in the research programme was limited by several practical considerations. Firstly, measurement with the mannually-operated model available for this study was hampered by the relatively large amount of time required for a full analysis. It was also found that addition to the samples of strongly electrolytic solutions promoted flocculation of the colloidal clay particles, resulting in erratic and unreliable readings. This latter consideration has been noted by other workers attempting to obtain size distributions of river water suspensions (70). Attempts to reduce this effect by dilution of the electrolytes provided decreased the accuracy of the instrument at low particle thresholds, resulting in incomplete distributions.

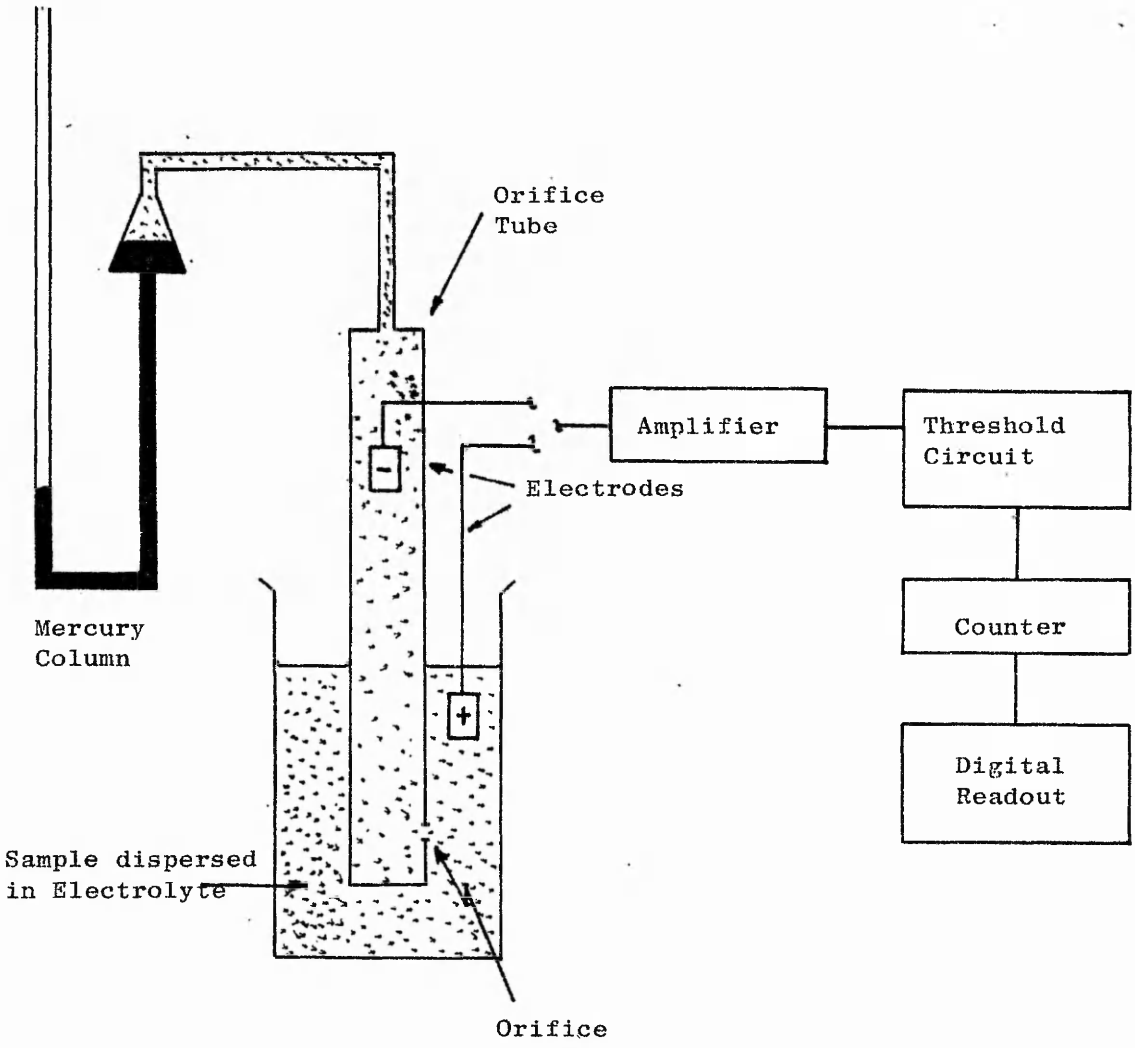


FIGURE 16: Principal Components of the Coulter Counter

The effects described above precluded the use of the Coulter Counter for most of the experimental programme. However, an automated version of the instrument was obtained for a short period of time, which enabled some investigation of particle size distribution to be carried out. In this case the time needed for a full analysis was so short that it was considered that very little coagulation of the samples would take place.

3.7.2 Measurement of Surfactant Concentration

The evaluation of the concentration of surfactant present during flotation was considered to be essential for accurate process control. This necessitated the analysis of a large number of samples and a method which was both fast and reliable was therefore required. The methylene blue method, which had been used by other workers (34) was utilised in the preliminary tests on River Trent water (see Section 3.2). However, it was judged to be unsatisfactory at the low levels of surfactant encountered since the end-point of the titration used in the method was not heralded by a clearly visible colour change, and the determination involved an unacceptably high degree of subjectivity. Two alternative analytical methods were therefore considered.

3.7.2.1 Spectrophotometric Method

This method (71) appeared promising due to its direct applicability to low concentrations of quaternary ammonium compounds.

The principle of the method is that quaternary ammonium salts combine with certain anionic dyes to form compounds which may be extracted with organic solvents. The resulting colouration may be measured spectrometrically. The first step of the analysis was the construction of a calibration curve. The following were introduced successively into a series of separating funnels:

0.5 ml Aqueous solution of methyl orange, 0.15%
1.0 ml Sodium hydroxide lye (SG 1.33), diluted 1:1
20.0 ml Chloroform, Analar

50 ml portions of standard solutions of the quaternary ammonium salt (in this case CTAB) were then added to the funnels to provide a range of surfactant concentrations from zero to 10 mg l^{-1}. The mixtures were shaken vigorously for three minutes and allowed to stand for two hours. After this period most of the aqueous layer had separated from the chloroform layer. The bottom 10 ml of the chloroform layer, which was now an orange colour, were transferred to another separating funnel and shaken with 25 mls of 2M hydrochloric acid. This transferred the orange colour into the aqueous layer, which was withdrawn. A spectrophotometric reading of each of the calibration mixtures was taken at 508 nm and a curve plotted. The results of such a calibration procedure are given under Test B33 and are analysed in Section 4.4.1.

The analysis of samples of unknown surfactant concentration followed a similar procedure. 50 mls of the sample were placed in a separating funnel and the determination was continued as described above. A spectrometric reading was taken and the result was read off the calibration curve. Samples with a surfactant concentration likely to be above the limit of the calibration (10 mg l^{-1}) were diluted before analysis and the final result multiplied by a suitable dilution factor.

Other methods similar to the above may also be used for the determination of cationic surfactants. One such method utilises bromophenol blue in the presence of a citrate buffer (72).

The spectrophotometric method was found to be accurate and reproducible. In addition the result of the analysis was a completely objective measurement unlike those of titration methods. However, the length of time needed before adequate separation of the two phases occurred in the first step of the analysis resulted in a relatively high time requirement when large numbers of samples needed to be analysed.

3.7.2.2 Two-Phase Titration Method

This method was adapted from the procedure recommended by the International Organisation for Standardisation for the determination of anionic-active matter (73).

The principle of the adapted method is the determination of cationic-active matter in a medium consisting of aqueous and chloroform phases by volumetric titration with an anionic-active solution. The indicator used in this technique was a mixture of a cationic dye (dimidium bromide) and an anionic dye (disulphine blue). Initially the cationic-active matter present in the sample to be analysed formed a salt with the anionic dye which dissolved in the chloroform to give this layer a blue-green colour. In the course of the titration the anionic-active matter added displaced the disulphine blue from this salt and the blue colour left the chloroform layer as the dye passed to the aqueous phase. The anionic-active matter, when added in excess, formed a salt with the cationic dye which dissolved in the chloroform layer and coloured it pink.

In the analytical procedure described below, a mixed indicator solution was used which was prepared by combining 20 ml of a stock solution with 20 ml of 5N sulphuric acid in a 500 ml volumetric flask and diluting to the mark with distilled water. The stock solution was prepared by dissolving a 0.5 g portion of dimidium bromide and a 0.25 g portion of disulphine blue in 60 ml of hot 10% ethanol. This was then transferred to a 250 ml volumetric flask and diluted to the mark with 10% ethanol.

During the initial evaluation of the two-phase titration method it was found that at low concentrations of cationic surfactant the recognition of the end point of the titration was to some extent subjective. This was because the colour change in the chloroform layer was not a discrete step from blue to pink but took place gradually as anionic surfactant was added. In order to minimise this effect a calibration procedure was adopted.

The following were introduced successively into a series

of 100 ml stoppered measuring cylinders:

10 ml Standard solution of cationic surfactant (CTAB)

5 ml Mixed indicator solution

15 ml Chloroform, Analar

Varying amounts of a solution of an anionic surfactant (sodium lauryl sulphate) were then added to give a range of colours around the end point. The most marked colour change was chosen as the standardised end point, and used thereafter as a standard colour. A calibration curve was then prepared by titrating various quantities of cationic surfactant solution against anionic surfactant solution until the correct end point, as indicated by the standard colour, was reached. The same quantities of mixed indicator solution and chloroform were used throughout the test.

The calibration procedure outlined above enabled a plot to be produced of the mass of anionic surfactant needed to bring about the standardised end point for a particular mass of cationic surfactant. The standard colour could be recreated at any time by choosing a point on the calibration curve and combining the required masses of cationic and anionic surfactants. All titrations throughout the experimental programme were therefore standardised and the accuracy of the method was increased significantly.

The analysis of solutions of unknown cationic surfactant concentration was carried out by a process similar to that described above. A known volume of sample was placed in a 100 ml stoppered measuring cylinder with mixed indicator solution and chloroform and titrated against the anionic surfactant solution until the standard colour was obtained. The unknown concentration could then be found from the calibration curve.

It was found that once the calibration procedure had been completed and a calibration curve obtained, analysis of samples could be carried out rapidly and yielded accurate and reproducible results. The two-phase titration technique was therefore adopted as the main method of analysis for cationic surfactant concentration.

The calibration procedure was repeated whenever a fresh stock solution was prepared. In addition, occasional spot checks were made between the results obtained by titration and those obtained by the spectrophotometric method. These showed that accuracy was maintained throughout the period of the experimental programme.

3.7.3 Determination of Mixing Characteristics

The mixing characteristics of both column and channel flotation systems were investigated using a tracer response method. Such techniques have been used extensively in the field of Chemical Engineering (58) and have also been found to be useful in the assessment of the performance of water treatment units (74).

There are several variations of the tracer response method which may be used, their common characteristic being the addition of tracer at some point in the system and its detection at another point. In the case of systems such as flotation circuits introduction of the tracer is usually carried out at the point of entry of the influent in the flotation cell and detection is carried out at the exit point of the effluent from the cell.

The variations in the technique depend on the method by which the tracer is introduced and may be classified as follows:

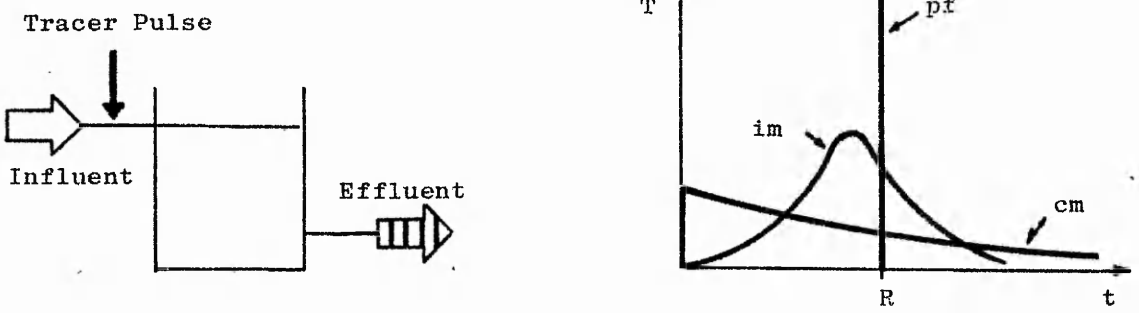
(i) Injection of the tracer into the system as a single pulse or as a series of pulses.

(ii) Steady addition of tracer solution into a system which is initially free of tracer.

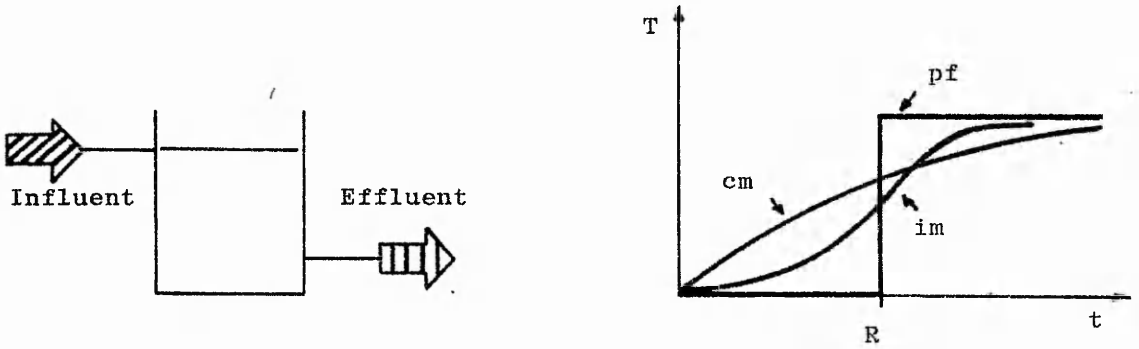
(iii) Steady addition of tracer-free solution into a system which is initially filled with tracer solution.

Option (i) is suitable for tracers such as radioactive isotopes, which are used in small doses and can be detected with accuracy at very low concentrations. In this case a plot of the tracer concentration of the effluent stream against time is known as an "E-curve". The E-curves for various mixing conditions are shown in Figure 17a. It

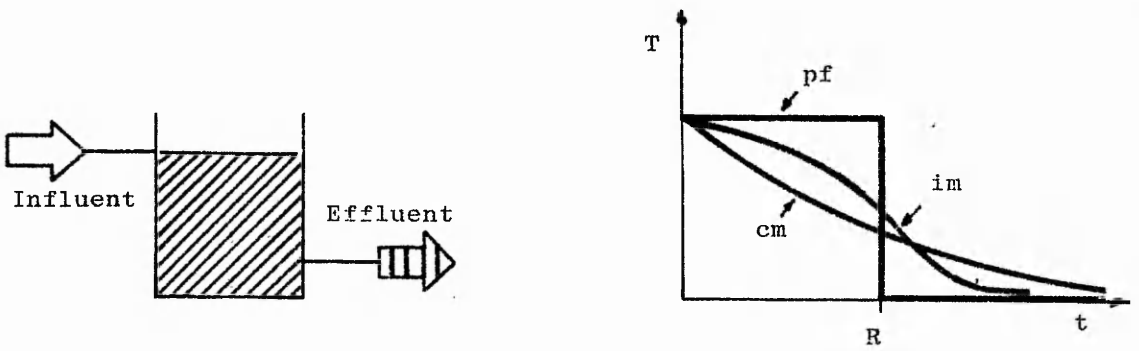
pf: plug flow cm: complete mixing im: intermediate mixing



a. "E-curves"



b. "F-curves"



c. "R-curves"

FIGURE 17: Tracer Response Methods

will be seen that for a perfect plug flow condition the tracer pulse for the influent at zero time is duplicated in the tracer concentration for the effluent after a period of time equal to R, the retention time of the vessel. At the other extreme condition, complete mixing, the tracer concentration in the effluent reaches a maximum immediately the tracer pulse is applied in the influent, after which it is subject to an exponential decrease. Any mixing regime which lies between these two extreme conditions results in an effluent tracer concentration which reaches a maximum at some intermediate time between zero and R.

Options (ii) and (iii) may be employed with tracers which need to be used in larger quantities in order to obtain an accurately measurable response. This was the case in the present study since the most convenient system available was the use of sodium chloride as a tracer with continuous monitoring of the response by on-line conductivity measurement of the effluent stream. The tracer response curves for various mixing conditions as shown in Figure 17b and Figure 17c and are known as "F-curves" or "R-curves". They will be seen to bear a reciprocal relationship to one another, and their various forms have been derived and discussed in Section 2.4.1.3. Option (iii) was preferred for the present study since the maximum tracer response occurred at the start of the test, and the recording equipment could therefore be adjusted to give full-scale deflection.

At the beginning of a mixing test the flotation cell was filled with tracer solution at a suitable concentration and thoroughly mixed by vigorous aeration. A sample of the homogenous mix was taken so that the initial conductivity of the solution could be measured. This sample was also used to adjust the recording equipment to full-scale deflection. The air flow rate to the cell was then adjusted to the value relevant to the test and tracer-free influent was fed into the cell at the required rate. The

correct water level in the cell was maintained by manipulation of the outlet valve. The concentration of tracer in the effluent stream could then be monitored.
Figure 18 shows details of the detection equipment. A small copper pot containing a conductivity electrode was inserted between the effluent outlet and the drain. Changes in tracer concentration were detected by a conductivity meter and logged on a chart recorder. This record of conductivity was later converted to tracer concentration using a calibration curve (see results of Test A1 and Section 4.3.1).

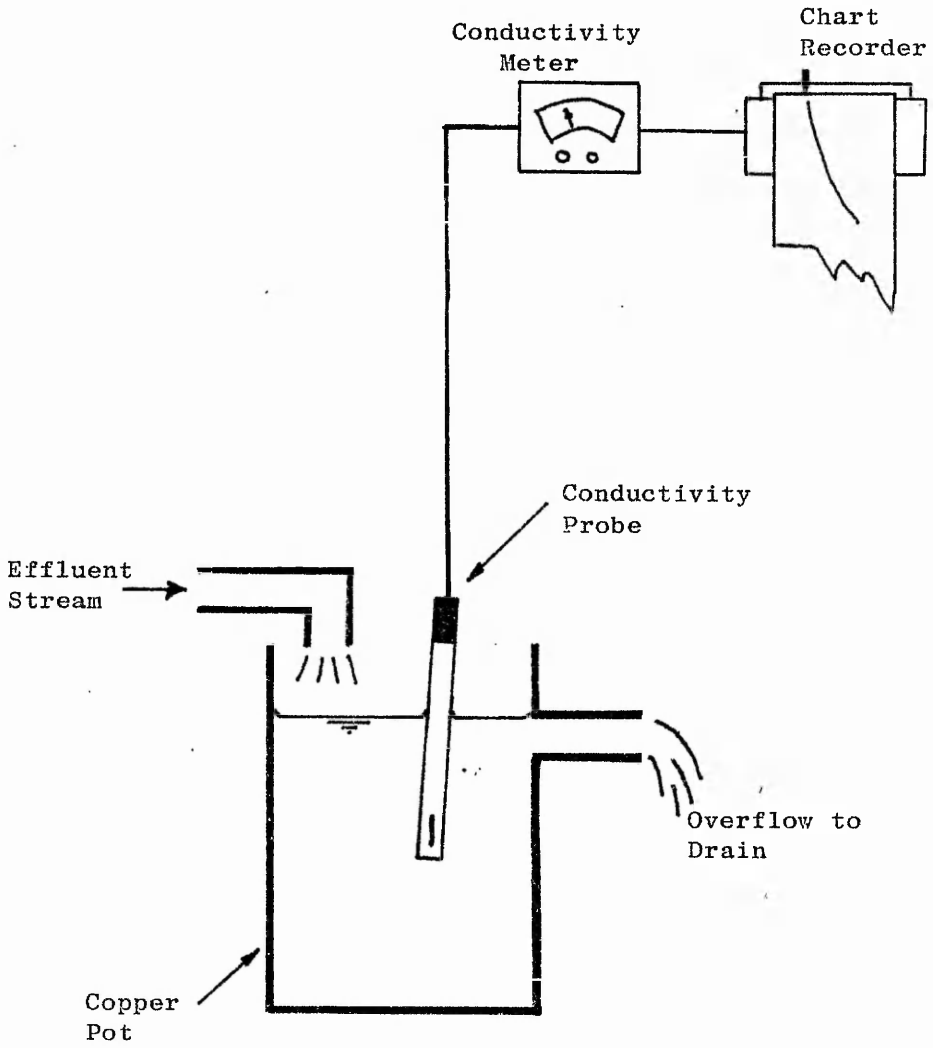


FIGURE 18: Detection Equipment for Tracer Tests

CHAPTER 4

ANALYSIS AND DISCUSSION OF EXPERIMENTAL RESULTS

4.1 INTRODUCTION

For convenience of presentation the raw data from all tests has been collected as Appendix 3. The analysis of each main group of tests is contained in the sections that follow. Finally, an overall assessment of the results and a general discussion are presented.

4.2 ANALYSIS OF GROUP P EXPERIMENTS

4.2.1 Continuous Tests (P1 - P15)

Figure 19.a. shows the results obtained for a typical continuous run using the Simon-Hartley pilot plant. The ratio:

$$\frac{\tau}{\tau_i} = \frac{\text{Turbidity}}{\text{Initial Turbidity}}$$

was used as a general measure of removal efficiency. It will be seen that the value of this ratio decreased with time in a manner similar to that expected from a continuous reactor in which a first-order removal process was occurring. Eventually a steady-state was reached.

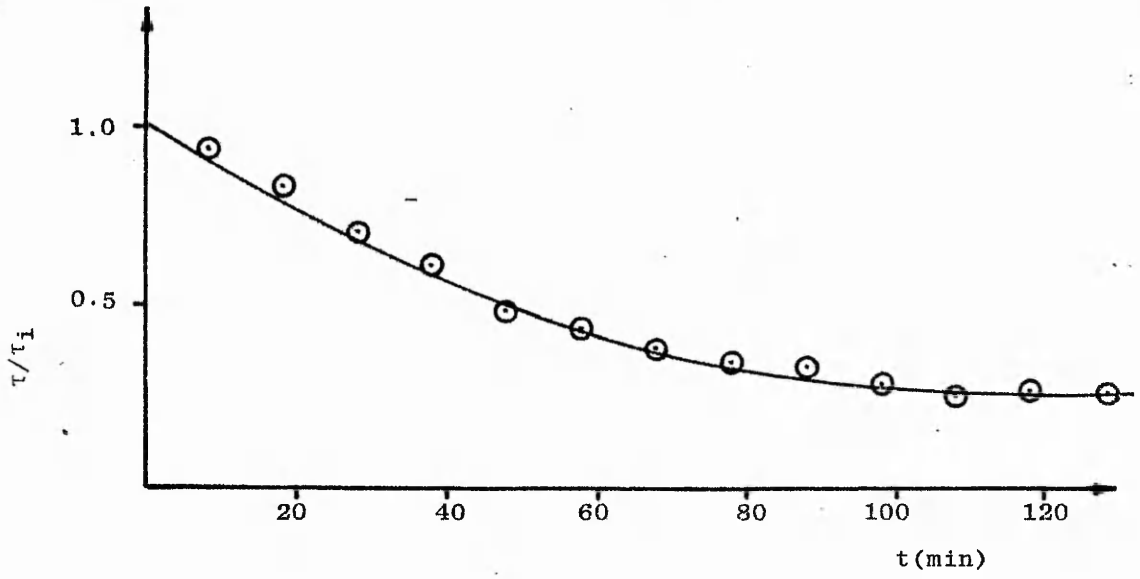
It was felt that the significance of the Group P tests was governed by a consideration of the experimental techniques employed. In particular the surfactant concentration in the unit was not controlled as accurately as in later experiments (see Section 2.4.3.2). As a result a constant surfactant concentration was likely only when steady-state had been reached. It was therefore decided to concentrate the analysis on steady-state values of the turbidity ratio. The pilot flotation unit was assumed to consist of two completely mixed stages in series, the first being 600 l in volume and the second 400 l (see Section 3.2). In addition it was assumed that a common flotation rate constant could be applied to both stages. Under these conditions the steady-state particle concentration achieved would be given by an extension of the theory outlined in Section 2.4.1.4:

$$\frac{c}{c_i} = \frac{1}{(R_1k+1)} \cdot \frac{1}{(R_2k+1)} \qquad \text{(XXV)}$$

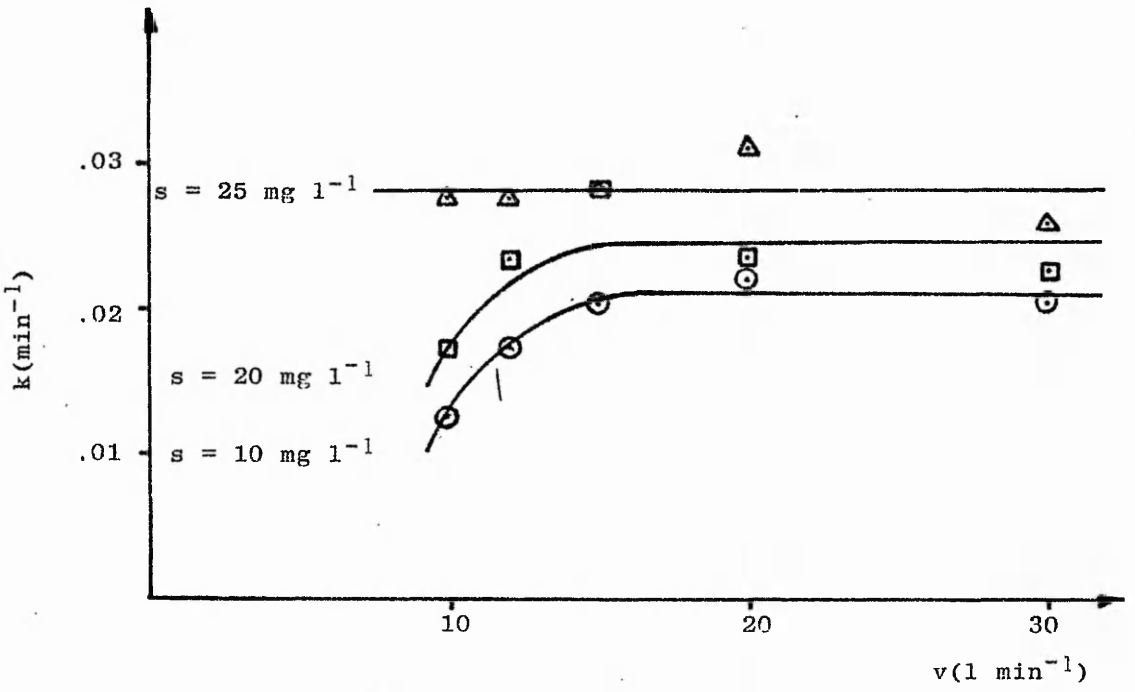
where R_1 = Retention time of first stage

R_2 = Retention time of second stage

k = Common Flotation rate constant



a. Typical Removal vs. Time Curve



b. Relationship between Rate Constant, and Flow Rate

FIGURE 19: Preliminary Experiments

c/c_i was assumed to be equal to the turbidity ratio τ/τ_i. Equation (XXV) was rearranged to give:

$$(R_1R_2)k^2 + (R_1 + R_2)k + (1 - \frac{c_i}{c}) = 0 \qquad \text{(XXVI)}$$

This was a quadratic equation from which values of k could be found for each test. Negative roots for equation (XXVI) were ignored. The results of such a procedure are given in Table 1.

TABLE 1: Calculation of Rate Constant k for Preliminary Experiments

Test Number	Nominal Surfactant Concentration (mg l^{-1})	Flow Rate v ($l\ min^{-1}$)	R_1 (min)	R_2 (min)	c/c_i	k (min^{-1})
1	10	30	20	13.3	0.56	0.0203
2	10	20	30	20.0	0.42	0.0291
3	10	15	40	26.7	0.36	0.0202
4	10	12	50	33.3	0.34	0.0173
5	10	10	60	40.0	0.38	0.0125
6	20	30	20	13.3	0.53	0.0225
7	20	20	30	20.0	0.40	0.0234
8	20	15	40	26.7	0.27	0.0280
9	20	12	50	33.3	0.26	0.0233
10	20	10	60	40.0	0.29	0.0173
11	30	30	20	13.3	0.49	0.0259
12	30	20	30	20.0	0.32	0.0310
13	30	15	40	26.7	0.27	0.0280
14	30	12	50	33.3	0.22	0.0275
15	30	10	60	40.0	0.18	0.0275

Figure 19.b. illustrates the relationship between the calculated rate constant, k, and the flow rate to the unit, v. For a first-order chemical kinetics analogy to apply k should have been constant for a particular surfactant concentration irrespective of v. This was approximately true at a nominal surfactant concentration of 25 mg l^{-1} and at lower surfactant concentrations when the flow rate exceeded 15 l min^{-1}.

4.3 ANALYSIS OF GROUP A EXPERIMENTS

4.3.1 Calibrations (A1 and A5)

Figure 20.a. shows the relationship between conductivity, Ω, and tracer concentration, T, for solutions of the tracer in laboratory tapwater. In order to use the curve produced for calibration purposes, a graph of $(\log_{10} \Omega)$ vs. $(\log_{10} T)$ was plotted and a linear regression on the resultant straight line produced the following equation:

$$\Omega = 1.93\ T^{0.7265} \qquad \text{(XXVII)}$$

The curve associated with equation (XXVII) is shown in Figure 20.a. The coefficient of correlation associated with equation (XXVII) had a value of 0.9999, indicating a high degree of fit.

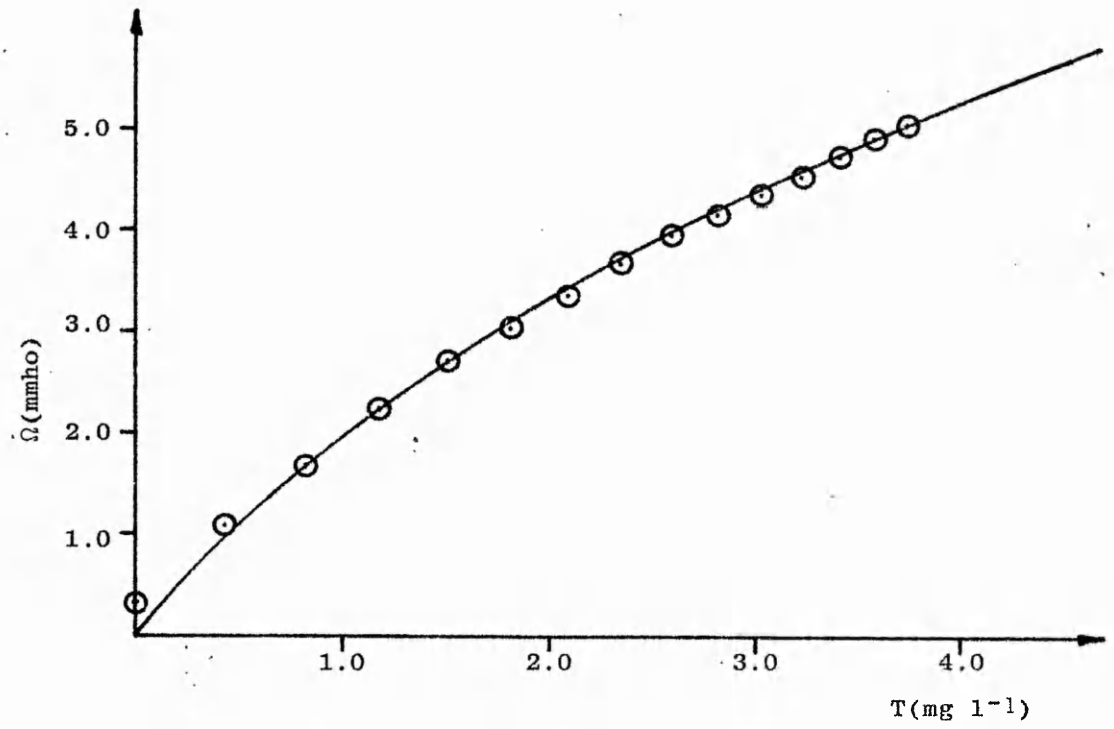
The dependence of turbidity, τ, on solids concentration, c, for the graded kaolinite used in following experiments is shown in Figure 20.b. The relationship was approximately linear, with an initial value of turbidity at zero solids concentration corresponding to the turbidity of the laboratory tapwater. A linear regression of τ vs. c yielded the following equation:

$$\tau = 0.3241\ c + 1.5452 \qquad \text{(XXVIII)}$$

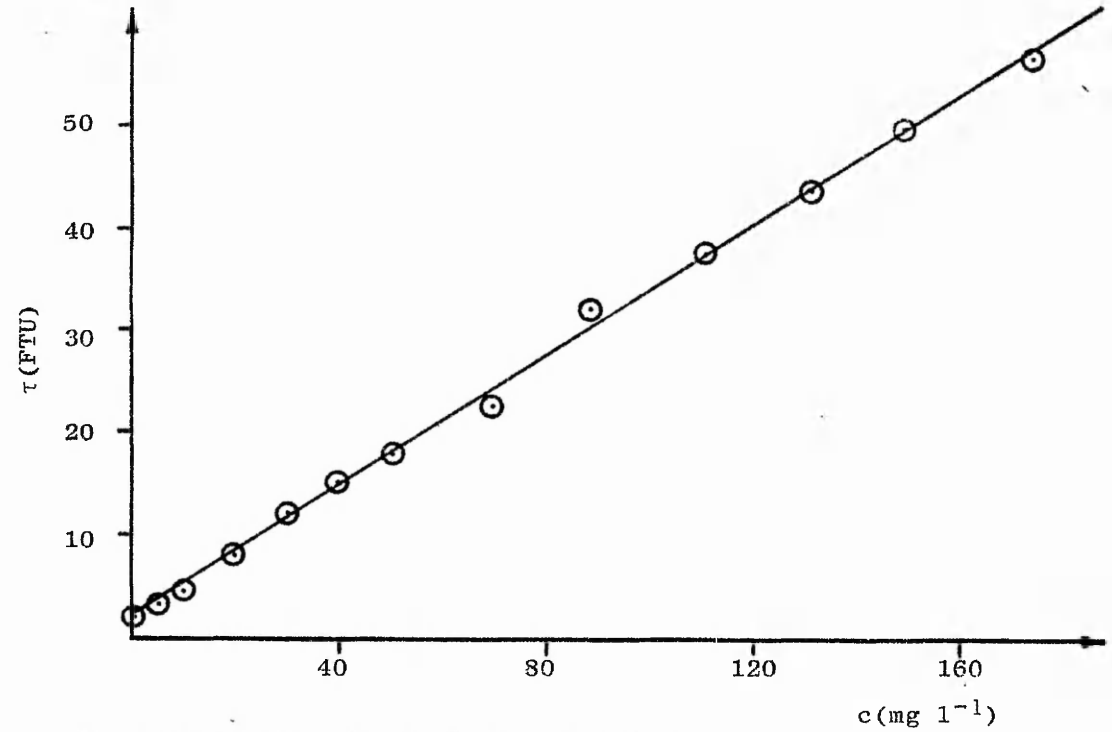
The coefficient of correlation for this relationship was 0.9991, indicating excellent fit. Values of clay concentration, c, could therefore be derived from experimentally determined turbidities, τ, by use of equation (XXVIII). This assumed that the particle size distributions of all samples remained the same throughout a test. Although this was not precisely correct, the narrow grading curve of the material justified this assumption (see Section 3.3.1).

4.3.2 Mixing Experiments (A2 - A4)

Tests on the mixing regimes in the flotation column caused by aeration at the two extreme experimental air rates were carried out. Figure 21.a. shows the tracer responses for both maximum and minimum air rates. The responses coincided, showing the mixing regimes prevalent in each case to have been the same. The responses took the form of a negative

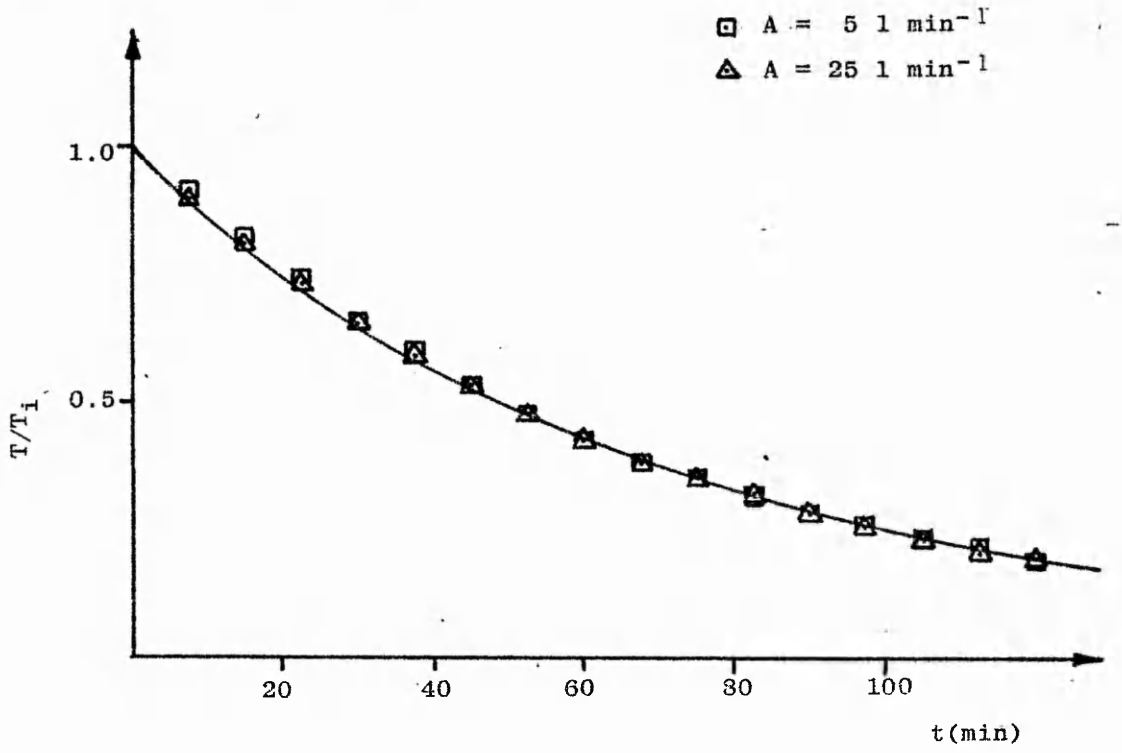


a. Conductivity vs. Tracer Concentration

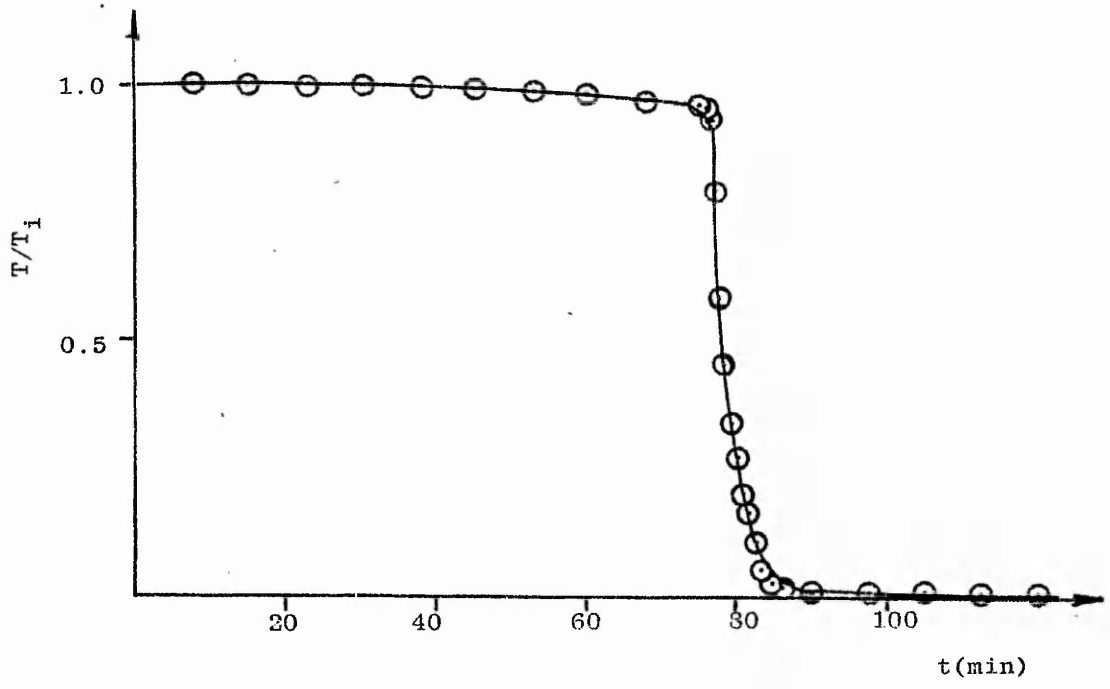


b. Turbidity vs. Clay Concentration

FIGURE 20: Calibration Curves



a. Aerated Column



b. Non-aerated Column

FIGURE 21: Mixing Experiments in Flotation Column

exponential decrease, indicating complete mixing in each case. Equation (X), Section 2.4.1.3, gives the mathematical description of this type of response, and consideration of the equation showed that a plot of the natural logarithm of T/T_i vs. time, t, should yield a straight line passing through the origin with a gradient of $-R^{-1}$. Linear regressions of the two sets of experimental points yielded the following:

Test A2: $\ln(T/T_i) = -(0.014112)t - 0.005429$

Test A3: $\ln(T/T_i) = -(0.014027)t - 0.005710$

The correlation coefficient was -0.9998 in each case, showing excellent fit to the straight line model. The theoretical gradient in each case was $-0.013333\ min^{-1}$, since the retention time was 75 min. This gave values for the ratio of experimental gradient to theoretical gradient as follows:

Test A2: (exptl. gradient)/(theor. gradient) = 1.0584

Test A3: (exptl. gradient)/(theor. gradient) = 1.0655

The intercepts in each case were considered to be negligible. It was concluded that complete mixing had taken place for both maximum and minimum air flow rates. To test if this uniformity of mixing regime was due in any way to the passage of water through the column, rather than the passage of air, a test (A4) was carried out at the same water flow rate as the two previous tests but with no aeration. The tracer response obtained is shown in Figure 21.b. Since this corresponded closely to the plug flow model, it was concluded that the effects of water flow rate on mixing were negligible.

4.3.3 Batch Flotation Tests (A6 - A14)

A number of tests were carried out on the removal of clay and surfactant by flotation. The column was operated in the batch mode at a variety of air rates. Since previous tests had shown water flow rate to have little effect on the mixing regime, the rate of recirculation was not considered as a variable. Tests were run under conditions of variable and constant surfactant concentration, as explained in Section 2.5.2.

The results of Tests A12 and A13 are shown in Figure 22, as an example of the type of behaviour encountered. Both clay and surfactant concentrations decreased in approximately exponential fashion, so that first order rate constants, k and m_1, could be found from plots of relative concentration vs. time. The theoretical gradient of such plots would correspond to -k or to $-m_1$, and the theoretical intercept would be zero. The results of such an analysis are given in Table 2.

TABLE 2: Calculation of Rate Constants k and m_1 for Batch Tests

Test Number	A ($l\ min^{-1}$)	k (min^{-1})	m_1 (min^{-1})
A6	25	0.089808	0.024402
A7	25	0.084113	
A8	20	0.070311	0.015539
A9	20	0.075742	
A10	15	0.054264	0.013578
A11	15	0.056660	
A12	10	0.042431	0.009860
A13	10	0.039228	
A14	5	0.019758	0.004208

The average value for the coefficient of correlation in this analysis was -0.9928, and the average value for the intercept was -0.0127. The nearness of both these values to the theoretical predictions (-1 and zero) was an indication of the suitability of the first order removal model.

There did not appear to be a definite trend distinguishing k values under variable surfactant conditions to those under constant surfactant conditions. In all cases the numerical values of k obtained from each pair of tests were close to each other. The provisional assumption was made that variations in surfactant concentration over the range encountered during the tests had little effect. Therefore for the purposes of comparison all the values of k derived from Tests A6 - A14 were considered together.

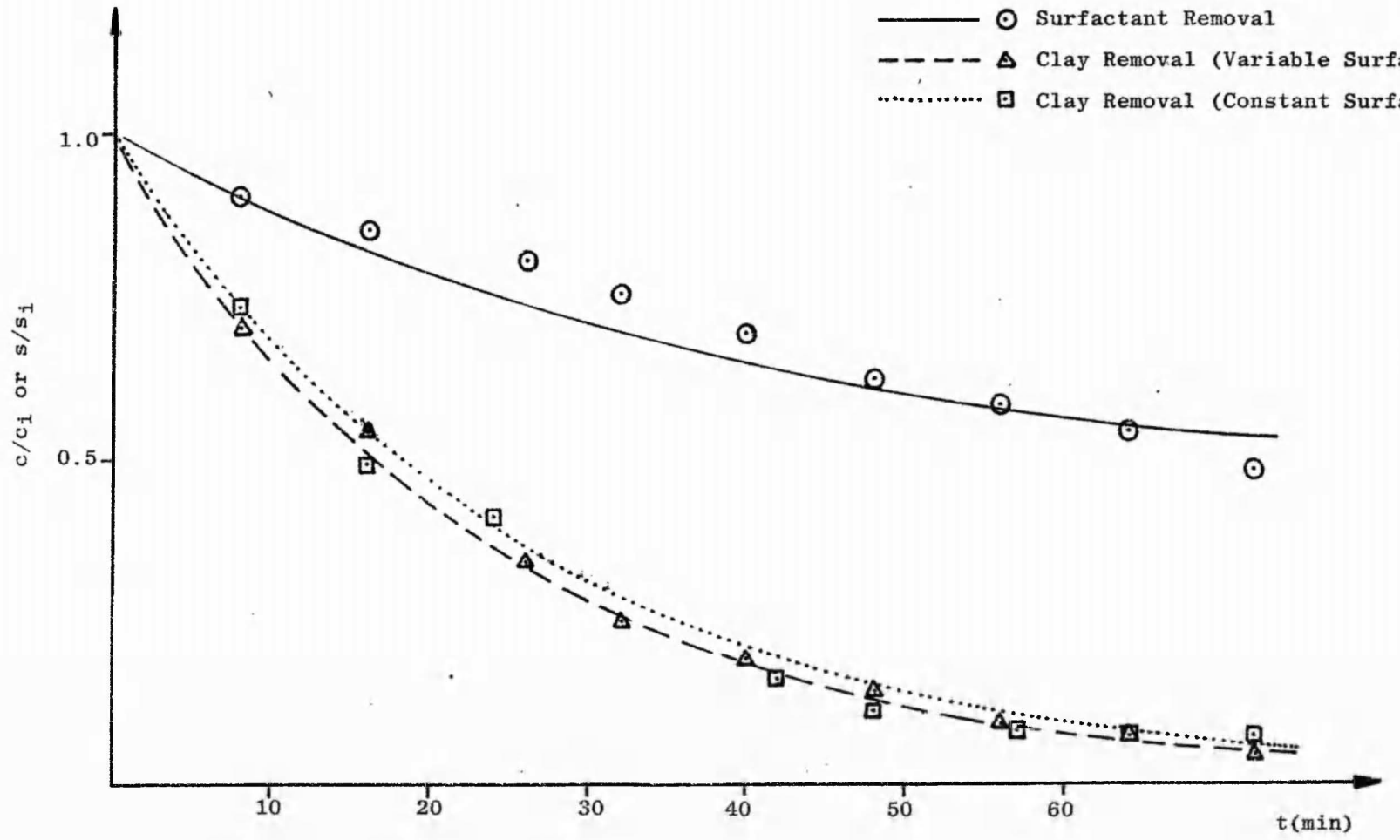


FIGURE 22: Typical Removal vs. Time Curves from Batch Flotation Tests

Figure 23 shows the relationship between the first order removal constants, k and m_1, and the air rate, A. There was a linear dependence of the first order constants on air rate, and a linear regression analysis gave the following characteristics for the lines of best fit:

$$k = (0.003271)A + (0.006443) \quad \text{(XXIX)}$$

$$m_1 = (0.000921)A + (0.000303) \quad \text{(XXX)}$$

Equation (XXIX) was utilised to calculate the most probable values of k for batch tests at the air rates used. These values, which are shown in Table 3, were used in the analysis of the continuous test results described in Section 4.3.4.

TABLE 3: Calculation of Rate Constant k for Various Air Rates

Air Rate A ($l\ min^{-1}$)	k (min^{-1})
5	0.022799
10	0.039155
15	0.055512
20	0.071868
25	0.088224

In order to assess the accuracy of the technique used to create conditions of constant surfactant concentration (see Section 2.4.3.2), the mean values of s/s_i were found for those tests in which the technique was employed. These are shown in Table 4. The overall mean value of s/s_i for all tests was 1.0656.

TABLE 4: Accuracy of Surfactant Dosing Technique (Batch Tests)

Test Number	Mean s/s_i
A7	1.1755
A9	1.0235
A11	1.0635
A13	1.0000

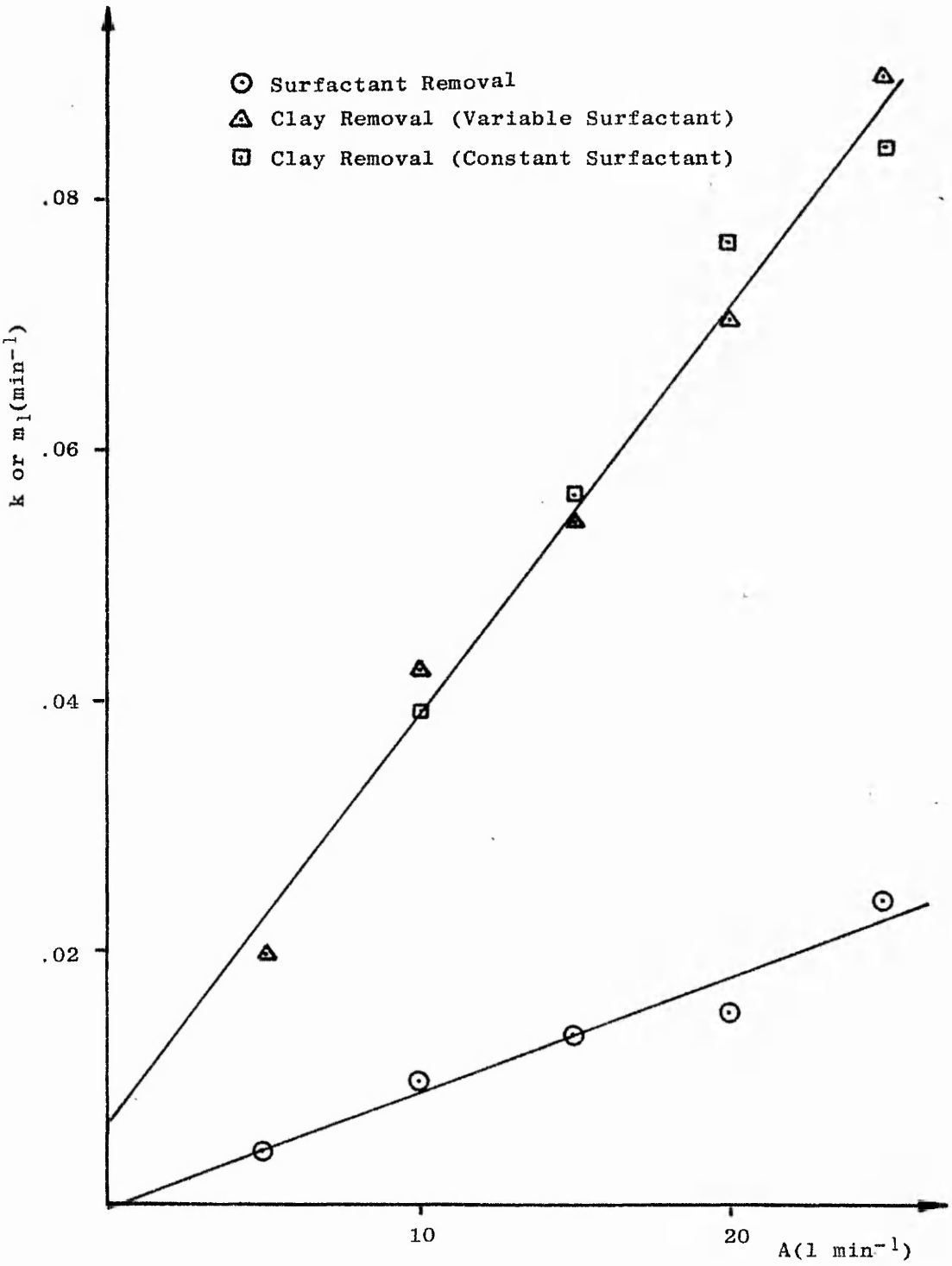


FIGURE 23: Relationship between First-Order Rate Constants and Air Rate

4.3.4 Continuous Flotation Tests (A15 - A30)

The observed closeness of the experimental mixing regimes to complete mixing suggested that equation (XV), Section 2.4.1.4, could be used to describe particle removal in continuous flotation. This hypothesis was tested over a range of air and water rates. A constant surfactant concentration was maintained for all tests using equation (XXIV), Section 2.4.3.2, and the values of m_1 obtained from batch tests (see Section 4.3.3).

An example of the type of removal encountered during continuous runs is shown in Figure 24.a, which utilises the data obtained in Test A22. The value of c/c_i decreased exponentially until a steady-state value was reached. Such behaviour confirmed the predictions of equation (XV).

In order to test the accuracy of the equation as a model for continuous flotation, a method was required for comparing experimental results from continuous tests with those predicted from equation (XV) and values of k derived from batch experiments. Three alternative schemes were examined.

The first method considered was the direct evaluation of values of k from the results of the continuous tests. This could be carried out using a log plot method similar to that used for the analysis of batch flotation results. Equation (XV) was rearranged into the following form:

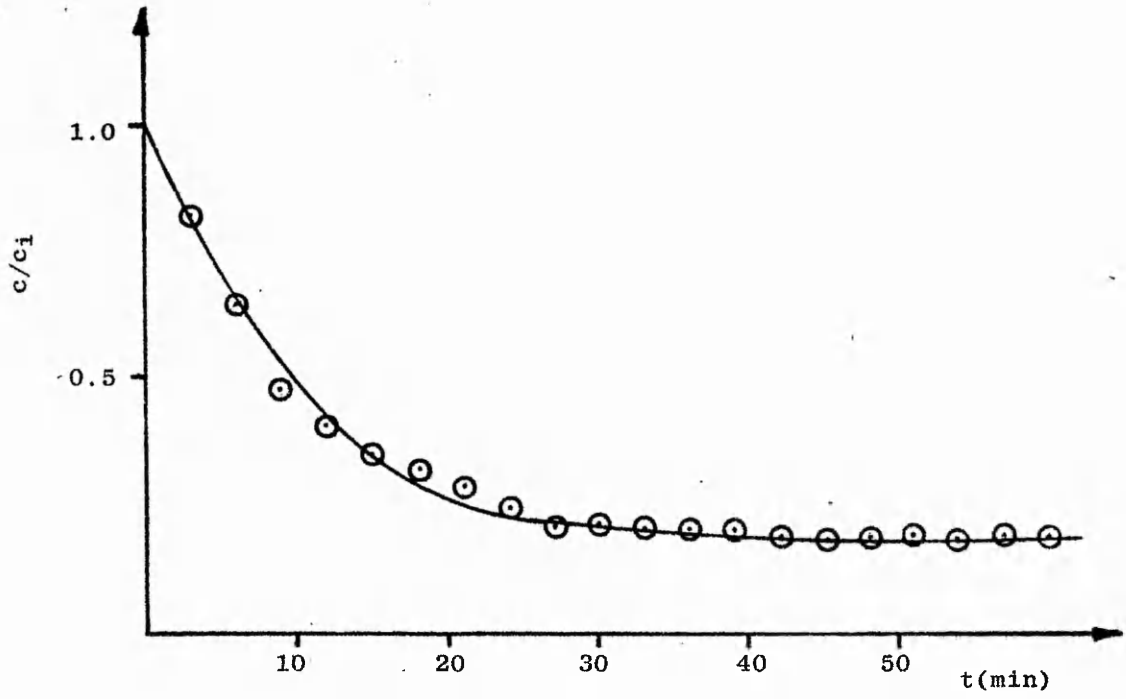
$$\ln\left[\frac{c}{c_i} - \frac{1}{(Rk+1)}\right] = \ln\left[1 - \frac{1}{(Rk+1)}\right] - \left[\frac{(Rk+1)}{R}\right] t \qquad \text{(XXXI)}$$

A plot of the L.H.S. of this equation vs. t should have produced a straight line with the following characteristics:

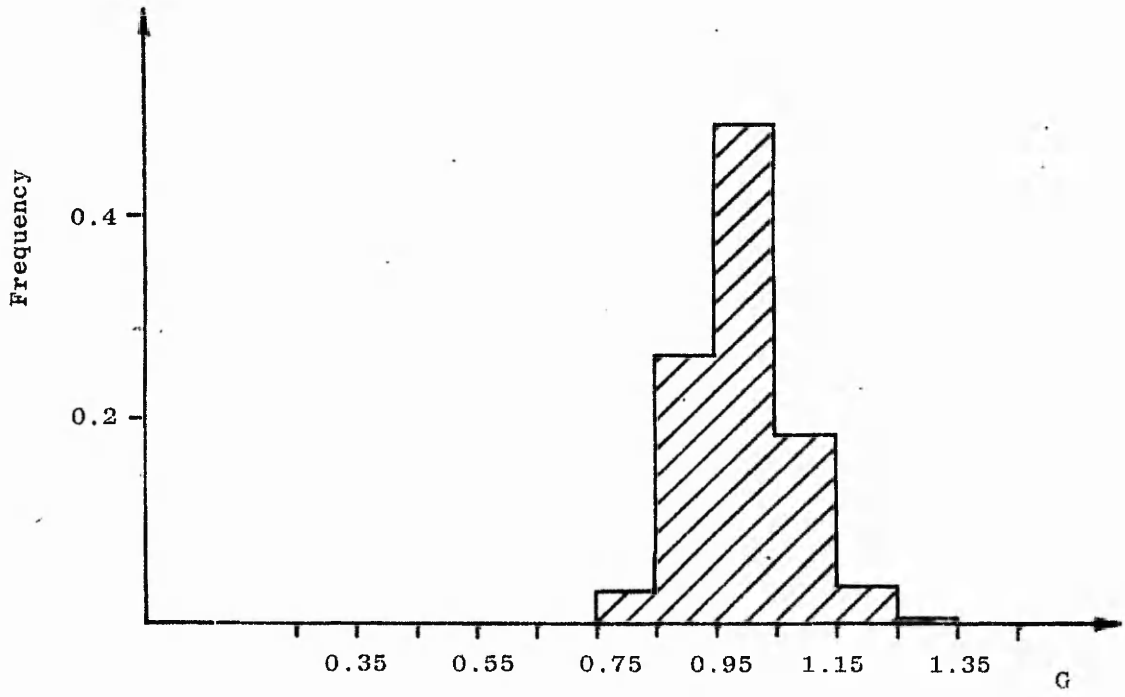
$$\text{gradient} = \ln\left[1 - \frac{1}{(Rk+1)}\right]$$

$$\text{intercept} = -\left[\frac{(Rk+1)}{R}\right]$$

There were two main problems associated with this method of analysis. Firstly, equation (XXXI) could not be separated to yield an expression with k on one side only and therefore an analytical solution for k could not be obtained directly. Secondly, as c/c_i approached the steady-state value $(Rk+1)^{-1}$, the L.H.S. of equation (XXXI) tended to a large negative value. Small errors in the measurement of c/c_i at this stage



a. Typical Removal vs. Time Curve



b. Frequency Distribution for Parameter G

FIGURE 24: Continuous Flotation Tests in Flotation Column

would therefore have been grossly exaggerated on the log plot, and would have caused an inaccurate measurement of the gradient.

The second analytical approach was the calculation of a parameter which would give a measure of the deviation of experimental points from their predicted values. The predicted values were calculated from equation (XV), Section 2.4.1.4, and the batch flotation data (see Table 3, Section 4.3.3). A parameter of deviation for the results of a continuous tests was defined as:

$$\text{parameter of Deviation} = \frac{1}{n} \sum_{i=0}^{n} (d_i)^2$$

$$\text{where } d_i = \frac{\text{(exptl. value) - (predicted value)}}{\text{(exptl. value)}}$$

The difference between experimental and predicted results was divided by the experimental result to give an equal weighting to all points regardless of size. The deviation parameter could therefore be used as a measure of the variation between the results of different tests. However, it did not provide a measure of the absolute accuracy of tests and could only be used for a relative assessment.

The third method of analysis did not have the disadvantages mentioned above and enabled an absolute value for the accuracy of all tests to be obtained. A dimensionless parameter, G, defined as

$$G = \frac{c/c_i \text{ (exptl.)}}{c/c_i \text{ (predicted)}}$$

was found for each point of time in every test. In the absence of experimental error the value of G would have been unity in all cases; values higher or lower than this indicated experimental deviations from predicted behaviour.

Values of c/c_i (predicted) were calculated using equation (XV), Section 2.4.1.4, and the values of k shown in Table 3, Section 4.3.3.

When G had been found for every experimental point, a frequency distribution of values of G was formed. This is shown in Table 5 and Figure 24.b.

TABLE 5: Frequency Distribution of Parameter G

Value of G	Frequency
1.35 - 1.25	0.0032
1.25 - 1.15	0.0356
1.15 - 1.05	0.1845
1.05 - 0.95	0.4887
0.95 - 0.85	0.2589
0.85 - 0.75	0.0291

The following characteristics were found to define the frequency distribution:

mean value of G , $\bar{G} = 0.9933$

S.D. of values of G from $\bar{G}$, $s_G = 0.0835$

total number of values of G, $n_G = 309$

The absolute accuracy of equation (XV) as a model for single-stage continuous flotation could be found by subjecting the distribution of G values to two elementary statistical tests.

The first statistical test was an examination of $\bar{G}$. The closeness of this value to unity gave a promising indication that the model was accurate.

The second test was an evaluation of the spread of the distribution about the mean. The null hypothesis, that the observed mean value, $\bar{G}$, coincided with the theoretical mean, μ, was tested using Student's t-distribution. The null and alternative hypotheses were formulated:

H_0: $\bar{G} = \mu = 1$

H_1: $\bar{G} \neq \mu$

The decision rule adopted was that if the modulus of t obtained from the frequency distribution was less than the theoretical value, then H_0 would be accepted at the significance level chosen (in this case 0.1). Since values of G could be greater or less than the mean value, the test was two-tailed.

The number of degrees of freedom was given by:

number of degrees of freedon = $n_G - 1 = 308$

(In the calculation that follows the statistical parameter t should not be confused with time, t, as used elsewhere in this thesis.)

The relevant theoretical value of t was obtained from statistical tables (140):

$t(0.05, 308) = 1.645$

The value of t calculated from the frequency distribution was:

$$t = \frac{\bar{G} - \mu}{s_G/\sqrt{n_G}} = \frac{0.9933 - 1}{0.0835/\sqrt{309}} = -1.4105$$

Since $| -1.4105 | < 1.645$, H_0 was accepted. Thus the use of equation (XV) as a model for continuous flotation was justified at a significance level of 0.1.

The accuracy of the surfactant dosing technique when applied to continuous tests was assessed by finding the mean values of s/s_i. These are shown in Table 6. The overall mean value for s/s_i for all tests was 1.0867.

TABLE 6: Accuracy of Surfactant Dosing Technique (Continuous Tests)

Test Number	Mean s/s_i
A15	1.0720
A16	1.2000
A17	1.1270
A18	1.0523
A19	1.0000
A20	1.0574
A21	1.1035
A22	0.9754
A23	1.0948
A24	1.0723
A25	1.0783
A26	1.3440
A27	1.1000
A28	0.9919
A29	1.0889
A30	1.0787

4.3.5 Particle Analysis (A31)

Samples of effluent taken during Test A30 were analysed to find their particle size distribution using a Coulter Counter (see Section 3.7.1.3). The number of particles in fifteen particle fractions was found for each of ten samples, from which the variations in the concentration of each particle fraction with time could be determined. In order to facilitate visual inspection of the data, the results for particle fractions which behaved in a similar fashion were grouped together. The variation of the total particle concentration for each group with time is shown in Figure 25.b, together with the cumulative curve for all fractions combined.

4.4 ANALYSIS OF GROUP B EXPERIMENTS

4.4.1 Calibrations (B33 and B34)

Figure 26.a shows the calibration curve used for the determination of surfactant concentration by the spectrophotometric method (see Section 3.7.2.1). The relationship between absorbance and the concentration of CTAB was approximately linear over the range of the calibration. A linear regression yielded the following characteristics for the line of best fit:

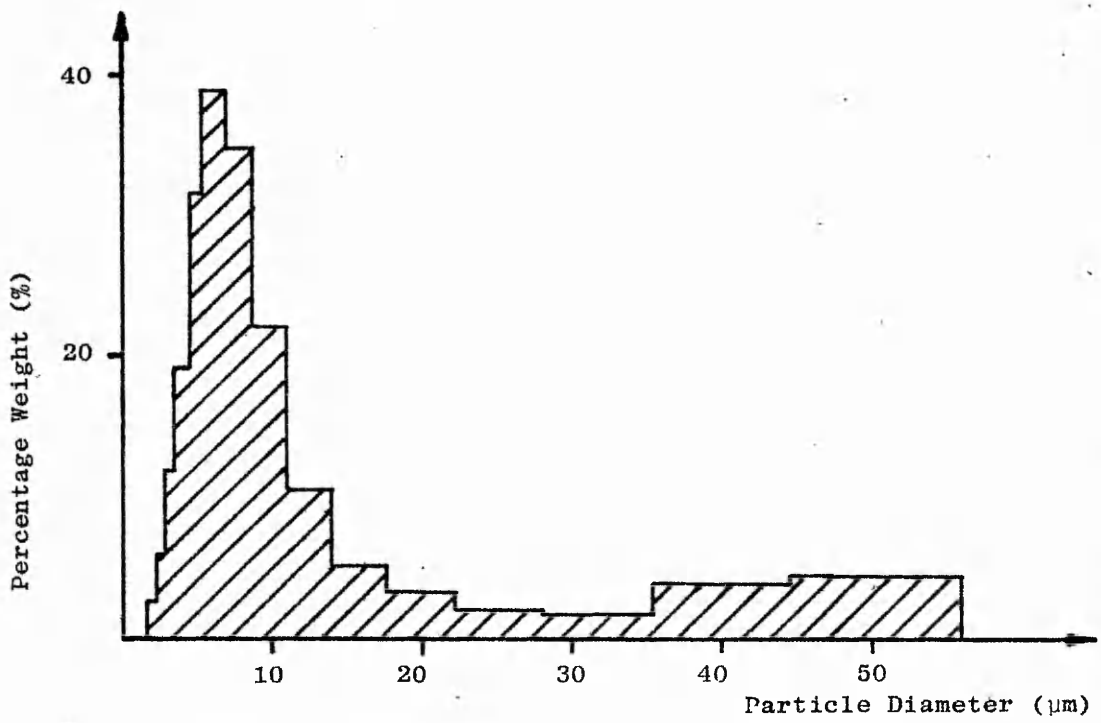
Gradient = 0.1278
Intercept = -0.0196
Coefficient of Correlation = 0.9976

$$\Rightarrow \text{(CTAB conc.)} = 7.8247\ \text{(absorbance)} + 0.1529 \qquad \text{(XXXII)}$$

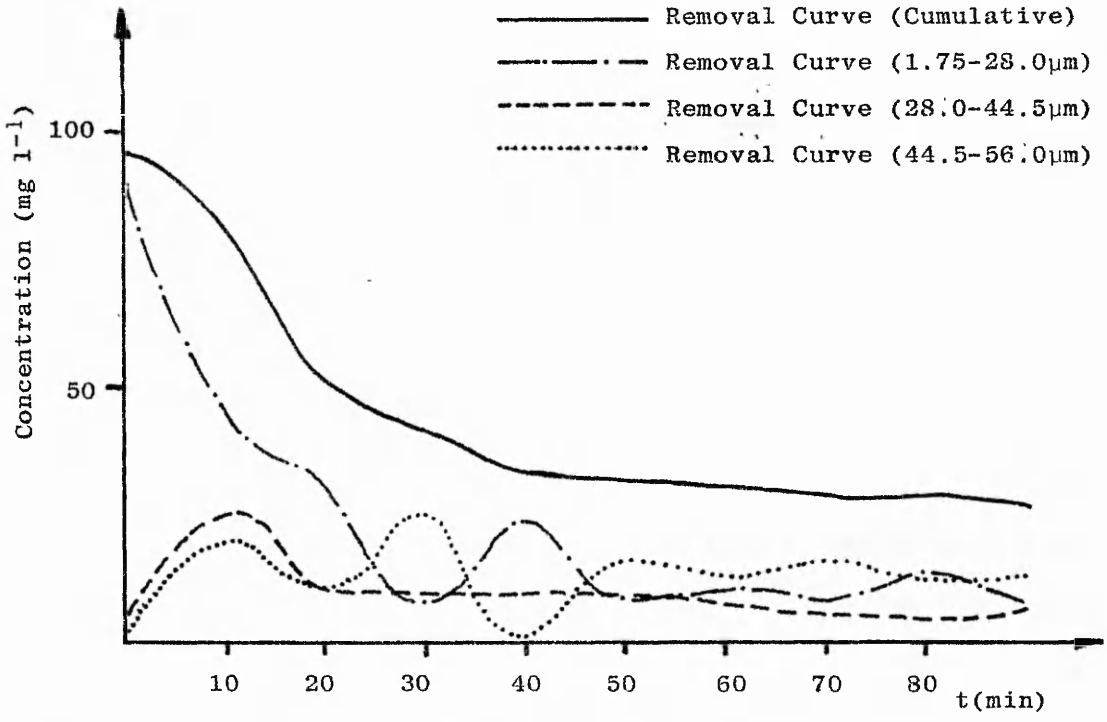
Figure 26.b shows the calibration curve for the two-phase titration technique (see Section 3.7.2.2). A linear dependance was found to exist between the masses of anionic and cationic surfactant needed to bring about an end-point. A linear regression yielded the following characteristics for the line of best fit:

Gradient = 0.7696
Intercept = 0.1447
Coefficient of Correlation = 0.9996

$$\Rightarrow \text{(mg (CTAB)} = 1.2994\ \text{(mg NaLS)} - 0.1880 \qquad \text{(XXXIII)}$$

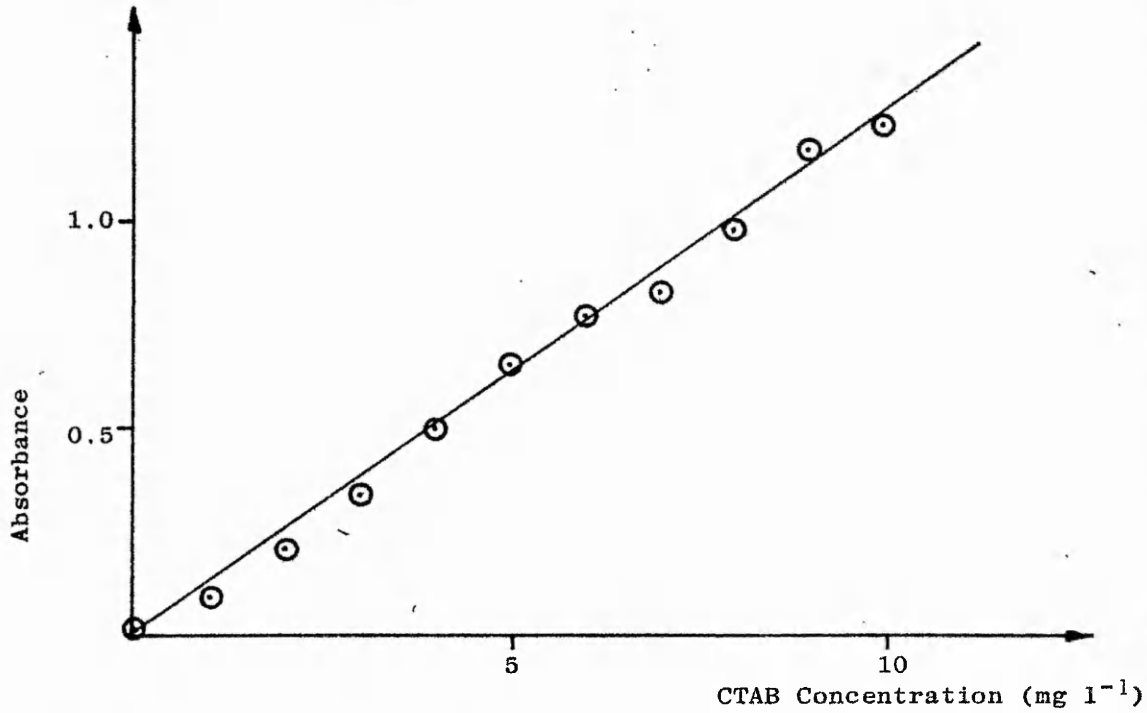


a. Particle Size Distribution of Refined Kaolinite (Initial Sample)

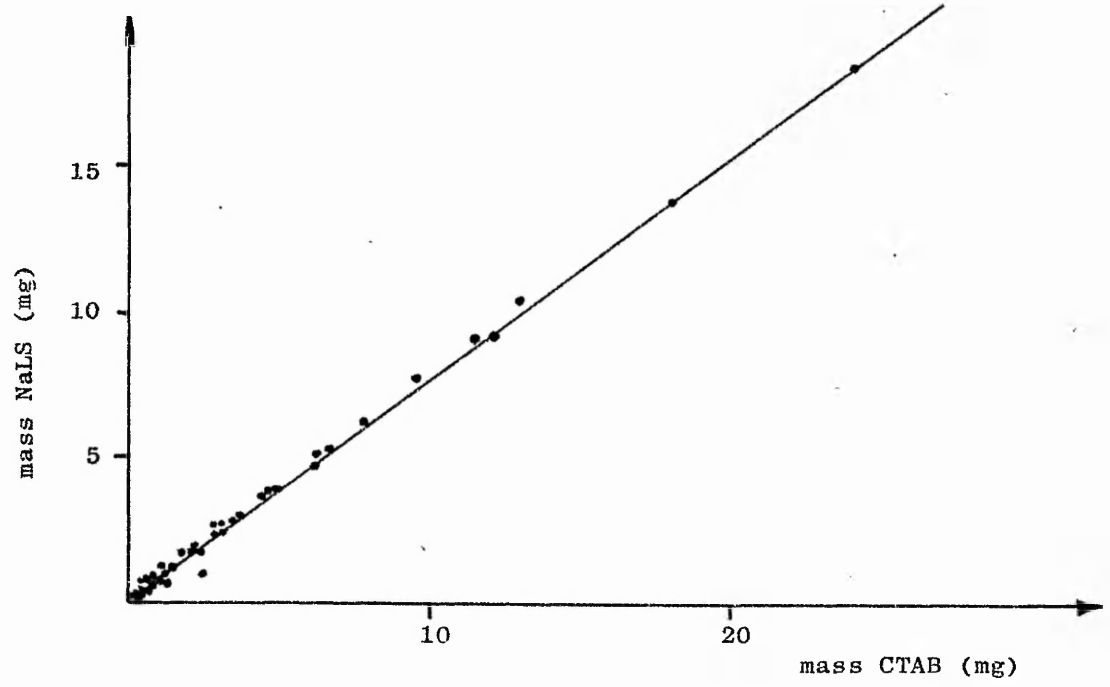


b. Particle Removal during a Continuous Run

FIGURE 25: Particle Removal by Flotation



a. Spectrophotometric Method



b. Two-Phase Titration Method

FIGURE 26: Calibration Curves for Determination of Surfactant Concentration

The correlation coefficients obtained for both calibration curves indicated an acceptable degree of experimental accuracy. Using molecular weights for CTAB and NaLS of 346.46 and 288.38 respectively, equation (XXXIII) was converted to:

(moles CTAB) = 1.0282 (moles NaLS) - (0.5×10^{-6})

ie approximately a mole for mole dependence.

4.4.2 Mixing Experiment (B1)

An experiment was carried out to check that alterations in the volume of the column did not affect the prevailing mixing regime. The results of this test were analysed in a similar fashion to those for tests A2 and A3 (see Section 4.3.2). The line of best fit through the points on a logarithmic-linear plot was characterised by the following values:

Gradient = -0.035352

Intercept = -0.048225

Coefficient of Correlation = -0.9996

In this experiment the theoretical gradient was -0.036364. Thus the ratio of experimental gradient to theoretical gradient was:

Test B1: (exptl. gradient)/(theor. gradient) = 0.9722.

The adoption of the complete mixing model was therefore considered to be justified.

4.4.3 Surfactant Removal Experiments (B2 - B6)

A series of experiments was conducted to examine further the removal of surfactant during batch flotation. Refinements in the analytical technique used (see Section 3.7.2) enabled absolute values of surfactant concentration to be found rather than the relative values which had been obtained in the Group A experiments (see Section 2.5.2). Figure 27 illustrates the results obtained during Test B3, which are used as an example of the removal behaviour encountered. After the adsorption period it was found that the concentration of surfactant remaining in the pool had dropped from its initial value of 45 mg l^{-1} to 38.9 mg l^{-1}. When aeration was commenced the surfactant concentration

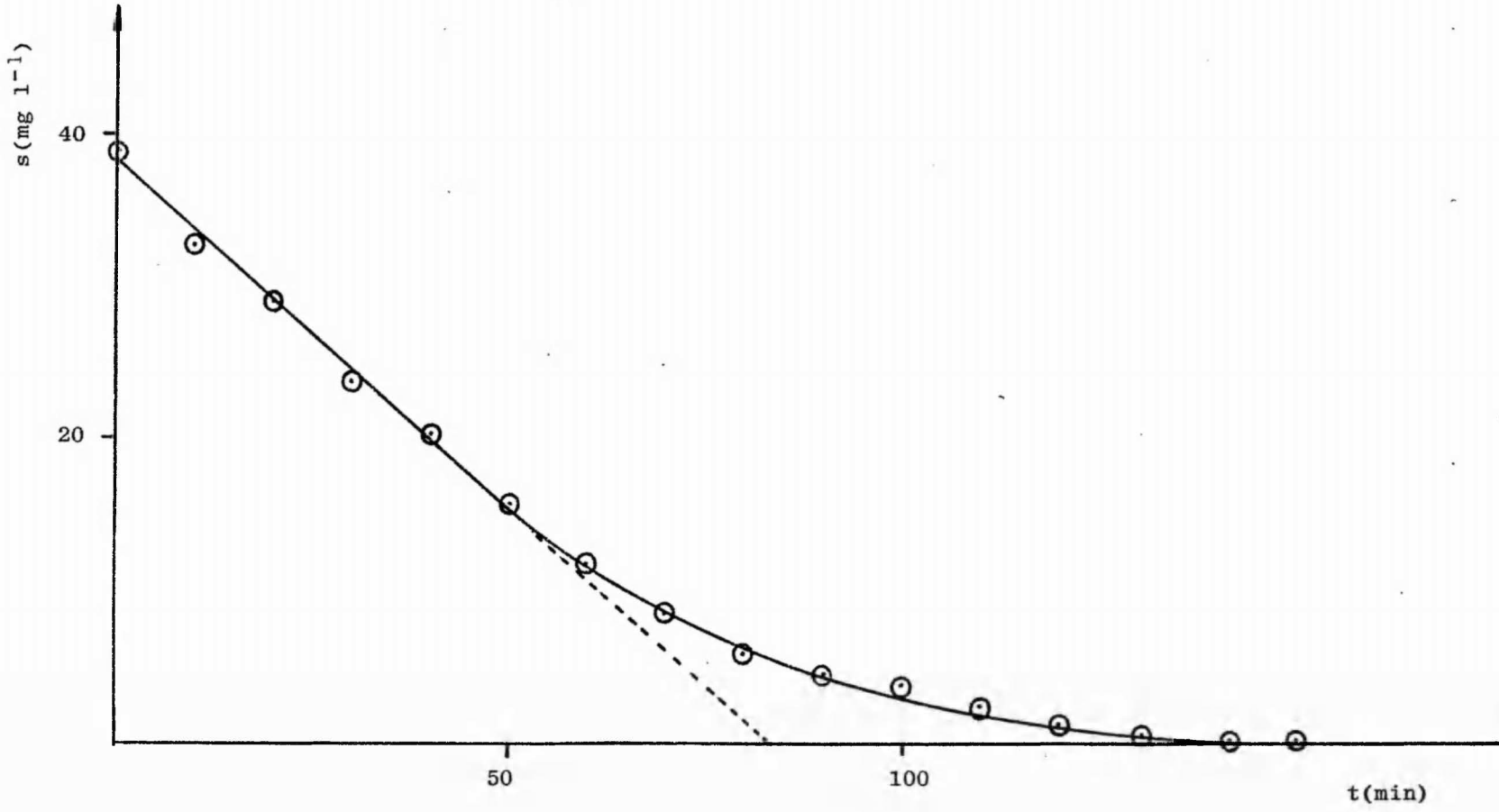


FIGURE 27: Typical Surfactant Removal vs. Time Curve from Batch Flotation Tests

decreased linearly with time until a level of approximately 15 mg l^{-1} was reached. After this point the concentration fell exponentially. It was clear that the original assumption of first-order kinetics was an oversimplification. It was therefore considered that whilst the first-order model:

$$\frac{ds}{dt} = -m_1 s \qquad \text{(XXXIV)}$$

was appropriate for concentrations below a critical level, the removal of surfactant above this level appeared to be more accurately described by the zero-order kinetic equation (see Section 2.4.1.1):

$$\frac{ds}{dt} = -m_0 \qquad \text{(XXXV)}$$

In equations (XXXIV) and (XXXV) the symbol s refers to the concentration of free surfactant, ie surfactant not adsorbed to particle surfaces.

Values for m_0 were obtained from the test results by a linear regression of s vs. t for experimental points lying above the critical surfactant concentration. Values of m_1 were obtained by a linear regression of $\ln(s/s_i)$ vs. t for points lying below this concentration. The results of these analyses are shown in Table 7.

TABLE 7: Calculation of Rate Constants m_0 and m_1 for Batch Tests

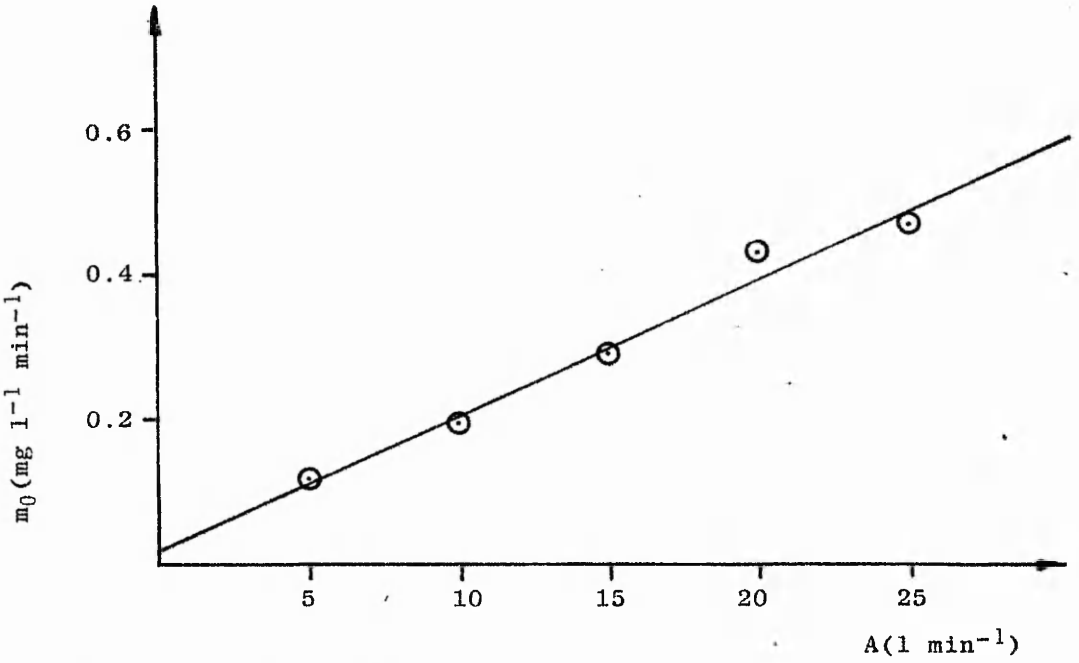
Test Number	A ($l\ min^{-1}$)	m_0 ($mg\ l^{-1}\ min^{-1}$)	m_1 (min^{-1})
B2	25	0.4647	0.06511
B3	20	0.4279	0.04877
B4	15	0.2897	0.04129
B5	10	0.1934	0.02804
B6	5	0.1173	0.02191

Figures 28.a and 28.b show the variation of the removal constants with air rate, A. Both relationships appeared to be linear, and could be defined by the following equations:

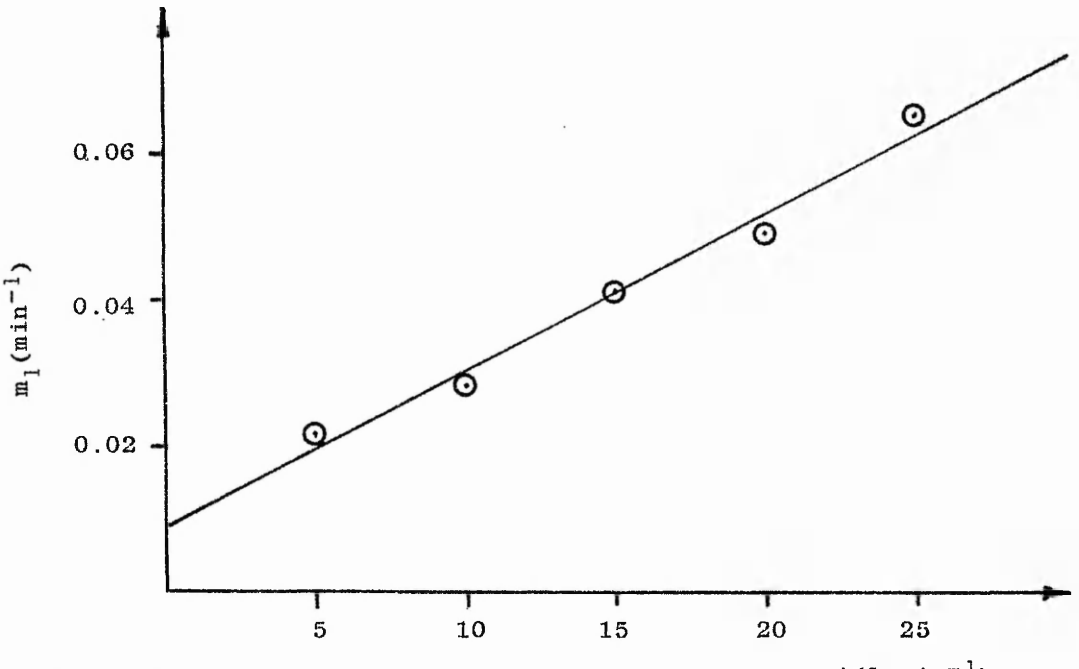
$$m_0 = 0.01859\ A + 0.01981 \qquad \text{(XXXVI)}$$

$$m_1 = 0.002143\ A + 0.008885 \qquad \text{(XXXVII)}$$

The coefficients of correlation for equations (XXXVI) and (XXXVII) were 0.9888 and 0.9887 respectively, and therefore



a. Surfactant Removal (Zero-Order)



b. Surfactant Removal (First-Order)

FIGURE 28: Relationship between Rate Constants and Air Rate

the assumption of linearity was considered to be justified.

4.4.4 Batch Flotation Tests (B7 - B32)

A series of experiments was carried out to find the effects of surfactant concentration on the removal of clay particles. A range of air rates was used.

The removal of clay was found in all cases to be best described by a first order expression, and the data from the tests was analysed by the same method as that described in Section 4.3.3. The results of this analysis are shown in Table 8, which shows the variation in the rate constant, k, with free surfactant concentration, s.

TABLE 8: Calculation of Rate Constant k for Batch Tests

Test Number	A ($l\ min^{-1}$)	s ($mg\ l^{-1}$)	k (min^{-1})
B7	25	23.1348	0.084045
B8	25	16.5175	0.090424
B9	25	9.9259	0.106186
B10	25	2.4307	0.117001
B11	25	1.1601	0.108590
B12	20	34.7922	0.053778
B13	20	24.9610	0.074183
B14	20	18.4814	0.085919
B15	20	11.8102	0.085541
B16	20	5.9477	0.101535
B17	20	3.8197	0.096035
B18	15	24.2633	0.044599
B19	15	16.3380	0.066610
B20	15	10.1311	0.069295
B21	15	5.1553	0.076163
B22	15	3.6164	0.070846
B23	10	24.1351	0.032675
B24	10	16.0559	0.039249
B25	10	10.1370	0.045774
B26	10	4.3090	0.048443
B27	10	2.1269	0.046581
B28	5	25.1354	0.018862
B29	5	18.5339	0.019631
B30	5	8.8388	0.027579
B31	5	3.5356	0.032001
B32	5	1.9611	0.029473

The average values for the intercept and coefficient of correlation for the analyses were 0.0116 and -0.9975 respectively, which were close to the theoretical values (0 and -1).

Figure 29 illustrates the dependence of k on s, for the various air rates used during the experiments. For each air rate the value of k increased sharply from zero over a narrow range of surfactant concentrations until a critical point was reached. Beyond this point k fell with increasing s; the critical point occurred at a free surfactant concentration of approximately 5 mg l^{-1}.

Figure 30 shows the relationship between k and air rate, A, for different surfactant concentrations. The points on this graph were derived from Figure 29 by selecting a particular value of s and reading off the corresponding value for k from each curve. There was a linear dependence between k and A, and linear regressions of the points in Figure 30. produced the following characteristic equations:

s = 5 mg l^{-1}: $k = 0.004348\ A + 0.00870$

s = 10 mg l^{-1}: $k = 0.004154\ A + 0.00719$

s = 15 mg l^{-1}: $k = 0.003868\ A + 0.00496$

s = 20 mg l^{-1}: $k = 0.=03598\ A + 0.00157$

The average coefficient of correlation for these equations was 0.9929, showing that an acceptable level of accuracy had been maintained.

It was observed during the tests that the concentration of surfactant in the pool dropped significantly from its initial value during the thirty minute adsorption period prior to flotation. The mass of surfactant adsorbed on to the particle surfaces during this period was calculated from this observed difference in concentrations.

$$\text{mass of surfactant adsorbed per unit mass of particles} = \frac{(s \text{ at start of adsorption period}) - (s \text{ at end of adsorp. period})}{(\text{concentration of particles, } c_i)}$$

The results of such a calculation are shown in Table 9 for each test.

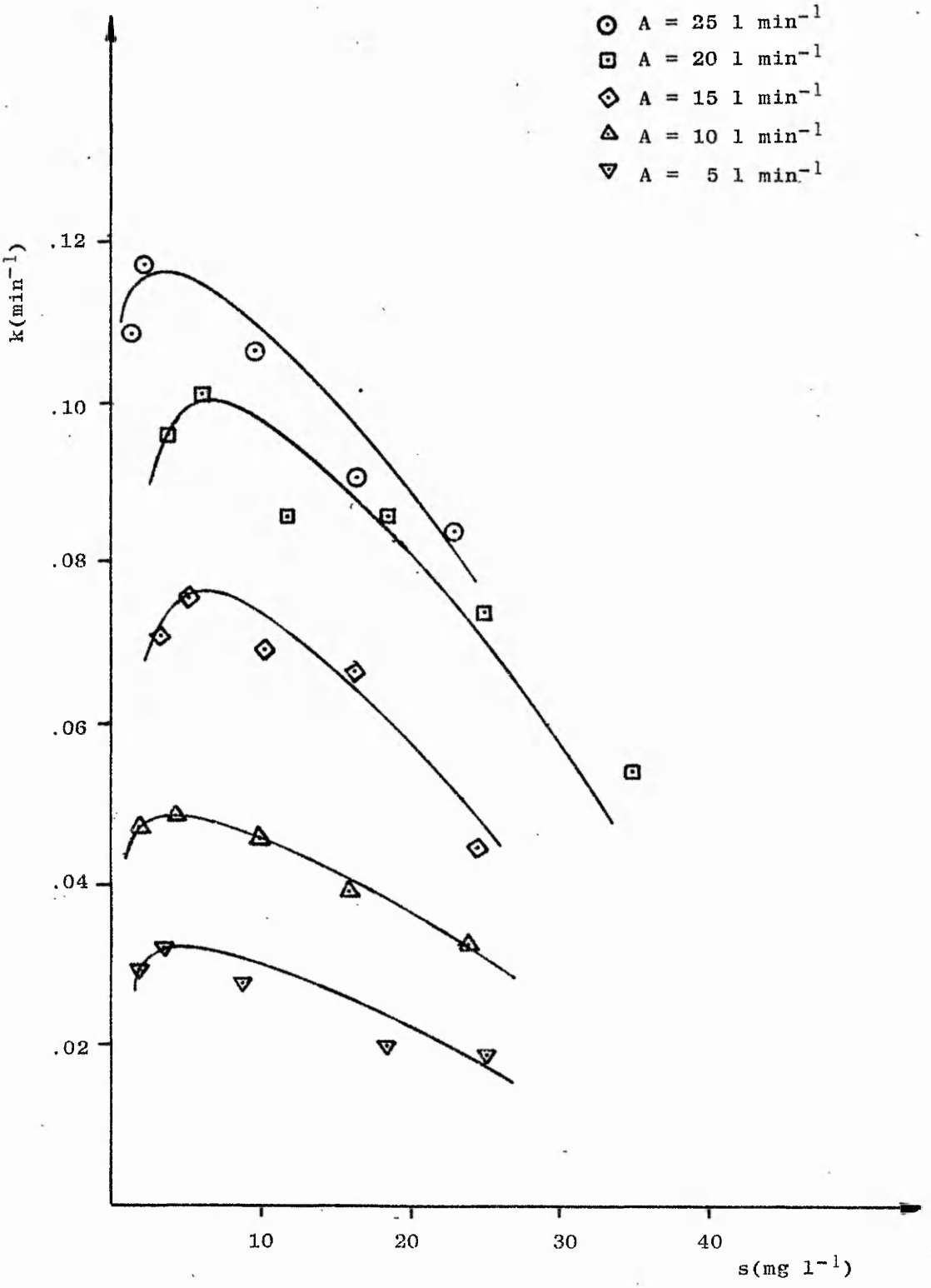


FIGURE 29: Relationship between Rate Constant and Surfactant Concentration

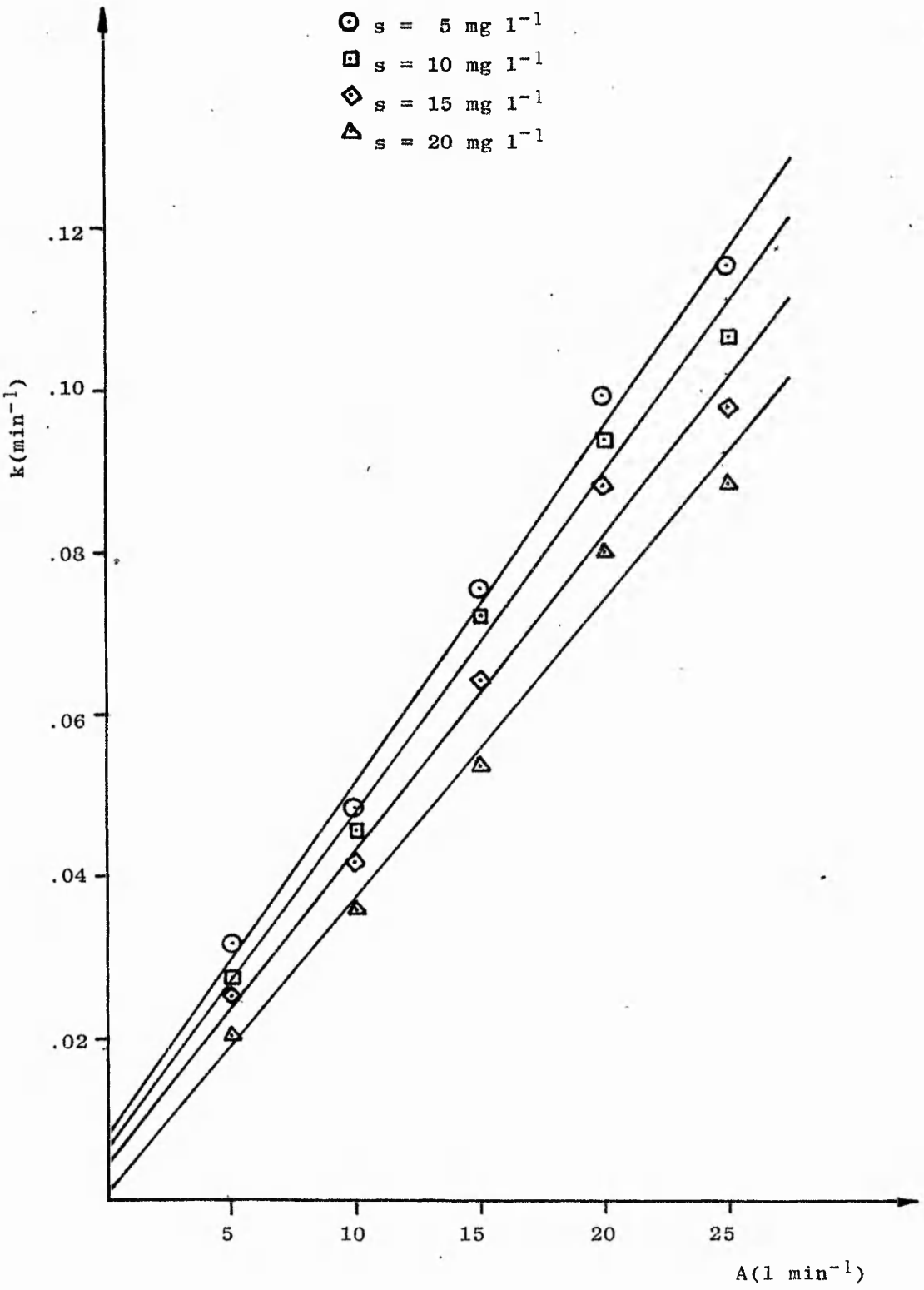


FIGURE 30: Relationship between Rate Constant and Air Rate (Derived from Figure 29)

TABLE 9: Surfactant Adsorption before Batch Tests

Test Number	(pre-adsorption) s (mg l^{-1})	(post-adsorption) s (mg l^{-1})	Mass adsorbed /unit mass ples. (mg mg^{-1})
B7	35.00	24.75	0.1025
B8	25.00	15.93	0.0907
B9	15.00	9.67	0.0533
B10	10.00	3.23	0.0677
B11	5.00	1.80	0.0320
B12	45.00	37.82	0.0718
B13	35.00	26.72	0.0828
B14	25.00	19.82	0.0518
B15	15.00	11.65	0.0335
B16	10.00	6.16	0.0384
B17	5.00	4.12	0.0088
B18	35.00	22.80	0.1220
B19	25.00	17.06	0.0794
B20	15.00	10.08	0.0492
B21	10.00	5.16	0.0484
B22	5.00	3.00	0.0200
B23	35.00	23.01	0.1199
B24	25.00	15.62	0.0938
B25	15.00	10.86	0.0414
B26	10.00	4.23	0.0577
B27	5.00	3.12	0.0188
B28	35.00	26.65	0.0835
B29	25.00	18.92	0.0608
B30	15.00	9.97	0.0503
B31	10.00	3.34	0.0666
B32	5.00	1.80	0.0320

An adsorption isotherm of surfactant on clay particles was constructed from the data in Table 9 by plotting the mass of surfactant adsorbed per unit mass of clay particles against the free surfactant concentration after the adsorption period had finished. This is shown in Figure 31. The line of best fit through the points was found to be

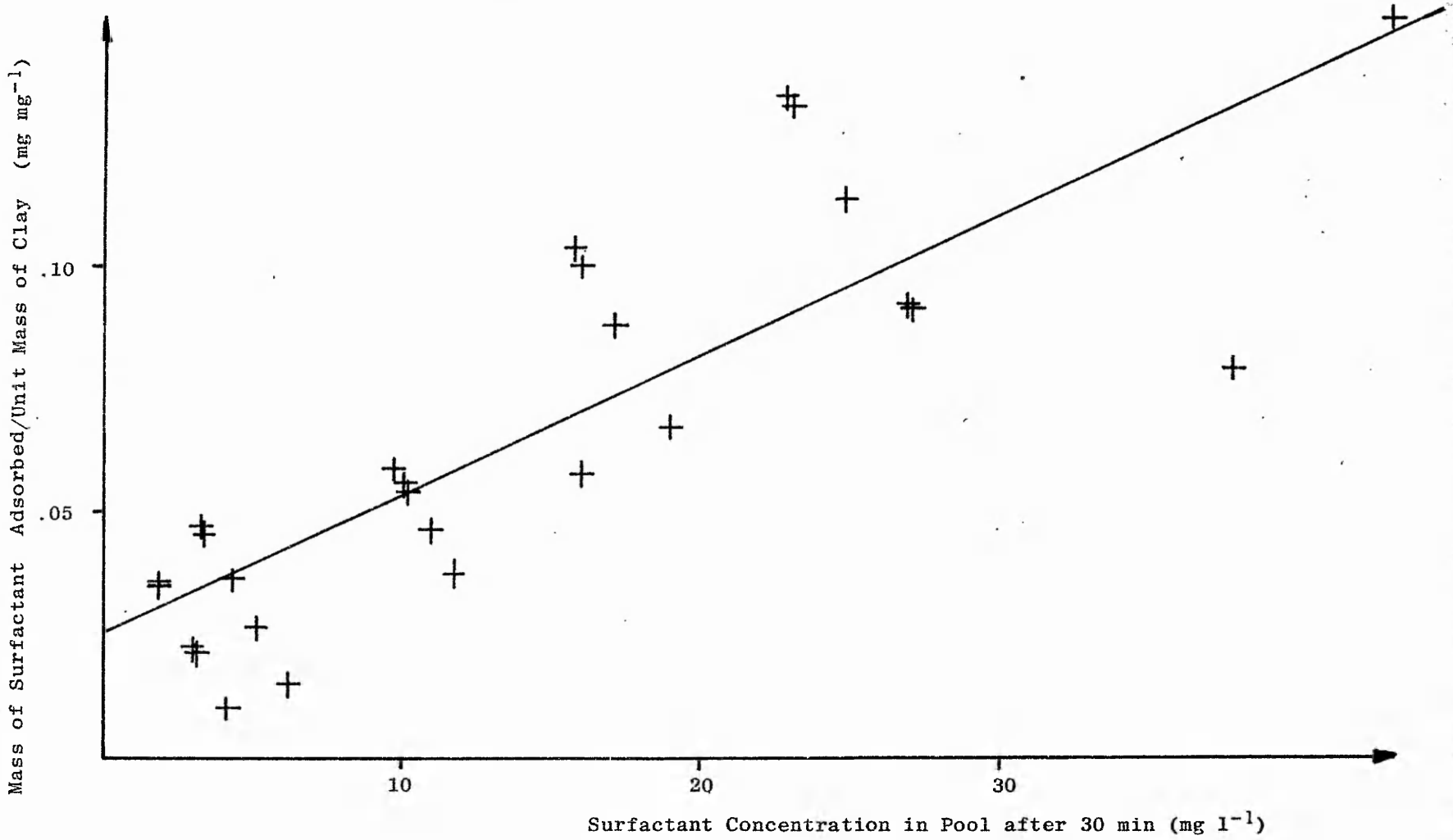


FIGURE 31: Adsorption Isotherm for Surfactant on Clay

characterised by the following:

Gradient = 0.002813

Intercept = 0.024957

Coefficient of Correlation = 0.7697

The low value obtained for the coefficient of correlation reflected the degree of scatter of the experimental data. Therefore only approximate predictions could be made regarding the initial loss of surfactant due to adsorption.

The alterations to the kinetic model of surfactant removal by flotation suggested by the results described in this section and in Section 4.4.3 necessitated modifications to the method used for ensuring constant surfactant concentrations during tests. In the region of zero-order removal, the mass of surfactant needed to be added per unit time was given by:

$S = Vm_0$

Thus in this region S was not determined by the surfactant concentration required. In the region of first order removal, S could be found from:

$S = Vm_1 s_i$

In this case s_i represents the surfactant concentration at the commencement of flotation (ie after the adsorption period had taken place). This was estimated from Figure 31, and was therefore subject to some error. To assess the significance of this error, the average value of surfactant concentration during each test was compared to the relevant value of s_i. The results of this analysis are shown in Table 10.

TABLE 10: Accuracy of Surfactant Dosing Technique (Batch Tests)

Test Number	s_i (mg l^{-1})	s(average) (mg l^{-1})	s/s_i
B7	24.75	22.60	0.9130
B8	15.93	16.71	1.0493
B9	9.67	10.01	1.0354
B10	3.23	2.16	0.6695
B11	1.80	0.95	0.5282
B12	37.82	33.78	0.8931
B13	26.72	24.38	0.9124
B14	19.82	18.03	0.9098
B15	11.65	11.86	1.0183
B16	6.16	5.91	0.9585
B17	4.18	3.76	0.9132
B18	22.80	24.75	1.0855
B19	17.06	16.10	0.9439
B20	10.08	10.15	1.0068
B21	5.16	5.16	1.0000
B22	3.00	3.82	1.2735
B23	23.01	24.51	1.0654
B24	15.62	16.20	1.0372
B25	10.86	9.90	0.9118
B26	4.23	4.34	1.0261
B27	3.12	1.32	0.4226
B28	26.65	24.63	0.9240
B29	18.92	18.40	0.9727
B30	9.97	8.46	0.8486
B31	3.34	3.60	1.0771
B32	1.80	2.02	1.1231

The average value of s/s_i for those tests where the critical surfactant level (assumed to be approximately 15 mg/l) was exceeded was 0.9737. In the region of first order surfactant removal the average value of s/s_i was 0.9208. It was concluded that whilst the uncertainty in predicing s_i had some detrimental effect on the accuracy of the method used

for ensuring a constant surfactant concentration during a test, values of s/s_i were close enough to unity to give an acceptably low level of experimental error.

4.5 ANALYSIS OF GROUP C EXPERIMENTS

4.5.1 Mixing Experiments (C1 - C4)

A series of experiments was carried out to assess the suitability of the mixing model described in Section 2.4.1.3.c for the characterisation of the regimes prevailing in the multi-stage flotation channel.

Figure 32 shows the experimental results obtained from the channel when it was divided into 1, 2, 3 and 6 stages. In addition, the response curves predicted from equations (XI) and (XII) are shown. The use of these equations was complicated by the experimental observation that after the insertion of baffles the volumes of the various compartments created were not exactly equal. This was due firstly to the difficulty of accurately positioning the baffles in the tank and secondly to the slight head loss that occurred across the baffles. In addition the total volume of the channel varied from test to test since the baffles themselves occupied a small volume (approxiately 2 l). The dimensions of individual compartments were therefore measured prior to each experiment and have been noted in Appendix 3.

It will be seen from Section 2.4.1.3.c that in the derivation of equations (XI) and (XII) it was assumed that each compartment of the multi-stage reactor was of equal volume. It was therefore necessary to evaluate the effects of the observed variations in volume on the results obtained from these equations if their use was to be justified. In order to do this a model of the mixing regime in a series of completely mixed cells of unequal volume was formulated (see Appendix 1.6). It was found by insertion of the relevant values for compartment volumes that there was no significant difference in the results obtained by either model for these values. When the discrepancy between volumes became large, however, significant deviations were encountered. Since the unequal volumes model involved a considerable amount of

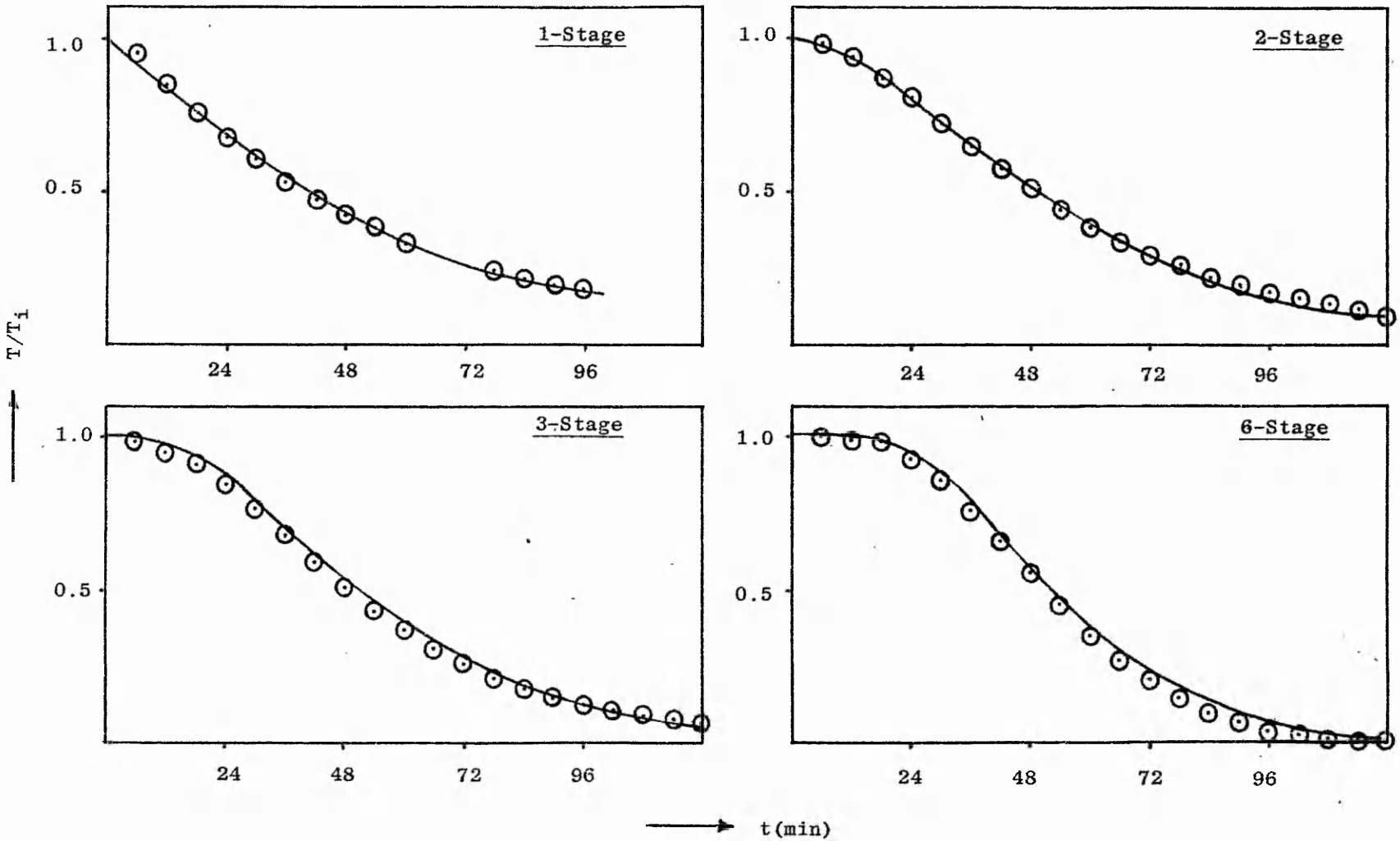


FIGURE 32: Mixing Experiments in Flotation Channel

additional computation, it was decided to use equations (XI) and (XII) to predict the theoretical tracer response curves. In each case the total retention time for the channel was calculated from the sum of the measured individual compartment volumes.

It will be seen from Figure 32 that the predicted curves correlated closely with the experimental points. In order to assess this numerically, a procedure similar to that used in Section 4.3.4 was adopted. A dimensionless parameter, F, defined as:

$$F = \frac{T/T_i \text{ (exptl.)}}{T/T_i \text{ (predicted}}$$

was found for all experimental points and the distribution of these values of F was subjected to a two-tailed t test. The distribution of F values is shown in Table 11 and in Figure 33.

TABLE 11: Frequency Distribution of Parameter F

Value of F	Frequency
1.45 - 1.35	0.0139
1.35 - 1.25	0.0139
1.25 - 1.15	0.0139
1.15 - 1.05	0.0972
1.05 - 0.95	0.5278
0.95 - 0.85	0.2778
0.85 - 0.75	0.0278
0.75 - 0.65	0.0139
0.65 - 0.55	0.0000
0.55 - 0.45	0.0139

The frequency distribution was found to have the following characteristics:

mean value of F , $\bar{F} = 0.9834$

S.D. of values of F from $\bar{F}$, $s_F = 0.1050$

total number of values of F, $n_F = 72$

The null and alternative hypotheses were formulated:

H_0 : $\bar{F} = \mu = 1$

H_1 : $\bar{F} \neq \mu$

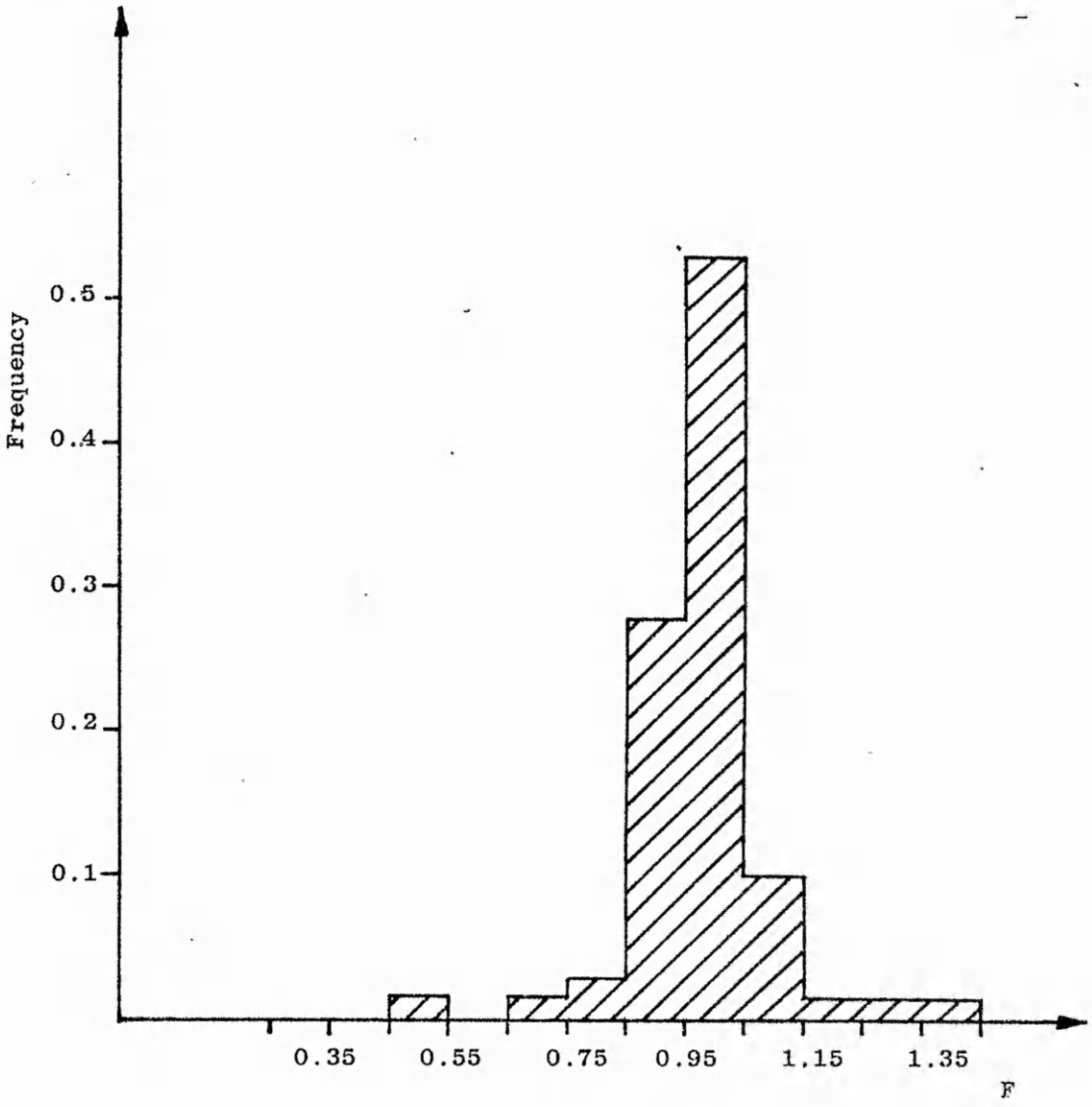


FIGURE 33: Frequency Distribution for Parameter F

A significance level of 0.1 was chosen and the number of degrees of freedom was 71. The test was two-tailed.
The value of t calculated from the frequency distribution was found:

$$t = \frac{\bar{F} - \mu}{s_F/\sqrt{n_F}} = \frac{0.9834 - 1}{0.1050/\sqrt{72}} = -1.3415$$

From statistical tables:
$t(0.05, 71) = 1.671$
Since $| -1.3415 | < 1.671$, H_0 was accepted. Thus it was concluded that equations (XI) and (XII) in Section 2.4.1.3.c adequately described the mixing regimes prevalent in the multi-stage flotation unit.

4.5.2 Surfactant Removal Experiments (C5 and C6)

The purpose of these experiments was to obtain values of the rate constants m_0 and m_1 for each of the air rates used for the remaining tests in Group C. These were then used to calculate the additions of surfactant necessary in order to achieve a constant surfactant concentration in later experiments.
In each case the surfactant removal curve followed the same pattern as that discussed in Section 4.4.3, and a similar analysis was applied in order to find the rate constants. This produced the values shown in Table 12.

TABLE 12: Calculation of Rate Constants m_0 and m_1 for Batch Tests

Test Number	m_0 (mg l^{-1} min^{-1})	m_1 (min^{-1})
C5	0.2594	0.02047
C6	0.4184	0.03881

The average coefficient of correlation for these calculations was -0.9961.

4.5.3 Batch Flotation Tests (C7 and C8)

These tests were conducted in order to find values of the rate constant, k, at each of the air rates used in subsequent experiments. The typical negative exponential removal curve was obtained in each case, from which k could be found from a plot of $\ln (c/c_i)$ vs. t. The values of k obtained are given in Table 13.

TABLE 13: Calculation of Rate Constant k for Batch Tests

Test Number	k (min^{-1})
C7	0.02537
C8	0.04038

The average coefficient of correlation for these tests was -0.9981.

The mean surfactant concentration during the two tests was 3.33 mg/l^{-1}

4.5.4 Continuous Flotation Tests (C9 - C16)

A series of experiments was carried out to examine the flotation process under the four different mixing regimes described in Section 4.5.1.

Figures 34 and 35 show the variations in relative clay concentration with time for each test. The curves in each plot refer to the relative concentrations in individual compartments and are numbered from the inlet end of the unit. The general trend was a decrease in the relative concentration in each compartment from its initial value of unity to some steady-state value. In order to test the applicability of equations (XVII) and (XVIII) as a description of the multi-stage flotation process, a statistical analysis was employed which was similar to that described in Section 4.3.4. A value of the dimensionless parameter G was found for every experimental point; the frequency distribution of these values is shown in Table 14 and in Figure 36.

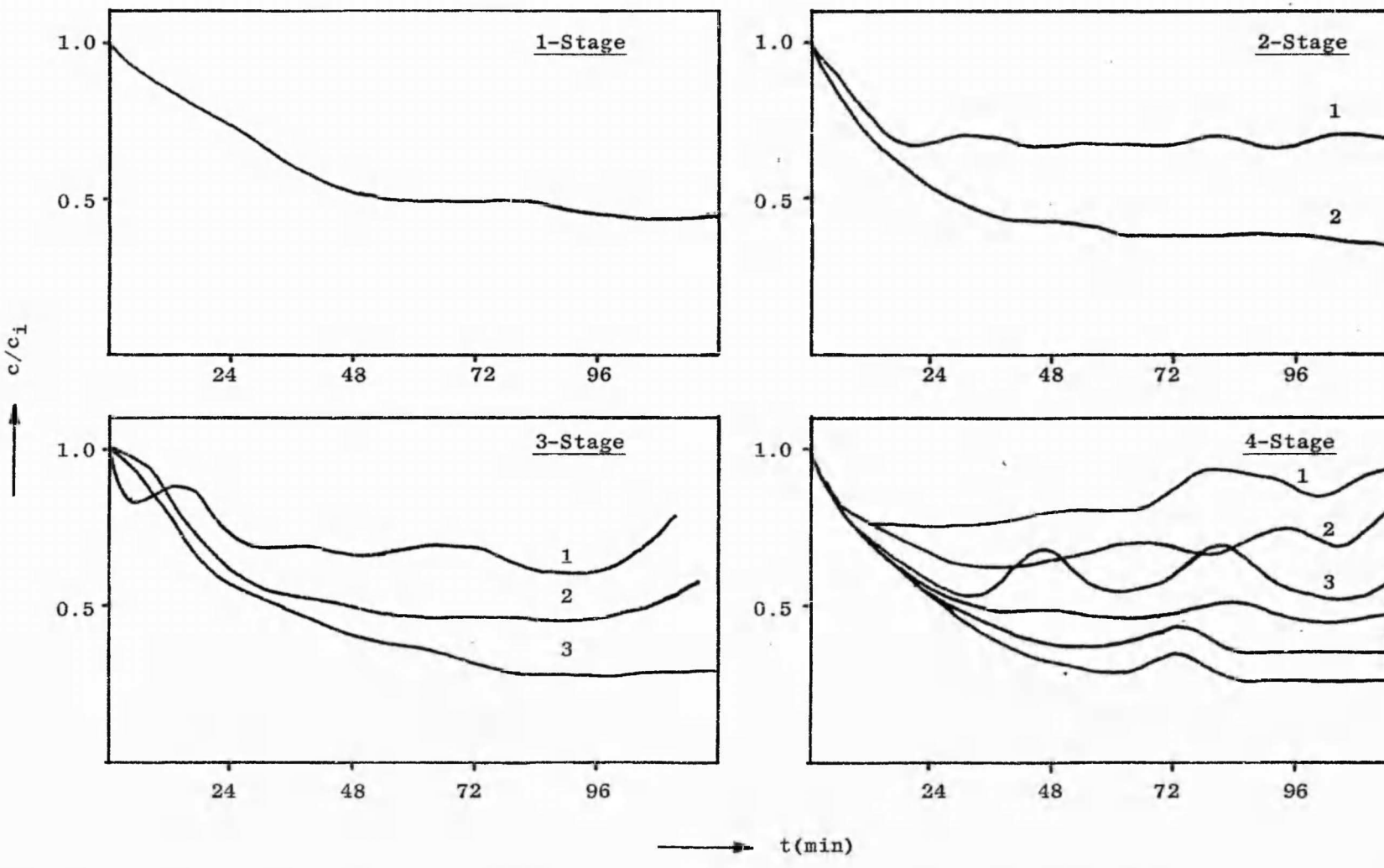


FIGURE 34: Continuous Flotation Tests in Flotation Channel (A = 30 l min^{-1})

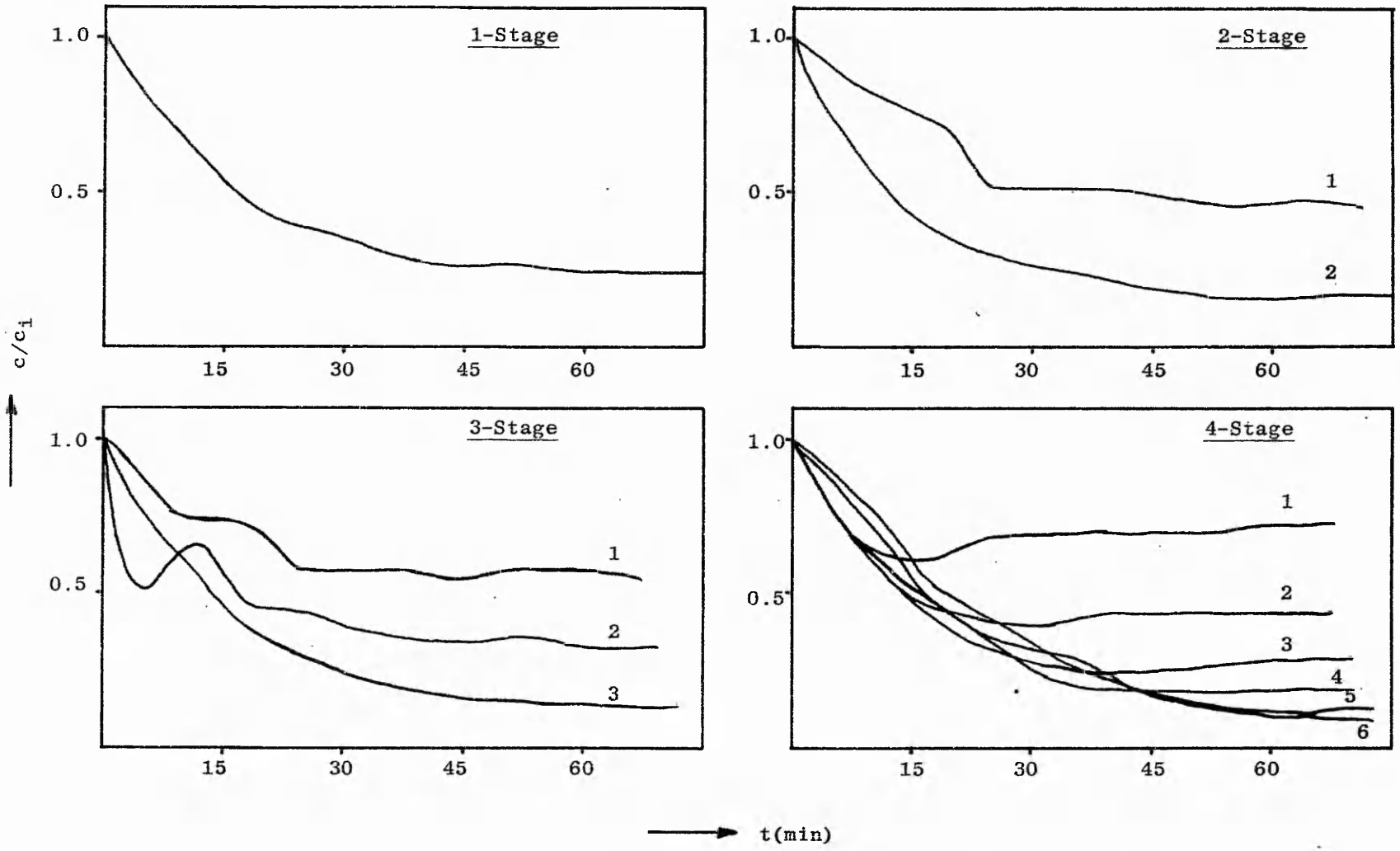


FIGURE 35: Continuous Flotation Tests in Flotation Channel (A = 50 l min^{-1})

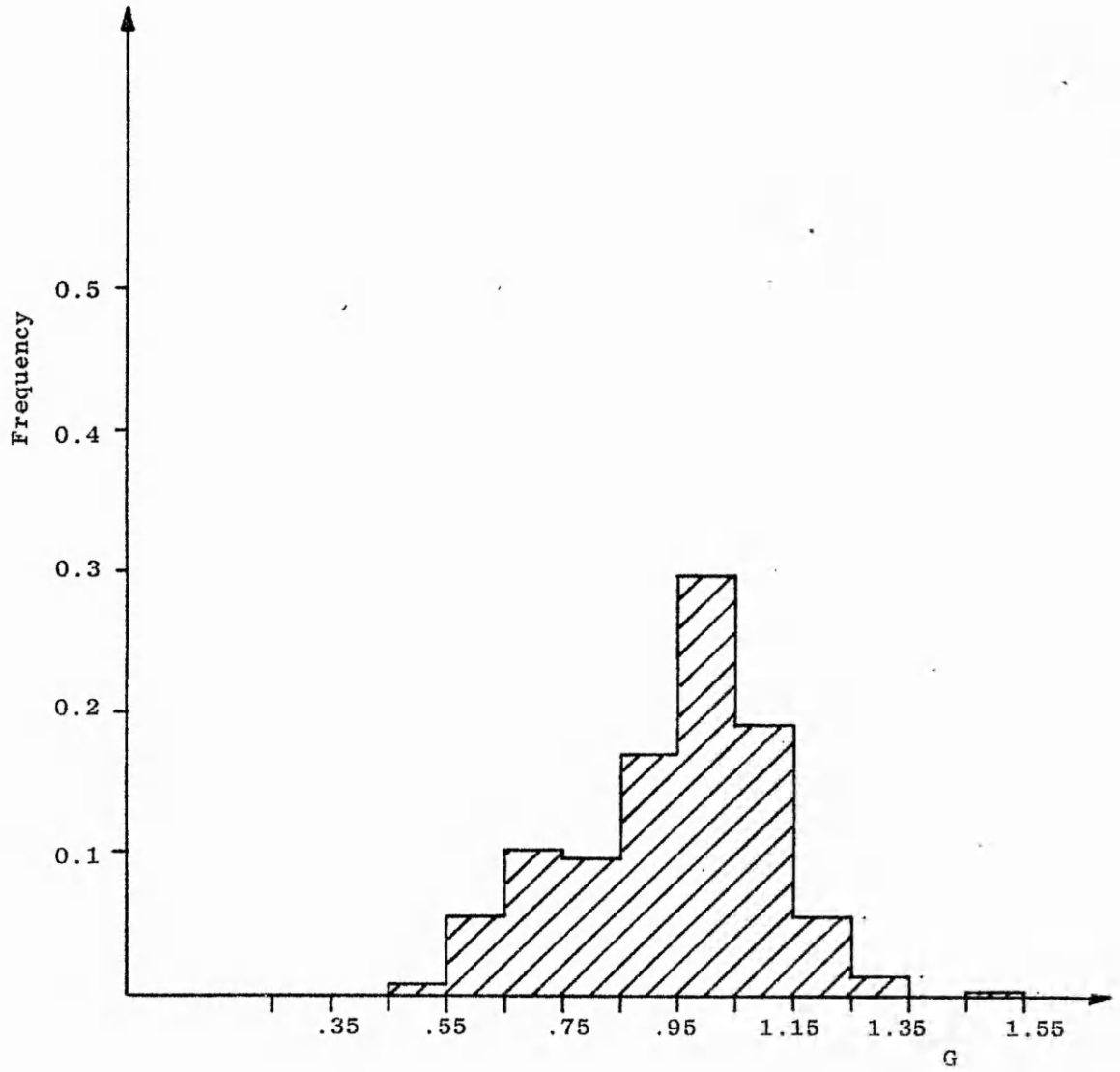


FIGURE 36: Frequency Distribution for Parameter G

TABLE 14: Frequency Distribution of Parameter G

Value of G	Frequency
1.55 - 1.45	0.0043
1.45 - 1.35	0.0000
1.35 - 1.25	0.0128
1.25 - 1.15	0.0556
1.15 - 1.05	0.1923
1.05 - 0.95	0.2992
0.95 - 0.85	0.1709
0.85 - 0.75	0.0983
0.75 - 0.65	0.1026
0.65 - 0.55	0.0556
0.55 - 0.45	0.0086

The following characteristics were calculated for this frequency distribution:

mean value of G , $\bar{G} = 0.9233$

S.D. of values of G from $\bar{G}$, $s_G = 0.1826$

total number of values of G, $n_G = 234$

The null and alternative hypothesis were formulated:

H_0: $\bar{G} = \mu = 1$

H_1: $\bar{G} \neq \mu$

The number of degrees of flotation was 233 and the test was two-tailed. A significance level of 0.1 was chosen. The value of t calculated from the frequency distribution was found:

$$t = \frac{\bar{G} - \mu}{s_G/\sqrt{n_G}} = \frac{0.9233 - 1}{0.1826/\sqrt{234}} = -6.425$$

From statistical tables:

$t(0.05, 233) = 1.645$

Since $| -6.425 | > 1.645$, H_0 was rejected. This conclusion held over the entire range of significance levels for which theoretical values of t were available. This suggested that equations (XVII) and (XVIII) did not adequately describe the multi-stage continuous flotation process.

The surfactant dosing technique employed during the experiments described in this section was similar to that adopted for

previous single-stage tests. The maintenance of a single constant surfactant concentration in all compartments of a multi-stage flotation unit would have required a separate dose to each individual compartment, and would have caused considerable operational difficulties. It was considered that these difficulties would have been magnified in any full-scale operation and therefore only a partial control of the surfactant concentration was attempted. The mass of surfactant required to be dosed into the unit was calculated from the relevant removal constant (see Section 4.5.2), assuming single-stage operation in all cases. It was found that during multi-stage operation this dosing procedure created a surfactant concentration gradient along the length of the flotation unit. This is shown in Table 15, which gives the mean surfactant concentration in each compartment of the unit during each experiment.

TABLE 15: Mean surfactant Concentrations in Channel Compartments

Test Number	Mean Surfactant Concentration, s ($mg\ l^{-1}$)					
C9	5.2248					
C10	5.5897			4.6411		
C11	4.9223		3.3754		2.2869	
C12	7.1082	6.4155	5.9701	4.7330	4.1887	3.5455
C13	3.8527					
C14	6.6654			2.7247		
C15	7.3572		3.9483		1.6076	
C16	8.3306	6.3801	2.7463	1.2487	1.5321	1.3976

It was observed that the relatively low surfactant concentrations present in the unit during these experiments caused a marked decrease in foam production. It was found that the foam layer only formed to a height of approximately 0.3 m, at which point its rate of production appeared to equal its rate of collapse. This resulted in a concentration of the floated particles in the upper layers of the foam. At the end of Test C11 a portion of this upper layer was removed

by scraping and a dry solids determination carried out. A container was weighed, filled with the foam sample, and then weighed again. This was then dried at 105°C in an oven for 2 hours and the container and contents weighed once more. The percentage of dry solids in the foam was then calculated from:

$$\% \text{ d.s.} = \frac{\text{(mass of container + contents after drying)} - \text{(mass of container)}}{\text{(initial mass of container + contents)} - \text{(mass of container)}} \times 100$$

$$= \frac{9.54 - 4.54}{12.03 - 4.54} \times 100 = 66.7\%$$

4.6 ANALYSIS OF GROUP D EXPERIMENTS

4.6.1 Surfactant Removal Experiments (D1 - D7)

Tests D1 - D4 were carried out in order to find the effects of column volumn, V, on the rate of removal of surfactant during batch flotation. The type of removal that occurred was found to be identical to that described in Section 4.4.3; an initially zero-order removal until a critical surfactant concentration was reached, followed by first-order removal. Values of m_0 and m_1 were found for each test. Experiments D5 and D6 were designed to test whether the concentration of clay particles in the flotation pool significantly affected surfactant removal. The initial clay concentration, c_i, was changed from its usual value of 100 mg l^{-1} to 200 mg l^{-1} for Test D5 and to zero for Test D6. Surfactant removal followed the usual pattern and values for m_0 and m_1 were calculated.

Finally, Test D7 was conducted under similar conditions to Test D1, but a naturally occurring river sediment was used instead of the refined kaolinite.

Values of m_0 and m_1 for these tests are shown in Table 16.

TABLE 16: Calculation of Rate Constants m_0 and m_1 for Batch Tests

Test Number	m_0 (mg l^{-1} min^{-1})	m_1 (min^{-1})
D1	0.5500	0.04266
D2	0.6344	0.04703
D3	0.8385	0.05154
D4	1.2193	0.07320
D5	0.5283	0.03579
D6	0.5829	0.04264
D7	0.5661	0.03115

Figure 37.a shows the variation of m_0 and m_1 with column volume, V, utilising the results of the analysis of Tests D1 - D4. It will be seen that the value of both types of rate constant decreased as V increased. A plot of m_0 and m_1 vs. 1/V (Figure 37.b) produced linear relationships with the following characteristic equations:

$m_0 = 62.5262\ (1/V) - 0.04119$

$m_1 = 2.7914\ (1/V) + 0.01558$

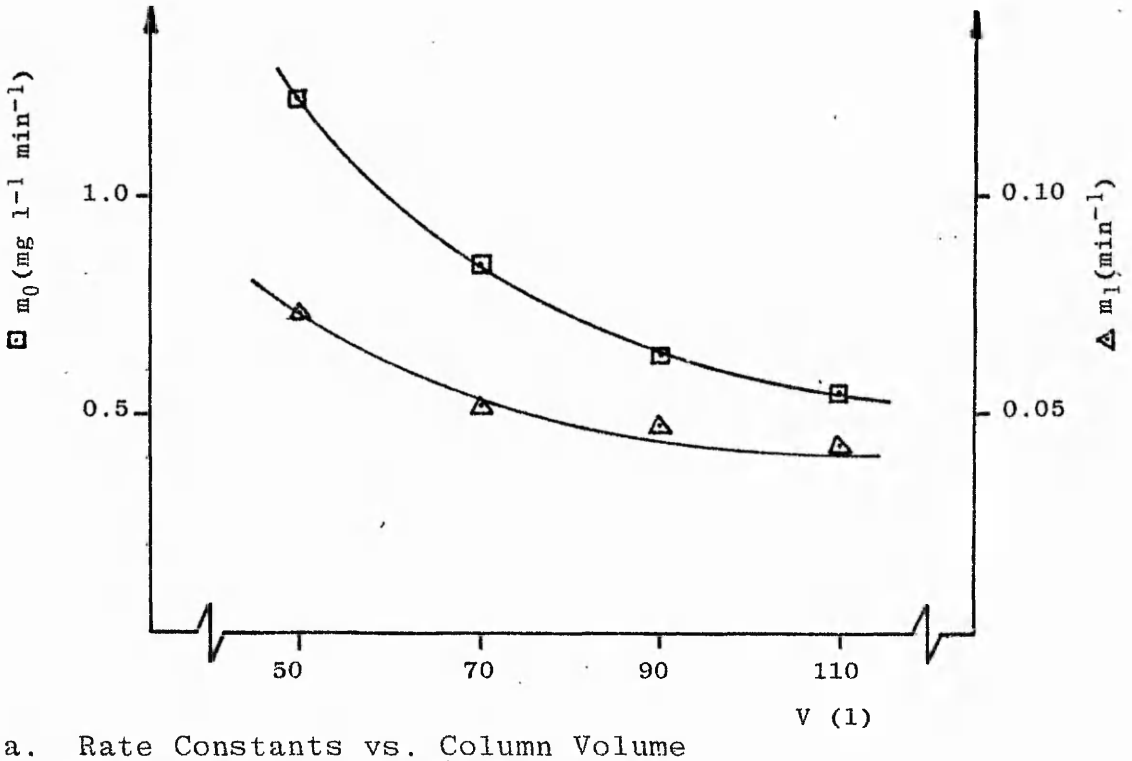
The correlation coefficients of these equations were 0.9978 and 0.9802 respectively.

Comparison of the rate constants calculated for Tests D1, D5 and D6 showed that clay concentration did not have a significant effect on surfactant removal.

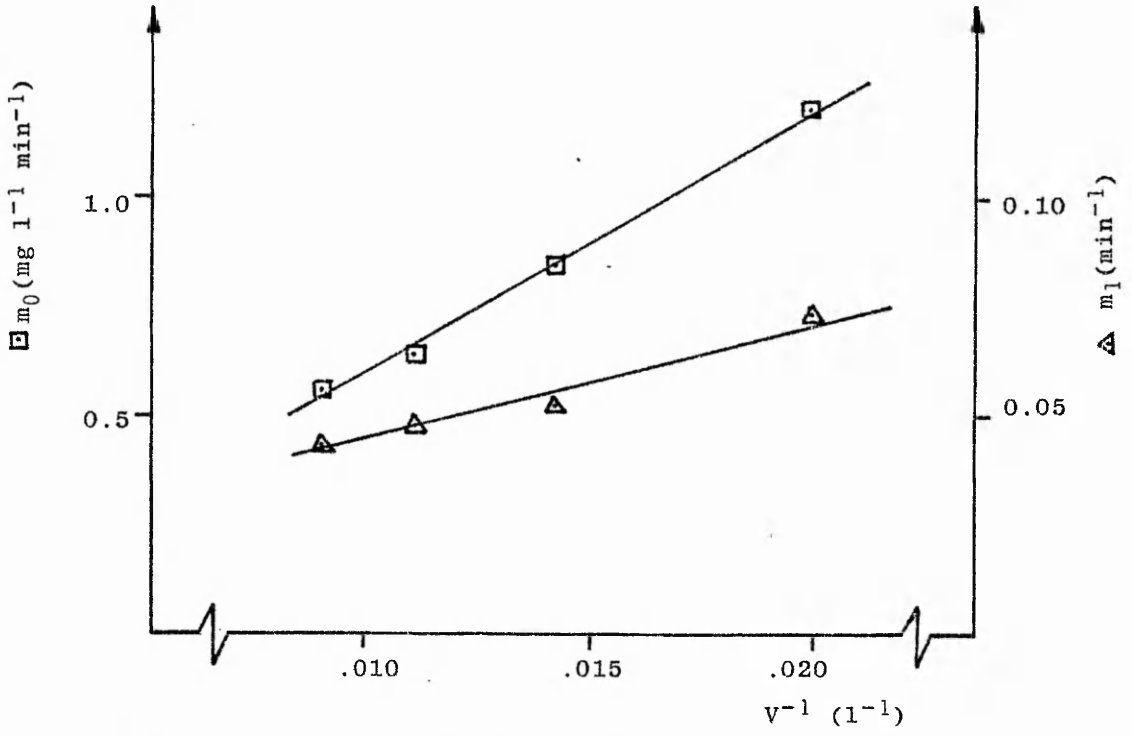
Comparison of Tests D1 and D7 showed that a change in the particles from graded kaolinite to river sediment did not result in any marked change in surfactant removal characteristics.

4.6.2 Batch Flotation Tests (D8 - D28 and D35)

Tests D8 - D19 and D24 - D28 were conducted in order to further investigate the effects of free surfactant concentration on the particle removal rate constant k. A range of surfactant concentrations was utilised at a single air rate. The removal of clay from the batch operated column followed the familiar first-order pattern. For each test the surfactant concentration was held steady by the addition



a. Rate Constants vs. Column Volume



b. Rate Constants vs. (Column Volume)$^{-1}$

FIGURE 37: Relationship between Rate Constants m_0 and m_1 and Column Volume

of concentrate, and the value of k was derived by linear regression of a plot of $\ln(c/c_i)$ vs. t. The results of Tests D8 - D19 are shown in Table 17. Tests D24 - D28 were a similar set of experiments using an initial clay concentration of 200 mg l^{-1}, so that the effects of c_i on the behaviour of k with s could be determined. The results of these tests are shown in Table 18.

TABLE 17: Calculation of Rate Constant k for Batch Tests

Test Number	s (mg l^{-1})	k (min^{-1})
D8	83.3779	0.005263
D9	68.2156	0.007152
D10	51.5114	0.013232
D11	42.0028	0.023775
D12	33.5222	0.039449
D13	25.3843	0.057716
D14	17.2463	0.085880
D15	13.3346	0.095819
D16	7.1526	0.116067
D17	4.6218	0.100529
D18	3.0975	0.100716
D19	1.4577	0.067187

TABLE 18: Calculation of Rate Constant k for Batch Tests

Test Number	s (mg l^{-1})	k (min^{-1})
D24	39.8060	0.042265
D25	31.9641	0.062696
D26	23.2372	0.089508
D27	15.0909	0.109399
D28	8.2683	0.125241

Figure 38 illustrates the results of both sets of tests. In each case the value of k decreased as s increased, except at low surfactant concentrations where k was subject to a rapid decrease as s was reduced. This behaviour was the same for

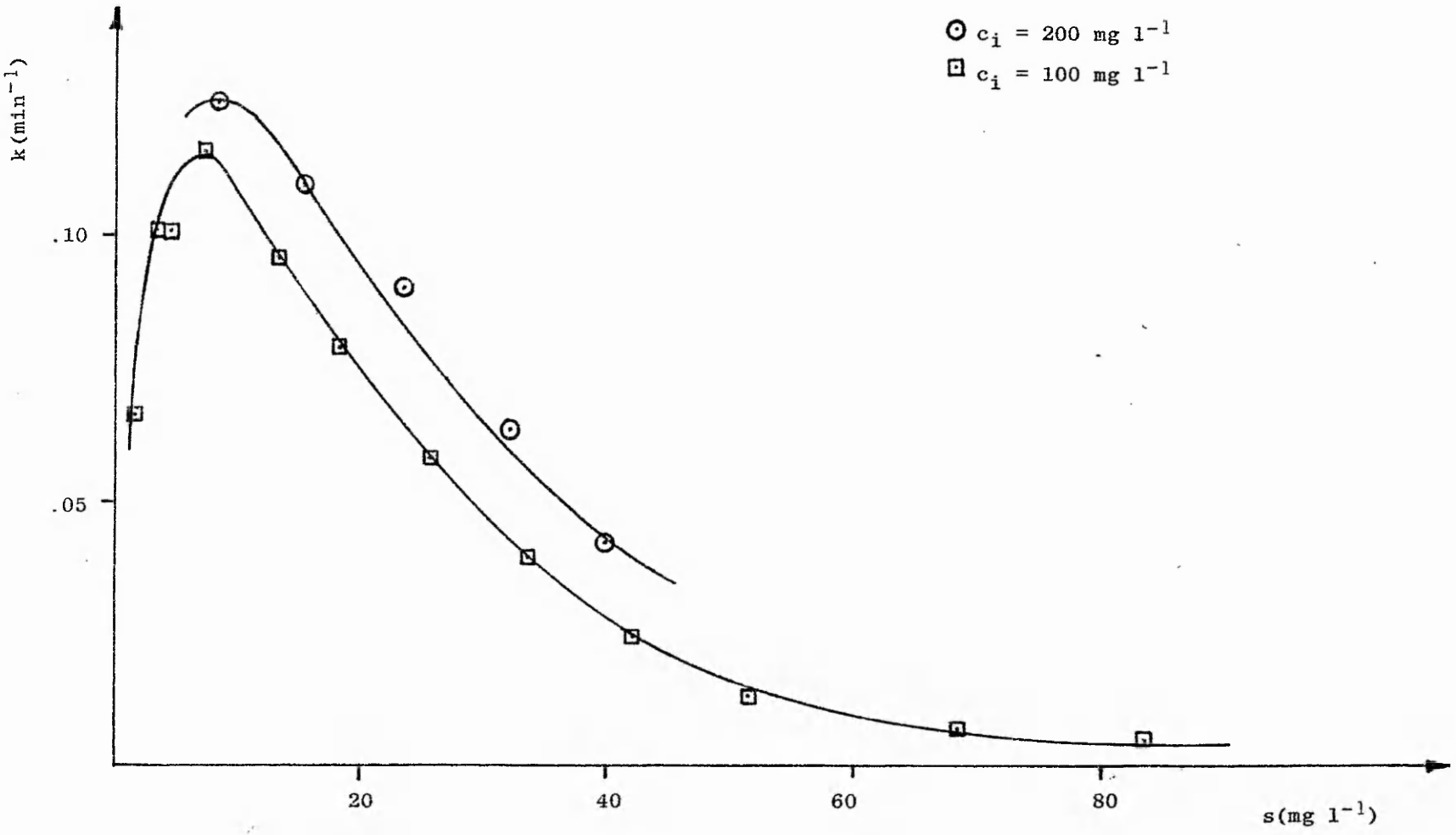


FIGURE 38: Relationship between Rate Constant k and Surfactant Concentration

both sets of tests, but numerical values of k were somewhat higher for the second set.

Adsorption isotherms were calculated for each initial clay concentration in a similar manner to that used in Section 4.4.4. These are shown in Tables 19 and 20.

TABLE 19: Surfactant Adsorption before Batch Tests

Test Number	(pre-adsorption) s ($mg\ l^{-1}$)	(post-adsorption) s ($mg\ l^{-1}$)	Mass adsorbed /unit mass ples. ($mg\ mg^{-1}$)
D8	100.0	87.8324	0.121676
D9	80.0	70.3572	0.096428
D10	60.0	52.6250	0.073750
D11	50.0	43.3734	0.066276
D12	40.0	34.1219	0.058781
D13	30.0	25.6413	0.043587
D14	20.0	16.6467	0.035330
D15	15.0	12.4351	0.025649
D16	10.0	8.4518	0.015482
D17	7.5	5.2684	0.022316
D18	5.0	3.0975	0.019025
D19	2.5	1.4577	0.010423

TABLE 20: Surfactant Adsorption before Batch Tests

Test Number	(pre-adsorption) s ($mg\ l^{-1}$)	(post-adsorption) s ($mg\ l^{-1}$)	Mass adsorbed /unit mass ples. ($mg\ mg^{-1}$)
D24	50.0	41.8101	0.040950
D25	40.0	33.9682	0.030159
D26	30.0	23.9500	0.030250
D27	20.0	16.0073	0.019964
D28	10.0	7.4537	0.017315

Figure 39 shows the two isotherms produced. The relationship between the relative mass of surfactant adsorbed and the surfactant concentration after the thirty minute adsorption period was approximately linear in each case and was characterised by the following equations:

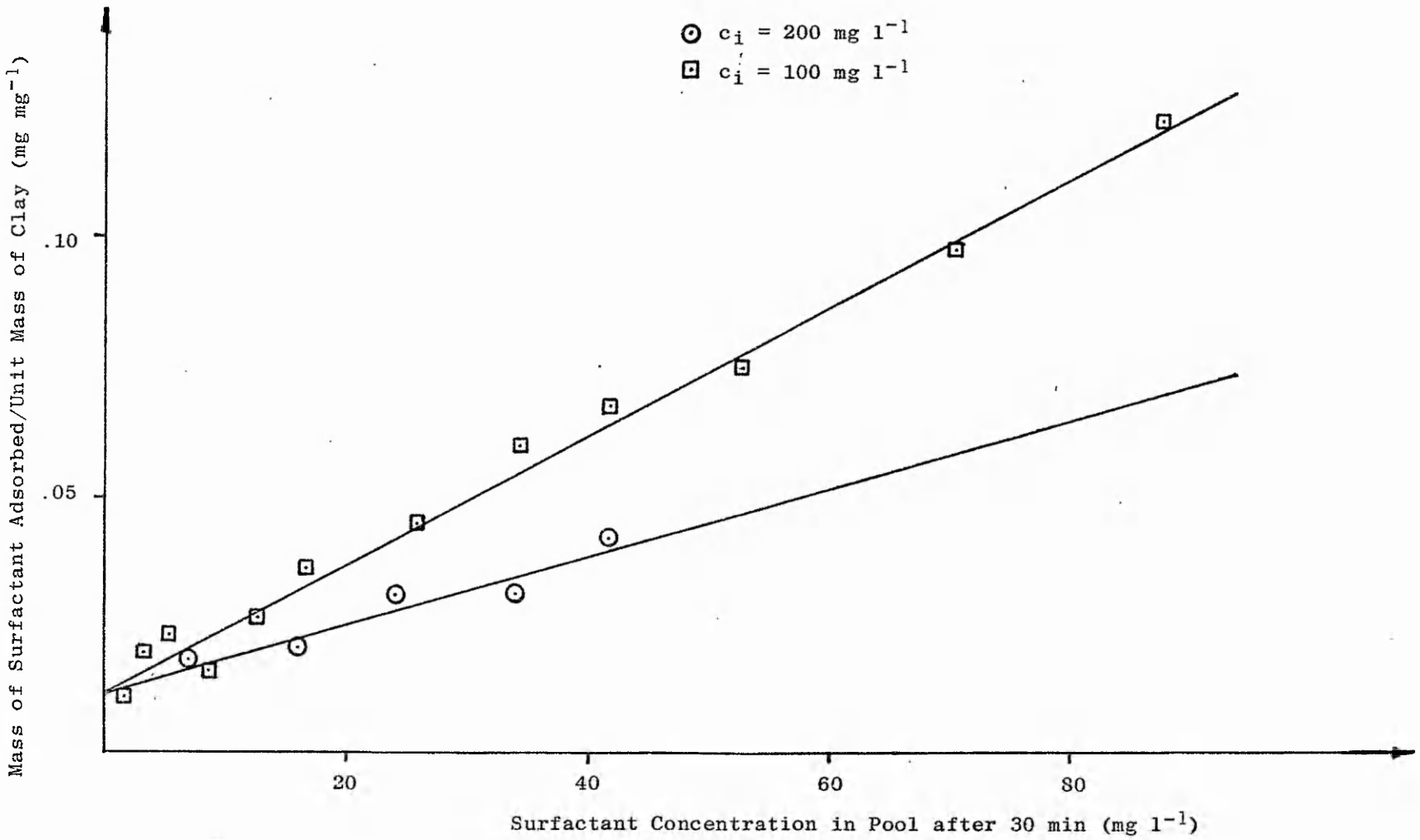


FIGURE 39: Adsorption Isotherms for Surfactant on Clay

c_i = 100 mg l^{-1}: relative mass adsorbed = 0.001233 s + 0.011927
c_i = 200 mg l^{-1}: relative mass adsorbed = 0.0006567 s + 0.011549
The correlation coefficients associated with these equations were 0.9950 and 0.9548 respectively.
In an ideal system the mass of surfactant adsorbed per unit mass of clay should not depend on the prevailing clay concentration, and a single isotherm would be produced. The observed disparity of the isotherms at different clay concentrations was not investigated further, but a suggested reason is the tendency for surfactants to act as coagulating agents. If larger agglomerates were to be formed then the particle surface area available for adsorption would be reduced.
Tests D20 - D23 were performed in order to examine the effect of column volume on the batch removal of clay. First order rate constants were derived, and are shown in Table 21.

TABLE 21: Calculation of Rate Constant k for Batch Tests

Test Number	V (l)	k (min^{-1})
D 20	110	0.069224
D 21	90	0.064983
D 22	70	0.061305
D 23	50	0.061734

The differences between these values of k were not judged to be significant. It was therefore concluded that column volume had no effect on the removal of clay particles by flotation. This is in direct contrast to the removal behaviour of surfactant (see Section 4.6.1).
Test D35 was carried out to check the similarity between results obtained in the flotation column and those obtained in the flotation channel. Since the plan area of the column was 0.1 m and that of the channel was 0.6 m , an air rate through the column of 5 l min^{-1} was considered to be comparable with an air rate of 30 l min^{-1} through the channel. Other pool conditions were identical to those for Test C7. The first order rate constant found from Test D35 was 0.02195

and that found from Test C7 was 0.02537. The mean surfactant concentrations were 2.6996 mg l^{-1} and 2.5292 mg l^{-1} respectively.

In order to test the accuracy of the surfactant dosing technique, an assessment similar to that described in Section 4.4.4 was carried out on the results of the tests. This is shown in Table 22.

TABLE 22: Accuracy of Surfactant Dosing Technique (Batch Tests)

Test Number	s_i (post-adsorption) (mg l^{-1})	s (average) (mg l^{-1})	s/s_i
D8	87.83	81.15	0.9239
D9	70.36	67.14	0.9543
D10	52.63	50.95	0.9683
D11	43.37	41.32	0.9526
D12	34.12	33.22	0.9736
D13	25.64	25.26	0.9850
D14	16.65	17.55	1.0540
D15	12.44	13.78	1.1085
D16	8.45	6.50	0.7694
D17	5.27	4.30	0.8159
D18	4.09	2.60	0.6358
D19	1.87	1.25	0.6672
D20	-	-	-
D21	20.52	17.91	0.8729
D22	20.66	18.87	0.9136
D23	19.83	17.77	0.8961
D24	41.81	38.80	0.9281
D25	33.97	30.96	0.9115
D26	23.95	22.88	0.9554
D27	16.01	14.63	0.9141
D28	7.45	8.68	1.1639
D35	4.41	1.84	0.4181

The average value of s/s_i was 0.8944, indicating a reasonable level of accuracy. It was found that the maintenance of a steady surfactant concentration during a test was more

difficult at low levels than at higher levels. This was probably caused by inaccuracies in the prediction of the value of s_i due to scatter on the adsorption isotherm.

4.6.3 Continuous Flotation Test (D29)

This test was carried out in order to assess the effect of variations in feed rate on the performance of a continuous flotation system.

Figure 40 shows the variation in feed rate, v, over the duration of the test. A stepped feed pattern was created by adjustment of the flowrate to the unit.

Figure 40 also shows the variation in the relative clay concentration in the effluent stream with time. An extension of the analysis described in Section 2.4.1.4 enabled a removal curve to be predicted (see Appendix 1.7), and this is also shown. In order to assess the correlation between observed and predicted results, a value of the dimensionless parameter G was calculated for each point of time. The frequency distribution of these values is shown in Table 23.

TABLE 23: Frequency Distribution of Parameter G

Value of G	Frequency
0.95 - 1.05	0.12
1.05 - 1.15	0.24
1.15 - 1.25	0.44
1.25 - 1.35	0.20

The following characteristics were calculated for this frequency distribution:

mean value of G , $\bar{G} = 1.1813$

S.D. of values of G from $\bar{G}$, $s_G = 0.08519$

total number of values of G, $n_G = 25$

The null and alternative hypotheses were formulated, and a value of t was calculated:

H_0: $\bar{G} = \mu = 1$

H_1: $\bar{G} \neq \mu$

$$t = \frac{\bar{G} - \mu}{s_G/\sqrt{n_G}} = \frac{1.1813 - 1}{0.08519/\sqrt{25}} = 10.6426$$

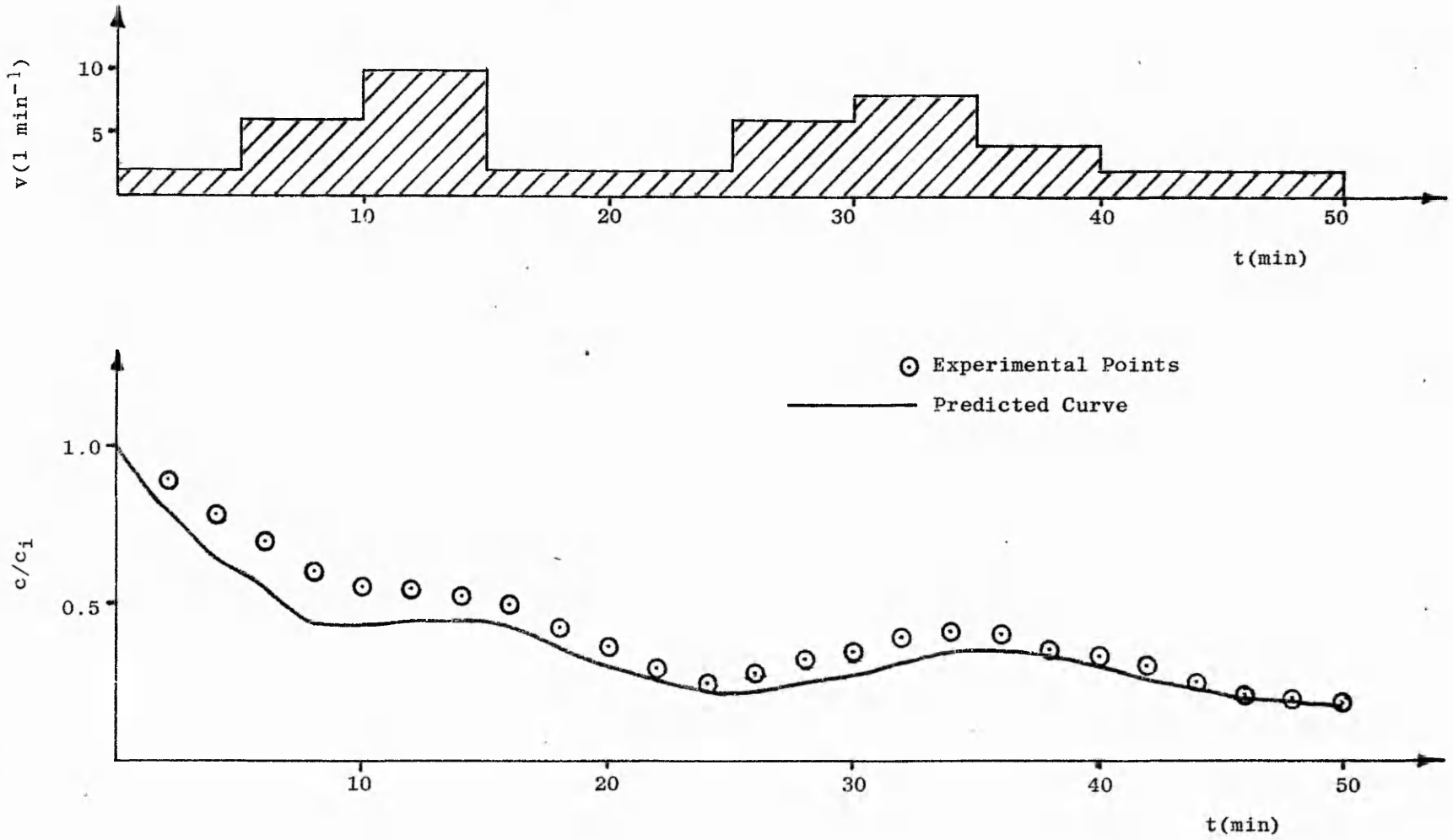


FIGURE 40: Continuous Flotation Test under Conditions of Variable Flow Rate

This value of t was greater than all the available theoretical values, and it was therefore necessary to reject H_0. The surfactant dosing technique adopted for this experiment differed slightly from the usual procedure. The mass of surfactant per unit time necessary to ensure conditions of constant surfactant was given by equation (XXIV), Section 2.4.3.2:

$$B = Vm_1 s_i + vs_i$$

The value of B varied during the course of this experiment since v was not constant. The required dose was therefore administered in two parts. The surfactant demand specified by the first term on the R.H.S. of the equation remained constant during the test, and was injected into the column at a constant rate. The surfactant demand specified by the second term was variable and dependant on v. It was found that this could be conveniently administered by initially setting the surfactant concentration in the holding tank at s_i. Variations in demand were then automatically provided for.

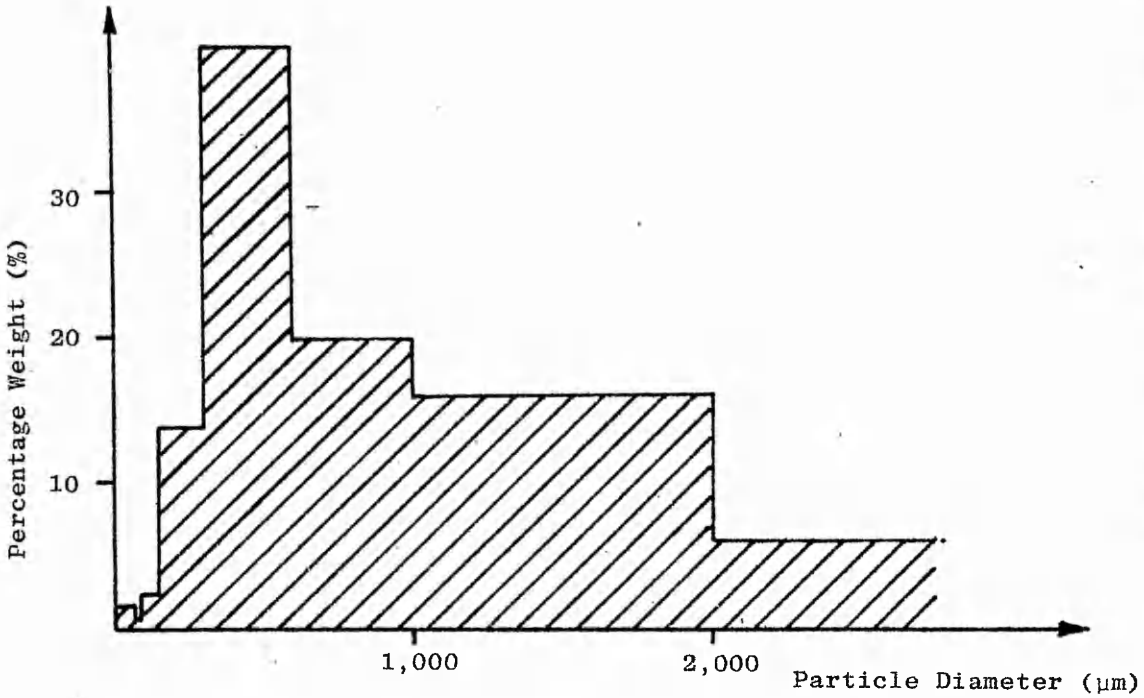
The average value of s/s_i measured during the test was 1.0505, demonstrating the level of accuracy achieved by the method to be satisfactory.

4.6.4 Experiments using the Model Sediment (D30 - D34)

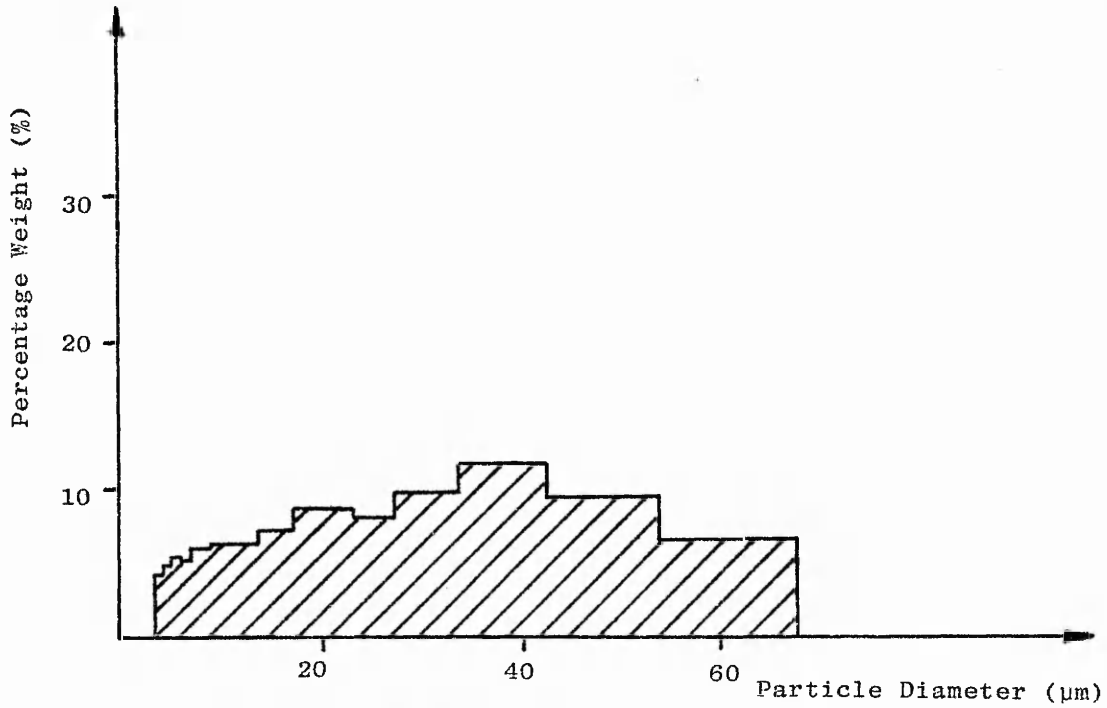
These experiments were conducted in order to give a preliminary demonstration of the applicability of flotation kinetics to the removal of naturally occurring materials. The choice and preparation of a suitable material for this investigation has been described in Section 3.3.1.

Figure 41 illustrates the results of Tests D33 and D34, which were carried out in order to find the distribution of particle sizes in the model sediment used. Figure 41.a shows the distribution of particle sizes above 75 μm diameter, which was determined by seiving. Figure 41.b shows the distribution below this level, determined using a Coulter Counter. These distributions indicate that the model sediment was a well-graded material.

In order that turbidity could be used as an analytical



a. Sieve Analysis of Fraction above 75 µm



b. Coulter Counter Analysis of Fraction below 75 µm

FIGURE 41: Particle Size Analysis of Model Sediment

technique during subsequent flotation experiments, the turbities of known concentrations of model sediment were found and a calibration curve was plotted. This is shown in Figure 42. It will be seen that the relationship between turbidity and solids concentration was approximately linear, and the following characteristic equation was found by linear regression:

$\tau = 0.2603\ c + 1.5424$

The correlation coefficient for this equation was 0.9990, showing the assumption of linearity to be justified. Two flotation experiments were conducted using the model sediment; a batch test to find the rate constant at a particular set of operational conditions, followed by a continuous test under identical conditions. The results of these experiments are shown in Figure 43. The removal of material by batch flotation was approximately first-order, and a linear regression of $\ln(c/c_i)$ vs. t yielded a value for the rate constant of 0.07174 min^{-1}. The coefficient of correlation associated with this analysis was 0.9974.

The value of the rate constant found from the batch test was used to predict the removal of material under continuous flotation conditions. In Figure 43.b this is compared with the experimental data obtained. It will be seen that a good correlation between predicted and observed behaviour only occurred when steady-state had been reached. This was confirmed by finding values for the dimensionless parameter G and subjecting the resultant distribution of values to a t-test. The value of t calculated from this procedure was in excess of any of the available theoretical values.

4.6.5 Mixing Experiments (D36 and D37)

The purpose of these experiments was to induce a degree of segregation into the mixing regime of the flotation column. Preliminary trials, using simple longditudinal baffles, were unsuccessful and complete mixing took place at all air rates. In an attempt to overcome this the column was filled with a honeycomb packing of the type used in air conditioning systems (see Figure 44). Tracer response tests were

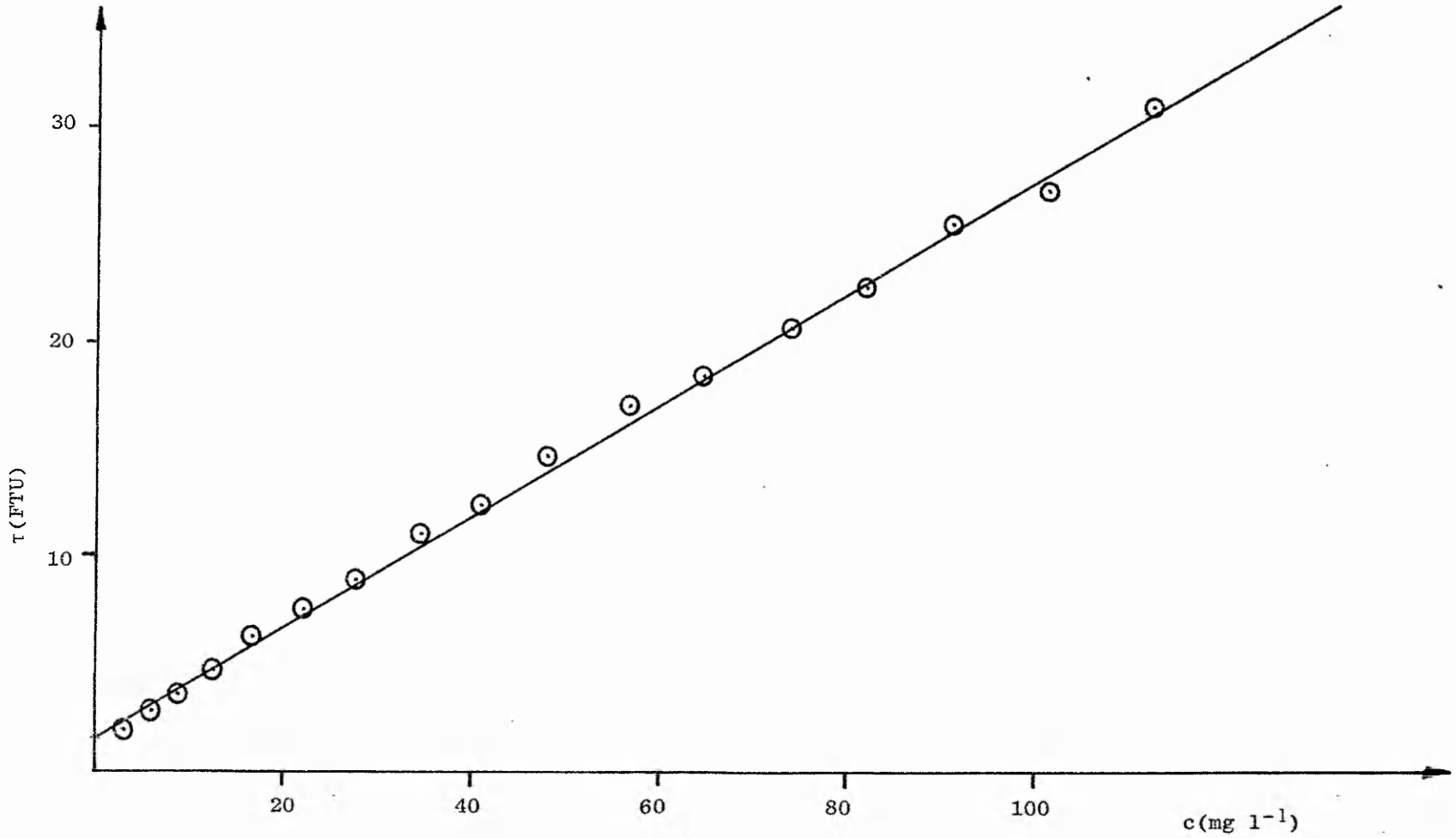
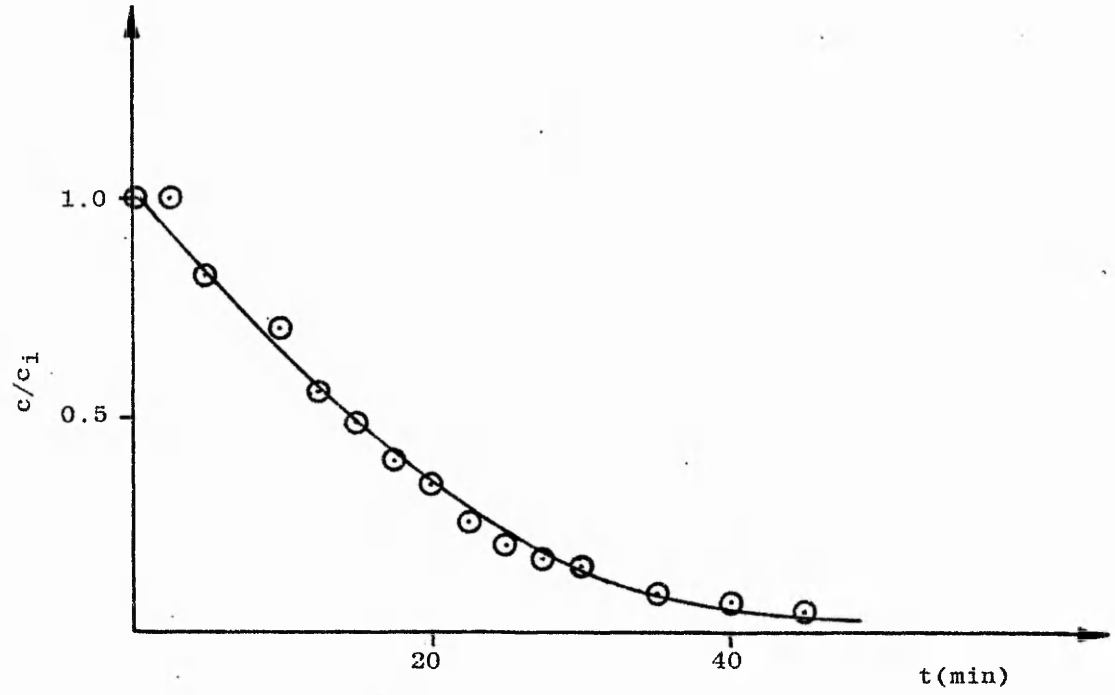
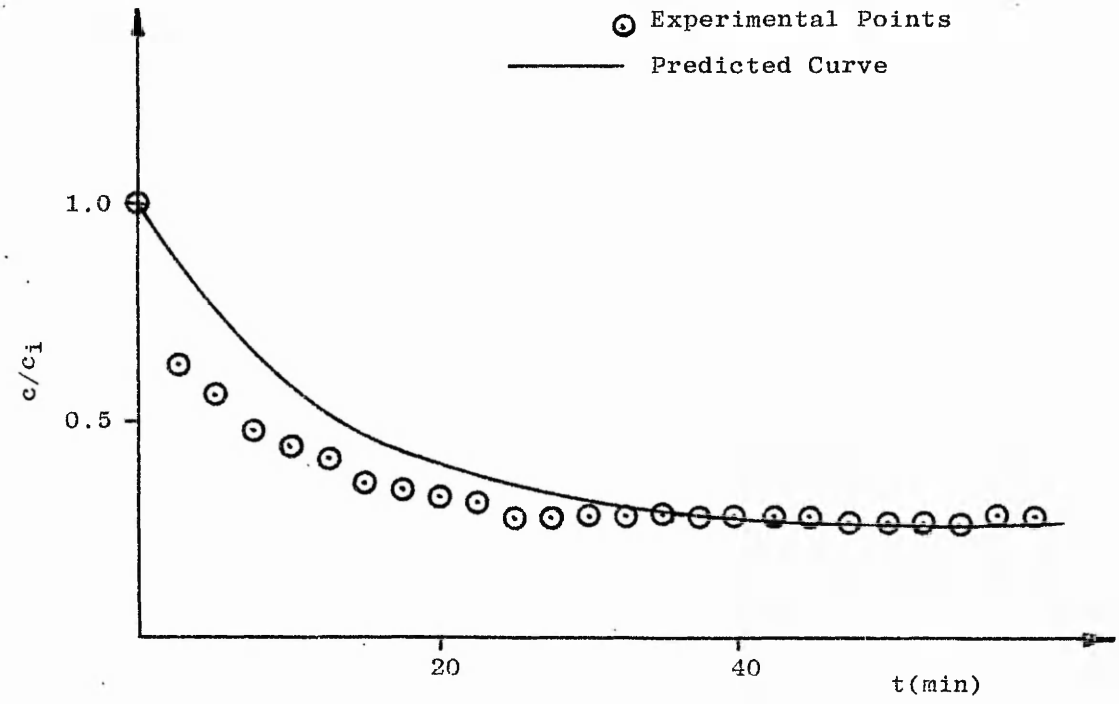


FIGURE 42: Turbidity Calibration for Model Sediment



a. Batch Test



b. Continuous Test

FIGURE 43: Flotation Experiments using Model Sediment

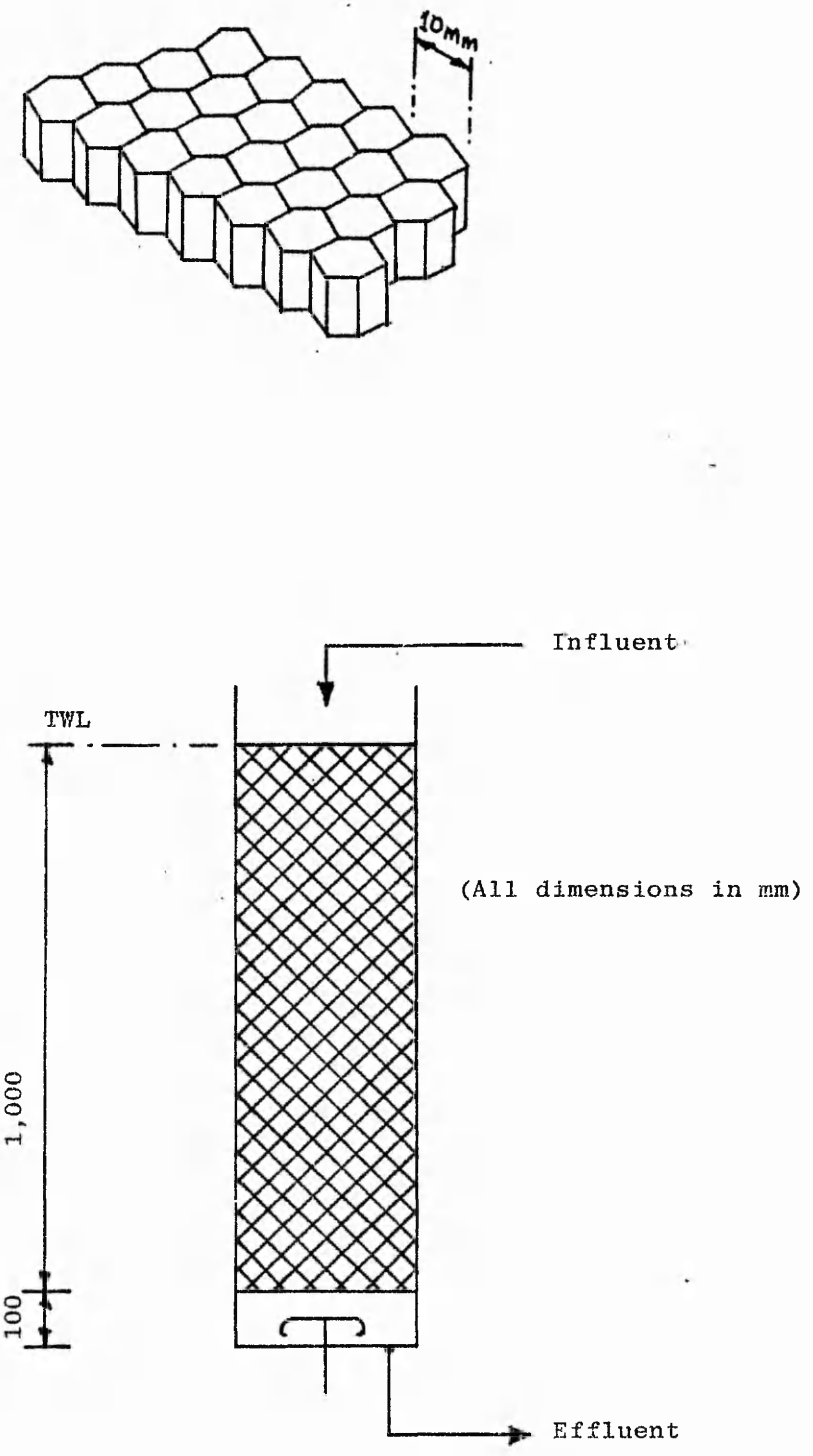


FIGURE 44: Details of Column Packing

then carried out at the maximum and minimum air rates used for flotation. In both cases the response curves closely fitted the complete mixing model, and a plot of $\ln(T/T_i)$ vs. t yielded the following:

D36: $\ln(T/T_i) = -0.04738\ (t) - 0.1292$

D37: $\ln(T/T_i) = -0.04936\ (t) - 0.0165$

The correlation coefficients associated with these equations were -0.9959 and -0.9993 respectively.

The value of the residence time of the column was approximately 20 min, since a flowrate of 5 l/min was used and the volume of the column (less the packing) was approximately 100 l. The theoretical value of the gradient of the log plots was therefore given by:

$$\text{gradient} = -\frac{1}{R} = -0.05$$

The closeness of the experimentally determined gradients to this figure provided firm evidence that the prevailing mixing regime was of the completely mixed type. It was therefore concluded that the insertion of the packing had not resulted in any segregation in the column.

4.7 DISCUSSION

The nomenclature used in the discussion which follows is illustrated in Figure 45.

4.7.1 Removal of Surfactant by Flotation

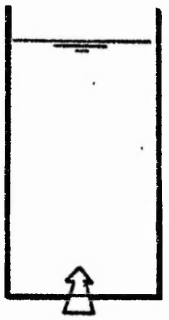
Previous investigations into the removal of surfactants by flotation (see Section 2.4.3.2) resulted in the conclusion that first-order kinetics adequately described the process. The observations made during the present study have shown that this is an oversimplification. An analysis is presented below which attempts to clarify the situation by considering the processes taking place in a flotation cell which affect surfactant removal. This analysis concerns the concentration of free surfactant in the flotation pool, ie surfactant which has not been adsorbed on to particle surfaces and is therefore present in the bulk solution in ionic form. The applicability of first-order kinetics to flotation systems has been considered by workers in the field of

Flotation Cell

V = Cell Volume
h = Pool Depth
a = Cell Plan Area

Clay Particles

c = Particle Concentration
c_i = Initial Particle Concentration
x_1 = Number of Particles in Unit Mass of Clay
k = First-Order Rate Constant for Particle Removal



Surfactant

s = Surfactant Concentration
s_i = Initial Surfactant Concentration
m_0 = Zero-Order Rate Constant for Surfactant Removal
m_1 = First-Order Rate Constant for Surfactant Removal

Air Bubbles

A = Air Rate
x_2 = Number of Bubbles in Unit Volume of Gas
b = Surface Area of One Bubble (Average)
u = Upward velocity of Bubble (Average)

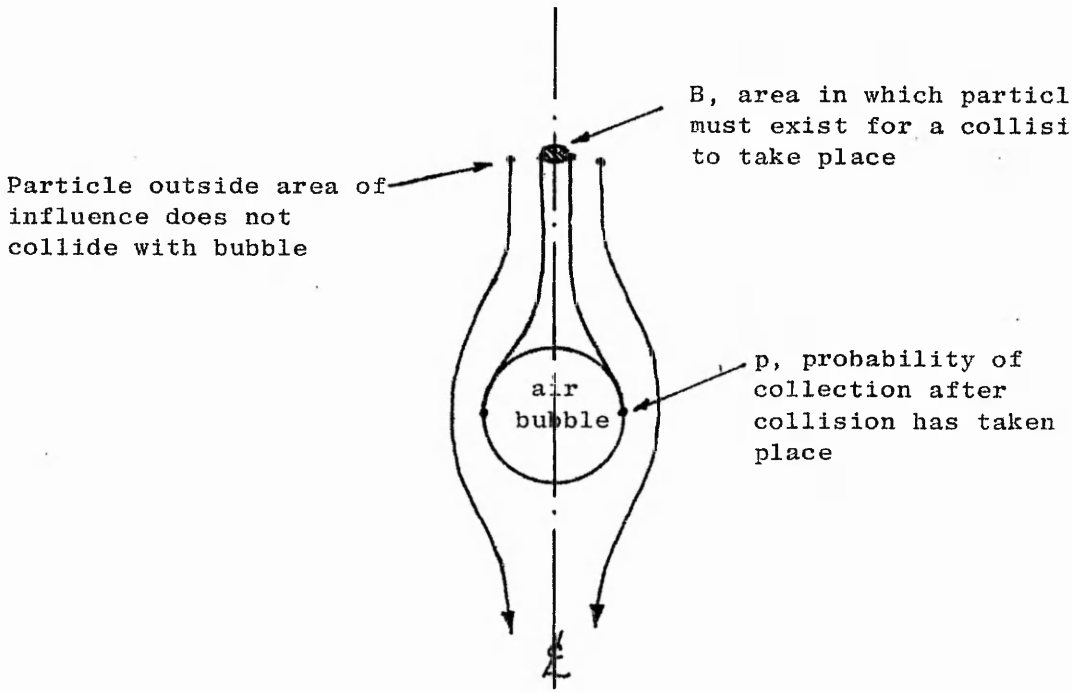


FIGURE 45: Nomenclature used in the Theoretical Development

particulate flotation to be an indication that some form of productive collision mechanism is responsible for collection. This is unlikely to be the mechanism responsible for the collection of molecular sized species such as surfactants, which are probably removed by a process of adsorption on to the surface of the air bubbles. The a priori assumption of first-order kinetics for surfactant removal cannot therefore be justified in this case.

If surfactant molecules are removed from the flotation cell by surface adsorption, the drop in free surfactant concentration over a period of time represents the mass of surfactant adsorbed on to the surfaces of all the bubbles which have passed through the pool during that period. Thus if in an incremental time period dt a drop in pool surfactant concentration of -ds is recorded, the following mass of surfactant will have been adsorbed:

Total mass of surfactant adsorbed = -ds V

The total area of bubble surface generated during the incremental time period dt is given by:

Total area of bubble surface generated = $Ax_2b\ dt$

Thus the mass of surfactant adsorbed per unit area of bubble surface is given by:

$$\text{Mass adsorbed per unit area} = -\frac{V}{Ax_2b} \cdot \frac{ds}{dt} \qquad \text{(XXXVIII)}$$

Provided air rate, bubble size distribution and liquid pool volume remain constant over the period of a test, an adsorption isotherm for surfactant on air bubbles may be derived from a plot of the R.H.S. of equation (XXXVIII) against s. If a mathematical expression can be found to describe the isotherm, it may then be used to evaluate the relationship between s and t.

It is not possible to construct the particular adsorption isotherm described above since the parameters x_2 and b were not measured during the experimental programme. However, a plot of -ds/dt vs. s gives a related curve since x_2 and b are both assumed constant, and this suffices for the purposes of the theoretical development. Such a plot is illustrated in Figure 46.a, using data from Test D6.

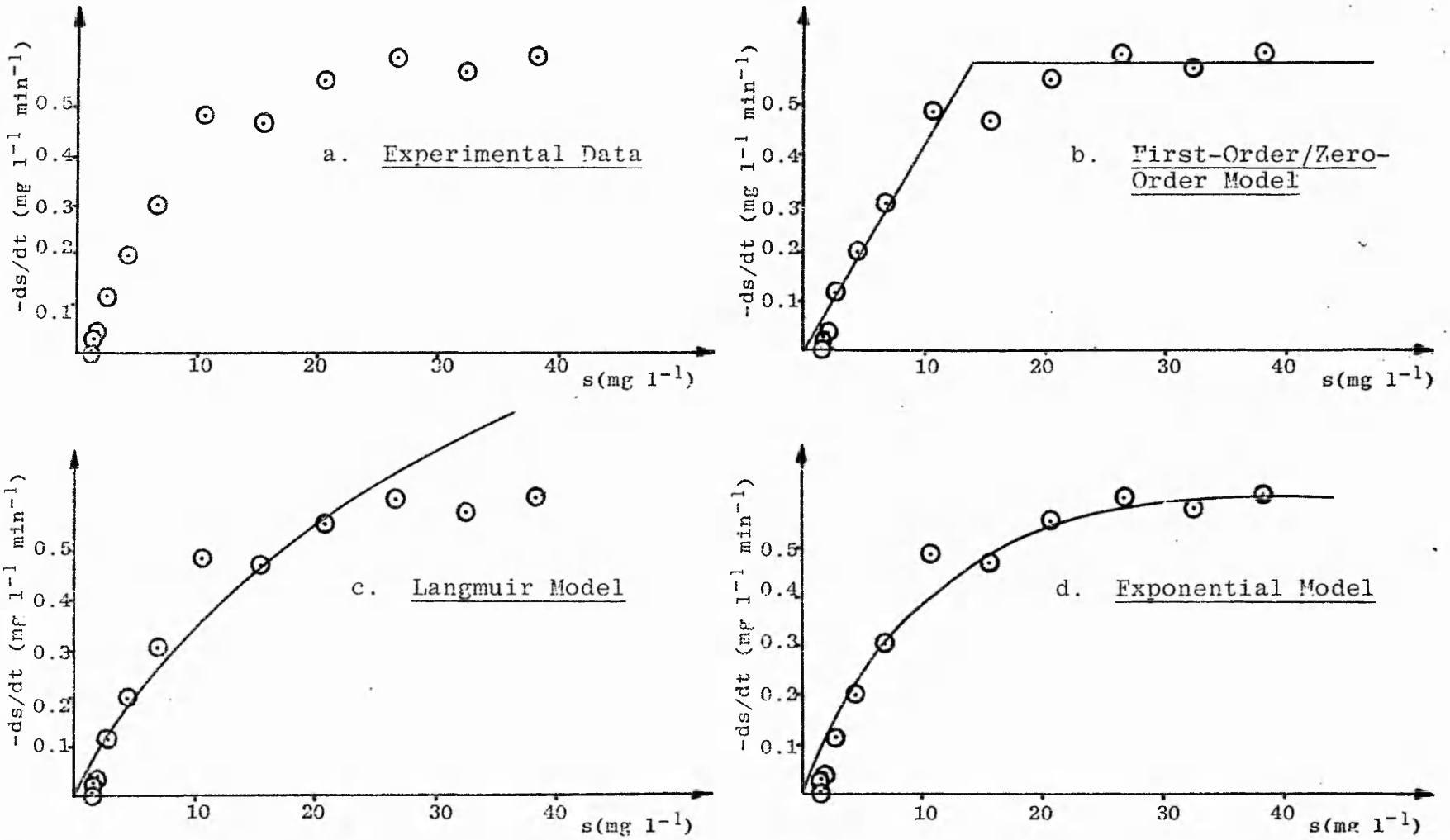


FIGURE 46: Development of a Theoretical Model for Surfactant Removal

If the first order/zero order model employed in previous sections (4.4.3 and 4.6.1) is chosen to represent the adsorption isotherm, the following mathematical expressions apply:

$$-\frac{ds}{dt} = m_1 s \qquad 0<s<s_{critical}$$

$$-\frac{ds}{dt} = m_0 \qquad s_{critical}<s$$

The value of $s_{critical}$ may be found from the equality:

$m_1 s_{critical} = m_0$

$\Rightarrow s_{critical} = \frac{m_0}{m_1} = 13.67$ mg l^{-1} in the present case.

It will be seen from Figure 46.b that the first order/zero order model fits the experimental data well except for values of s in the area of $s_{critical}$. One disadvantage in using the model to characterise the adsorption isotherm is that the resulting mathematical relationship is discontinuous. This precludes the formulation of a single equation for the relationship between s and t.

An alternative mathematical expression which is commonly used to describe adsorption isotherms of the general shape shown in Figure 46.a is the Langmuir model. In the present case this would take the form:

$$-\frac{ds}{dt} = \frac{X^{11} s}{Y^{11} + s}$$

The coefficients X^{11} and Y^{11} are constant and may be evaluated from a plot of $(-ds/dt)^{-1}$ vs. $(s)^{-1}$. If the Langmuir model accurately fits the experimental data the resultant curve should be linear with the following characteristics:

gradient $= 1/X^{11}$

intercept $= Y^{11}/X^{11}$

When the experimental data shown in Figure 46.a is utilised in this fashion a curve is produced which is non-linear. An attempt may be made at fitting the Langmuir model to the experimental data if a portion of the curve is chosen and approximated by a straight line. This allows values for X^{11} and Y^{11} to be calculated. Insertion of these coefficients into the Langmuir model enables a plot of (-ds/dt) vs. s to be drawn. This is shown in Figure 46.c. It will be seen

that whilst reasonable correlation is obtained at low values of s, the curve deviates sharply from the experimental data at higher values.

An expression which provides a more acceptable degree of fit to the experimental data than either of the above models has the form:

$$-\frac{ds}{dt} = X^1 \ (1 - e^{-Ys})$$

This is shown in Figure 46.d. The coefficient X^1 and Y are constants and may be evaluated by multiple linear regression analysis. In the present case the values of X^1 and Y are 0.6177 and 0.1018 respectively.

Since the parameters V, A, x_2 and b are assumed to be constant, the true adsorption isotherm for surfactant on to air bubbles may be expressed in a similar form, viz:

$$-\frac{V}{Ax_2b} \cdot \frac{ds}{dt} = X \ (1 - e^{-Ys}) \qquad \text{(XXXIX)}$$

Equation (XXXIX) may be solved to obtain an expression for the surfactant concentration in the flotation cell, s at any time, t (see Appendix 1.8):

$$Y\left[s-s_i\right] + \ln\left[\frac{(1 - e^{-Ys})}{(1 - e^{-Ysi})}\right] = -XY \cdot \frac{Ax_2b}{V} t \qquad \text{(XXXX)}$$

At high values of s, the second term on the L.H.S. of equation (XXXX) approaches zero, resulting in:

$$s = s_i - X \cdot \frac{Ax_2b}{V} t \qquad \text{(XXXXI)}$$

ie a zero order removal process. Thus the zero-order rate constant will be approximately:

$$m_0 = X \cdot \frac{Ax_2b}{V} t \qquad \text{(XXXXII)}$$

Equation (XXXXII) predicts that the zero-order rate constant, m_0, is directly proportional to air rate, A, and inversely proportional to column volume, V. This has been confirmed experimentally during this research programme (see Sections 4.4.3 and 4.6.1).

At low values of s, it is not possible to approximate equation (XXXX) to a zero-order expression since none of the terms in the equation tend to zero. The experimental

evidence indicates that a first-order expression gives an acceptable approximation. This may be deduced from equation (XXXX), which can be rearranged to give:

$$\ln\left[\frac{e^{Ys} - 1}{e^{Ysi} - 1}\right] = - X Y \cdot \frac{Ax_2b}{V} t$$

e^{Ys} may be represented by the series:

$$e^{Ys} = 1 + Ys + \frac{Y^2s^2}{2!} + \frac{Y^3s^3}{3!} + \ldots\ldots\ldots\ldots\ldots$$

Therefore:

$$e^{Ys} - 1 = Ys + \frac{Y^2s^2}{2!} + \frac{Y^3s^3}{3!} + \ldots\ldots\ldots\ldots\ldots \qquad \text{(XXXXIII)}$$

If both Y and s are sufficiently small, all the terms on the R.H.S. of equation (XXXXIII) other than the first one may be ignored. Therefore under these conditions equation (XXXX) reduces to:

$$\ln\left[\frac{s}{e^{Ysi} - 1}\right] = - XY \cdot \frac{Ax_2b}{V} t$$

Since $(e^{Ysi} - 1)$ is a constant, a plot of $\ln(s/s_i)$ vs. t should yield a straight line with the following characteristics:

$$\text{gradient} = - XY \cdot \frac{Ax_2b}{V}$$

$$\text{intercept} = \ln\left[\frac{e^{Ysi} - 1}{s_i}\right]$$

In the analysis of results contained in Sections 4.4.3, 4.5.2 and 4.6.1 the value of this gradient was assumed to be equal to $-m_1$, where m_1 was the first-order rate constant. Therefore:

$$m_1 = XY \cdot \frac{Ax_2b}{V} \qquad \text{(XXXXIV)}$$

Equation (XXXXIV) predicts that m_1 is directly proportional to air rate, A, and inversely proportional to column volume, V. This has been confirmed experimentally (see Sections 4.4.3 and 4.6.1). Equation (XXXXIV) also agrees with the observations of Grieves and Wood (141), who found that the first-order rate constant for the removal of surfactant mass from a colume during flotation was independant of the volume of the liquid pool. It will be seen that equation (XXXXIV) complies with this since:
rate constant for the removal of surfactant mass

$= Vm_1$

$= XY\ Ax_2b$

Therefore the mass of surfactant removed is a function of the production of bubble surface area and does not depend on the dimensions of the flotation vessel. Grieves and Wood have suggested that this implies that an adsorption equilibrium is rapidly established between the bubble and the surrounding bulk medium. The observation made during the present research, that surfactant removal is independant of particle type and concentration (see Section 4.6.1), may also be explained. The removal of particles in flotation relies on a collision mechanism, which takes place much more slowly than the surface adsorption mechanism by which surfactant is removed. Therefore surfactant adsorption on to a bubble surface is virtually complete before any appreciable amount of particle collection has taken place, and surfactant removal is largely independant of the properties of the particles in the flotation cell.

4.7.2 Removal of Particles by Flotation

Tomlinson and Fleming have stated that under conditions of "free" flotation the removal of particles by flotation is a first order process with a rate constant which represents the product of the probabilities of the successful completion of a number of sub-processes (see Section 2.4.2.1). In the analysis which follows the effects on these probabilities of variations in the operating parameters of the flotation system are examined.

The current theoretical treatments of the process of collision were reviewed in Section 2.4.2.2. The approach of Reay and Ratcliffe is the most suitable for the present study, since it is concerned with the collection of small particles. However, the detailed relationships developed by Reay and Ratcliffe are not required for the analysis contained in this section, only their general conclusions. They found that the streaming effect of the liquid in the flotation pool around a rising bubble surface created an

"area of influence" in which particles had to exist if they were to effect a collision. This area was only a fraction of the plan area of the bubble and was defined by the distance from the centre line of the bubble trajectory that a particle had to be in order to just graze the bubble at its widest point. This is illustrated in Figure 45, where the magnitude of the area of influence is B.

In incremental time dt the average distance a bubble will rise through the flotation pool is given by the following:

average distance risen through pool = udt

where u is the average upward velocity of the bubbles in the pool (see Figure 45). During this incremental rise the bubble will sweep through a volume of liquid equal to the product of the distance risen and its plan area. However, since only particles lying in area B will collide with the bubble, the incremental volume swept out in which collisions may occur is given by:

incremental volume = B udt

The number of particles lying in this volume, and therefore the number of collisions which occur, is given by:

number of collisions = x_1 c B u dt

The number of these collisions which result in capture of the particle by the bubble is calculated by multiplying the number of collisions by p, the probability collection after collision has taken place:

number of particles collected = p x_1 c B u dt

The above equation describes the collection efficiency of a single bubble. The total removal of particles during the incremental time period dt is assumed to be given by this individual removal efficiency multiplied by the total number of bubbles in the pool at any time.

The average time spent by a bubble in the flotation pool is given by:

average time spent in pool = $\frac{h}{u}$

The volume of air injected into the pool during this time is given by:

volume of air injected = A $\frac{h}{u}$

This is equivalent to the following number of bubbles:

number of bubbles = $x_2 \; A \; \frac{h}{u}$

This is the number of bubbles present in the pool at any time and does not vary providing the air rate and bubble size distribution remain constant. If conditions of "free" flotation prevail for the particles then every bubble is capable of effecting productive collisions throughout its time in the pool.

The total number of particles removed from the pool in time dt may now be calculated:

number of particles removed = $x_2 \; A \; \frac{h}{u} \; . \; px_1 \; c \; B \; u \; dt$

This removal of particles causes an incremental loss in pool concentration, -dc:

$$-dc = x_2 \; A \; \frac{h}{u} \; . \; px_1 \; \frac{cBu}{x_1 V} \; . \; dt$$

$$\Rightarrow \frac{-dc}{dt} = x_2 \; \frac{A}{a} \; . \; B \; . \; p \; . \; c \qquad \text{(XXXXV)}$$

$$\Rightarrow k = x_2 \; \frac{A}{a} \; . \; B \; . \; p$$

Equation (XXXXV) describes a first-order removal process with a rate constant that is a function of the probabilities of collision and adhesion (represented by B and p respectively). It predicts that the rate constant is linearly dependant on the air rate for a given cell plan area. This has been demonstrated experimentally (see Sections 4.3.3, 4.4.4 and 4.6.2). Furthermore, it predicts that the same value of k will be obtained for any combination of A and a, provided their ratio is constant. This has been verified for both flotation units used in the present study (see Section 4.6.2). The experimental observation that k is independant of V, the column volume, may also be deduced from equation (XXXXV).

The probability of collection after collison, p, is primarily a function of the chemical parameters of the system, which control the suitability for reaction of the particle and bubble surfaces. In the present study the use of purified synthetic components eliminated many of the chemical variables, and the most important factor remaining

was the surfactant concentration. Sections 4.4.4 and 4.6.2 describe the observed effects of surfactant concentration on the particle removal rate constant. Since other operating parameters (eg air rate, A) were fixed during a set of experiments, the observed variations in the rate constant, k, actually represent a variation in the probability of collection after collision, p. An example of the type of behaviour encountered is shown in Figure 47.a. It is assumed that the variation of p with s is the product of the effects of two conflicting mechanisms. Firstly, the rapid adsorption of free surfactant on to the surface of a bubble reduces the number of sites which are available for the subsequent collection of particles. Therefore if a high concentration of free surfactant is present in the pool, its adsorption at any available air/water interface will inhibit the collection of particles. The second factor, which counterbalances this effect, is the need to create particle hydrophoby. The mass of surfactant adsorbed on to the surfaces of the particles in the pool is directly proportional to the free surfactant concentration in the pool (see Sections 4.4.4 and 4.6.2). Therefore low concentrations of free surfactant will result in reduced adsorption by the particles and consequently a loss in hydrophobicity. This may result in a reduction in p despite the relatively high availability of collection sites on the bubbles.

The relationship between free surfactant concentration and the number of bubble sites available for particle collection may be deduced from an extension of the analysis contained in Section 4.7.1. Equations (XXXVIII) and (XXXIX) are combined to give:

mass of surfactant adsorbed per unit area of bubble surface $= X (1 - e^{-Ys})$

It has been noted that as s increases a point is reached where no further adsorption of surfactant can take place. This corresponds to the condition;

mass of surfactant adsorbed per unit area of bubble surface $= X$

It is assumed that at this point all the available bubble surface area is saturated with adsorbed surfactant molecules and that no sites are available for particle collection. At lower surfactant concentrations only a fraction of the available bubble surface area will be utilised for surfactant adsorption and some sites will be available for particle collection. The fraction of available bubble surface area used for surfactant adsorption at any value of s is given by:

fraction of bubble surface area used in surfactant adsorption

$$= \frac{X(1 - e^{-Ys})}{X} = 1 - e^{-Ys}$$

Therefore the remaining fraction of the bubble surfactant area, which is available for particle collection, is given by:

fraction of bubble surface area available for particle collection $= 1 - (1 - e^{-Ys})$

$$= e^{-Ys}$$

The probability that particles which have collided with a bubble will adhere to it and be collected (p) is a function of this fraction:

$$p = W^1(e^{-Ys})^Z$$

$$= W^1 e^{-YZs}$$

Thus a relationship between p and s has been derived. Its validity may be tested by examining the experimentally determined relationship between the rate constant, k, and s, since under constant collision conditions (ie constant values of x_2, A, a and B in equation (XXXXV)), k will be directly proportional to p. Thus:

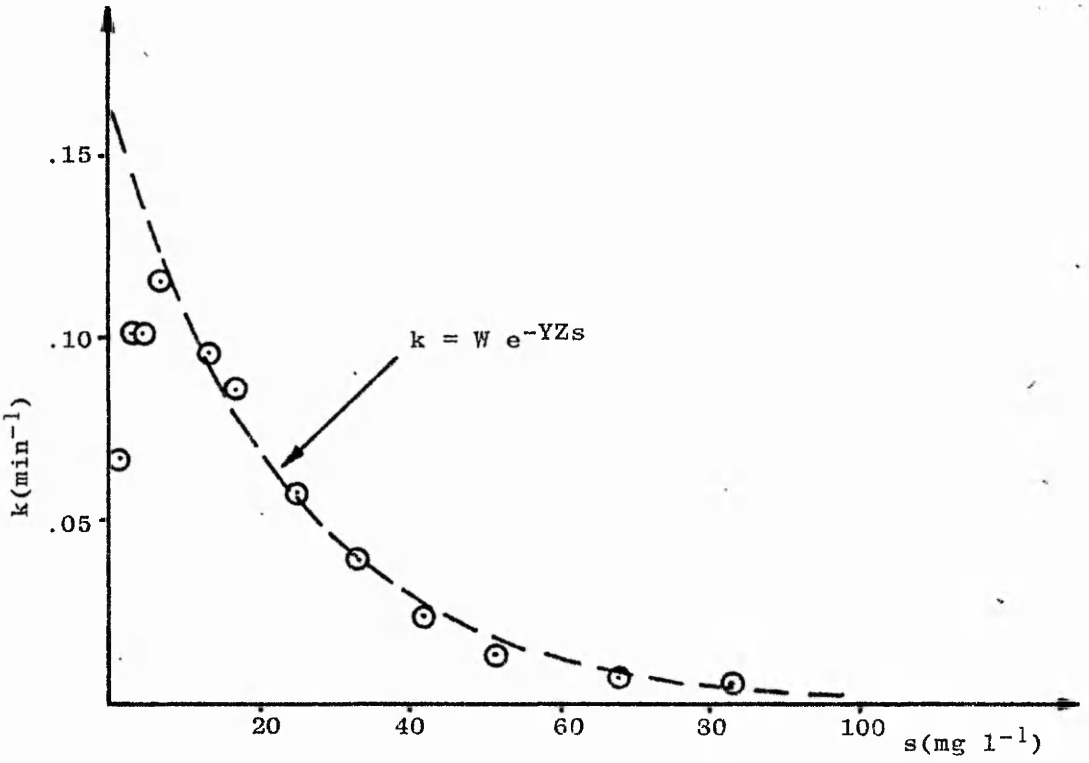
$$k = W e^{-YZs} \qquad \text{(XXXXVI)}$$

Equation (XXXXVI) may be tested by attempting to fit an exponential curve to the experimental data. In Figure 47.a this has been carried out using the results of Tests D8 - D19, and it will be seen that the equation gives good correlation for all values of s above a level of approximately 7.5 mg l^{-1}. Below this level the effects of reduced particle hydrophobicity become significant.

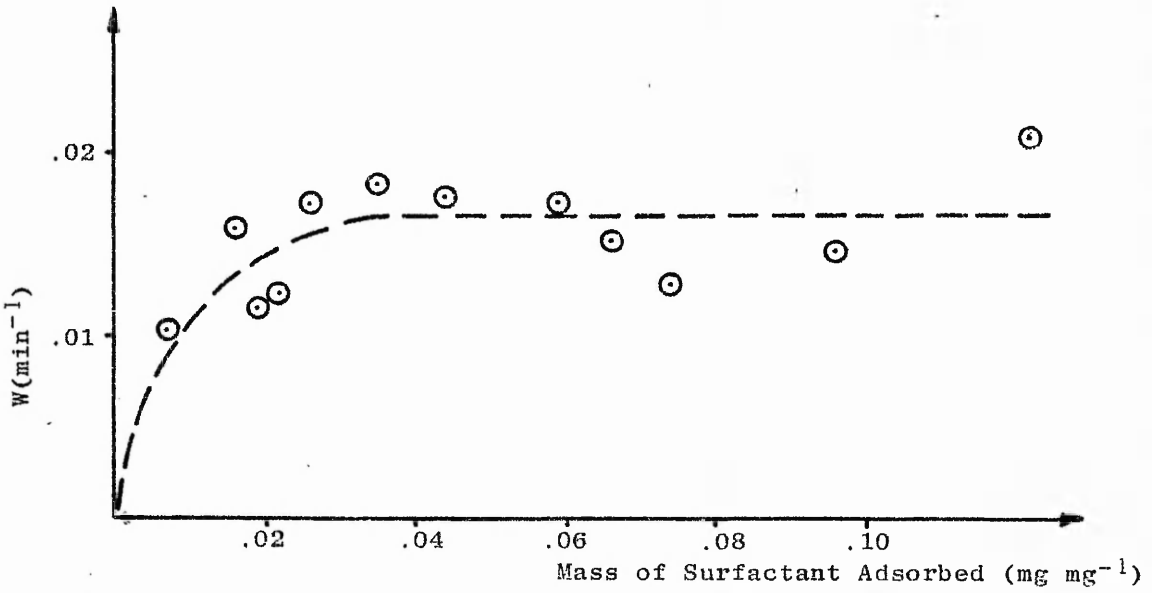
The curve shown in Figure 47.a has the following characteristics:

$W = 0.1655$

$YZ = 0.04419$



a. Relationship between Rate Constant and Surfactant Concentration



b. Relationship between Parameter W and Mass of Surfactant Adsorbed

FIGURE 47: Development of a Theoretical Model for Particle Removal

An approximate value of Z may be calculated using the value of Y derived in Section 4.7.1:

$Z = 0.4341$

$\Rightarrow k$ (or p) $\propto$ (available bubble surface area)$^{0.4341}$

It is possible to speculate that the theoretical value of Z should be 0.5 (ie a square-root relationship). If this were the case then p would depend on the availability of suitable collection sites in a particular linear direction (ie along a particular particle trajectory). However, it is considered that there is insufficient experimental evidence to make a firm conclusion.

The value of W found for the curve in Figure 47.a represents the value of k which could be achieved if the collector was so strongly adsorbed to the surfaces of the particles that no free surfactant remained in the pool. This situation would not be possible for the components used in the present study, but seems to have been achieved by Anfuns and Kitchener (63, 97) using surface methylated quartz.

The relationship between W and the mass of surfactant adsorbed on to the surfaces of the particles is shown in Figure 47.b. Values of W have been calculated for each experimental point using the formula:

$W = k\ e^{YZs}$

Examination of Figure 74.b shows a certain amount of scatter in the experimental points. However, it would appear that a relationship of the following form fits the data reasonably well:

$W \propto 1 - \exp$ (constant x mass adsorbed)

The adsorption isotherm for surfactant on clay particles has been found to exhibit a linear relationship between mass adsorbed and the concentration of free surfactant (see Sections 4.4.4 and 4.6.2). The relationship above may therefore be re-expressed as:

$W \propto 1 - \exp$ (constant x s)

This is a similar equation to that derived by Rubenshtein and Filippov (98) for the probability of attachment of air bubbles to fine coal particles. However, they did not

report that any inhibiting effects occurred at higher surfactant concentrations and it must be concluded that the phenomenon of bubble saturation was not significant with the particle/collector systems used. This would also appear to be the case for the flotation of oil/water emulsions (Angelidou et al (135)). However, Crandall and Grieves (23) noted that flotation efficiency was reduced by the use of high surfactant doses and attributed this observation to competition for bubble surface area between surfactant molecules and particles. Their experimental system was similar to that used in the present study, ie clay particles and a quaternary ammonium salt.

The observation that the particle flotation rate constant (k) decreases with increasing free surfactant concentration (s) may be explained by an alternative approach to the one developed above. This alternative has been used to account for the decreased recovery rates obtained in some mineral flotation systems after the addition of excess collector (146). It is postulated that as collector is added a point is reached where the particle surface becomes saturated, and maximum hydrophobicity is obtained. When additional collector is added a second adsorbed layer forms by means of the van der Waals attractions between the hydrocarbon chains of the collector molecules. The orientation of the collector molecules in this second layer is such that their polar groups are directed away from the surface of the particle; this is known as "hemimicelle formation". There is a resultant loss in particle hydrophoby and the probability of particle collection after collision with an air bubble (p) is reduced.

There are two main factors which mitigate against hemimicelle formation being the reason for the behaviour observed during the present study. Firstly, it seems likely that the point where a second layer of surfactant molecules begins to form would be marked by a change in the slope of the surfactant/particle adsorption isotherm. This was not observed in the present case; the adsorption isotherm was

linear across the range of surfactant concentrations tested. Secondly, measurements by Jaycock et al (142) on the adsorption of cationic surfactants gave a value in the region of 2×10^{-3} M for the minimum surfactant concentration at which hemimicelles begin to form. For CTAB this is equivalent to approximately 700 mg l^{-1}; the maximum surfactant concentration used in the present study was considerably below this figure.

In Section 4.6.2 it is stated that an increase in the initial particle concentration in the flotation cell (c_i) was found to result in a higher value for the removal rate constant (k). This observation cannot be explained simply by competition between surfactant molecules and particles for bubble collection sites. However, it was also noted that the surfactant/particle adsorption isotherm for the higher initial clay concentration differed significantly from the isotherm recorded for the lower value. In the absence of additional data it is concluded that some effect involving particle/particle interactions during the initial adsorption period (eg coagulation) is responsible for both these differences in behaviour.

4.7.3 Assumptions made in the Development of the Theory

The theory developed in Sections 4.7.1 and 4.7.2 constitutes a description of the batch flotation process based on various operational parameters. The validity of the assumptions made concerning these parameters is examined below.

The assumption is made that the properties of the bubble swarm (upward velocity, surface area and probability of collision with particles) can be characterised by average values. The use of an average value for bubble velocity, u, does not affect the validity of the theory of particle capture since although u appears in the early stages of the theoretical development, it cancels out later and does not appear in equation (XXXXV). The adoption of an average value for the surface area of a bubble, b, is considered to be justified because the important parameter in surfactant removal is the total surface area available from all bubbles,

x_2b. The conclusion of Reay and Ratcliffe, that the area of influence of a rising bubble is virtually independant of its size, is exploited in the analysis of particle flotation by the assumption that a single value for the term B applies to all bubble sizes. It should be noted that B is derived from the observed removal efficiency of the bubble swarm and does not strictly apply to the behaviour of a single bubble. Flint and Howarth showed that it was possible for this cumulative collision efficiency to exceed the sum of the individual collision efficiencies of component bubbles. In addition to assumptions regarding the bubble swarm, it is assumed that all particles in the pool are equally floatable. The results of Test A31 (see Section 4.3.5) showed this to be a realistic assumption for the majority of particles in the particular experimental system employed. The larger particle size fractions exhibited markedly different removal characteristics but only accounted for a small proportion of the total mass of particles in the cell and therefore did not significantly alter its operation. Finally, during the assessment of the effects of free surfactant concentration on particle removal it is assumed that all sites remaining on the bubble surface after adsorption of surfactant can be utilised for particle collection. However, it may not be possible for particles to collect on the upper hemisphere of the bubble due to the turbulence caused by the rise of the bubble through the liquid pool. This phenomenon would alter the value of W in equation (XXXXVI), but would not affect the basic form of the relationship between k and s.

4.7.4 The Continuous Flotation Process

The results of the experiments described in Section 4.3.2 show that the mixing regime prevalent in a single-stage continuous flotation cell approximates closely to the complete mixing model. An extension of this model has been demonstrated to be applicable to the case of a multi-stage flotation cell (see Section 4.5.1).

It would appear that the persistence of perfect mixing is due predominantly to the aeration of the pool and is not caused by the passage of the process stream through the cell (see Section 4.3.2). Attempts to create a degree of segregation in the single-stage unit by the use of packing (see Section 4.6.5) were not successful. It is felt that in such a situation segregation might be achieved if either the bubble size was reduced or the height of the cell was increased. The former method has been utilised by Valdes-Krieg et al (143) in a bubble fractionation column of similar plan dimensions to the single-stage flotation unit used in the present study. The pilot trials described by Boutin and Wheeler (129) suggest that the latter alternative may have an application in the mineral processing field. However, the increase in height necessary to effect segregation would make this alternative uneconomic in most wastewater treatment situations.

The use of chemical reactor theory for describing the performance of continuous flotation circuits has been tested extensively during this research programme. The results of the experiments described in Section 4.3.4 have shown that the removal of material from a single-stage continuous flotation cell may be predicted using chemical reactor theory combined with the relevant batch data. The control of the surfactant concentration in the cell is considered to be the main reason for the accuracy of these predictions. Although the zero order/first order model of surfactant removal has been shown to be an oversimplification (see Section 4.7.1) it appears to be sufficiently accurate to be used for process control and is preferred because the application of the more rigorous model would require an excessive amount of computation.

Chemical reactor theory was less successful in predicting the performance of multi-stage flotation units (see Section 4.5.4). An examination of the distribution of the parameter G for these experiments indicates that in general the removal achieved was in excess of that predicted from theory.

The explanation for this may be found by a consideration of the prevailing surfactant concentration in each compartment of the multi-stage unit. Since surfactant is removed at each stage, the free surfactant concentration in successive compartments decreases. If sufficient time is allowed, these reductions in free surfactant concentration would cause desorption of surfactant molecules from the particle surfaces until an equilibrium was re-established. However, since this desorption is a relatively slow process, the passage of the process stream through the unit prevents an equilibrium from being attained. A condition is therefore created in the latter stages of the unit where the free surfactant concentration is low but the mass of surfactant adsorbed to the particles is relatively high. This condition is highly advantageous to flotation and particle removal is enhanced.

It is felt that if a further investigation of this phenomenon was conducted, chemical reactor theory would be shown to be fully applicable to the analysis of multi-stage units.

The flexibility of chemical reactor theory provides significant advantages over the methods of analysis used in previous studies of wastewater flotation (see Section 2.4.3). These produce equations which can only be used when a steady-state has been reached. In the event of a variation of any process parameter such equations become invalid until another steady-state condition is reached. An investigation into the use of chemical reactor theory in a situation where one process variable (the influent flow rate, v) was not constant with time is described in Section 4.6.3. Despite a disparity between observed and expected values, it is felt that this application of the theory merits further investigation.

It is possible to explain some of the observations of previous workers by a combination of chemical reactor theory and the analysis developed in Sections 4.7.1 and 4.7.2. For example, Grieves and Wood (141) found that the removal of surfactant from a continuous flotation cell was independant of column volume and related to the value of the dimensionless parameter:

$$\frac{A}{v} = \frac{\text{air feed rate}}{\text{water feed rate}}$$

Batch tests under similar experimental conditions showed the rate of removal to be proportional to the prevailing surfactant concentration. This would suggest that the investigations were carried out in the region where surfactant removal is approximately first-order and the following rate constant can be applied (see Section 4.7.1):

$$m_1 = XY \cdot \frac{Ax_2b}{V}$$

This rate constant may be incorporated into the relevant equation for a single-stage continuous cell to give:

$$\frac{s}{s_i} \text{ (at steady state)} = \frac{1}{Rm_1 + 1}$$

$$= \left[R \cdot XY \cdot \frac{Ax_2b}{V} + 1\right]^{-1}$$

$$= \left[XY \cdot x_2b \cdot \frac{A}{v} + 1\right]^{-1}$$

Thus a relationship between s/s_i at steady state and the dimensionless parameter A/v has been derived. Figure 48 shows a plot of this relationship using values for m_1 obtained in Tests A6, A8, A10, A12 and A14. The curve obtained experimentally by Grieves and Wood is also shown. The similarity in the shape of the two curves will be noted; the actual values of s/s_i obtained are different because of variations between the two experimental systems (eg different bubble size distributions and an alternative cationic surfactant (ethylhexadecylammonium bromide)).

4.7.5 Treatment of River Water by Flotation

The results obtained during the preliminary tests on the treatment of water from the River Trent (see Section 4.2.1) showed several promising indications that a chemical kinetics analogy could be used for the analysis of wastewater flotation systems. The general shape of the removal-time curves obtained complied with the expectations of chemical reactor theory. In addition, the apparent independance of the derived rate constant, k, to variations in the turbidity of the feed to the unit indicated that the flotation process was approximately first order. If the predictions of chemical reactor

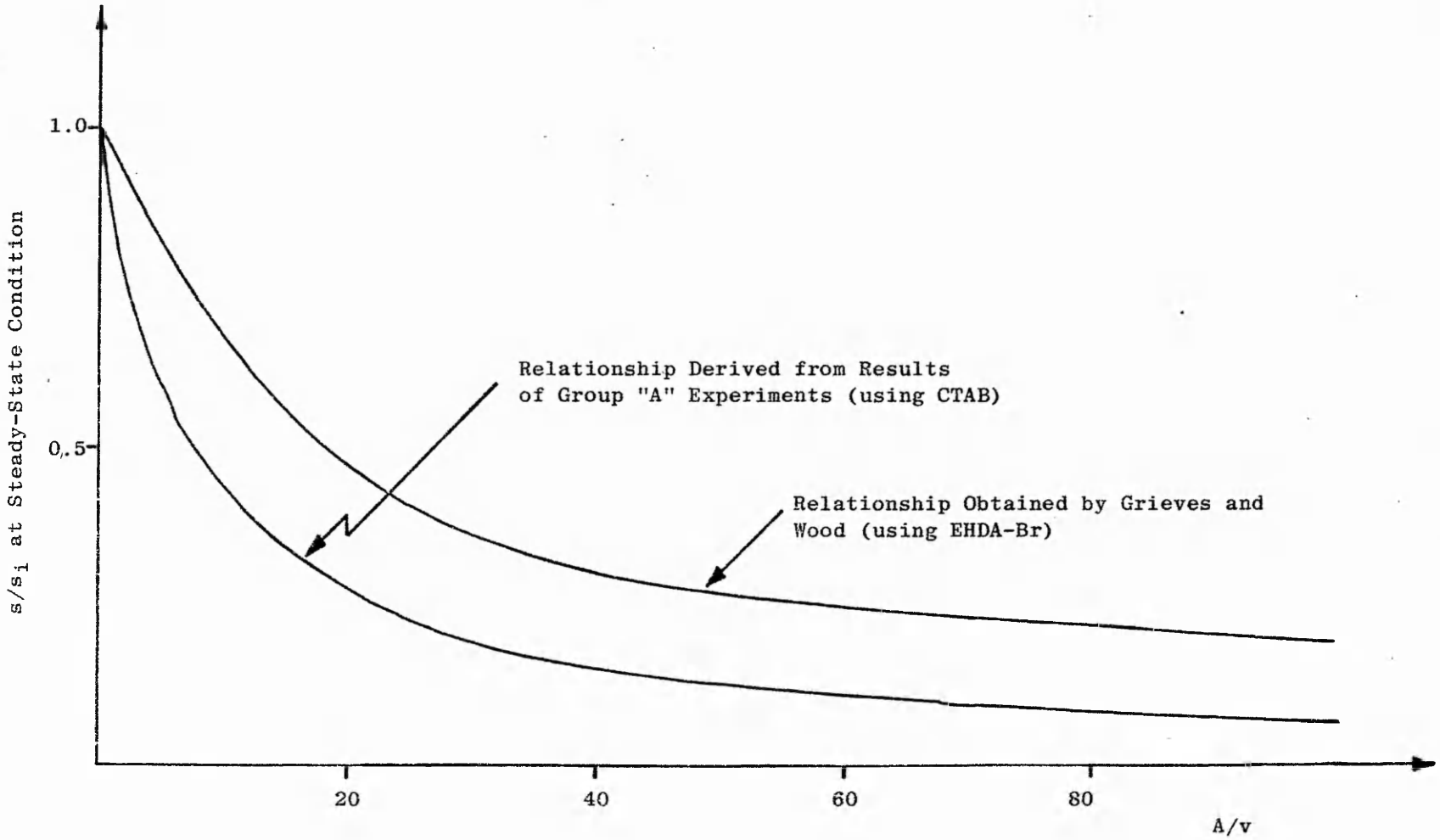


FIGURE 48: Relationship between Surfactant Removal and Air Flow/Water Flow Ratio

theory had been fully complied with, k would have been independant of the flow rate to the unit, v. This was not found to be the case at low values of v. It is suggested that the reason for the discrepancy between observed and expected behaviour is due to the method by which the unit was dosed with surfactant. Surfactant concentrate was fed into the inlet weir of the unit at a rate which was proportional to the flow rate, v. At high values of the retention time, R (ie low values of v) this produced a relatively low surfactant concentration in the pool. This low concentration was disadvantageous to flotation in this case since the dosing method adopted did not allow time for surfactant adsorption on to the particles prior to entry to the cell. Therefore the surfactant tended to be removed before it had produced adequate hydrophoby on the particle surfaces. It is noticeable that at the highest surfactant dose k exhibited complete independance from v, and this is considered to provide further evidence that an effect such as that described above was significant.

The flotation tests carried out using the model sediment (see Section 4.6.4) did not produce a positive correlation between observed and expected removal. Considerable experimental difficulties were encountered using this material due to rapid settlement of the larger fractions. It is felt that the use of reconstituted wastewaters is not satisfactory and that future research on the practical application of flotation should be conducted using naturally occurring raw waters.

4.7.6 Design Procedure and Process Optimisation

It has been shown that the theoretical approach adopted holds considerable promise as a method for predicting the behaviour of wastewater flotation systems. This makes it possible to formulate a rational design method which would allow a high degree of process optimisation and would result in substantial savings in construction and operating costs.

The first stage of the design of a flotation plant for the treatment of a particular wastewater should be a programme of

pilot trials using a small batch flotation apparatus. The purpose of the trials would be twofold. Firstly, the effects of the various chemical parameters could be assessed in order to find the most favourable treatment conditions. Secondly, the effects on the process of variations in the characteristics of the influent could be determined. In a river water treatment situation important characteristics might be suspended solids concentration, pH and volumetric throughput.

When the pilot trials have been completed, it should be possible to decide on a realistic minimum value of the rate constant, k. This value should be used for design purposes to allow excess capacity within the treatment plant and thereby ensure an acceptable factor of safety. Various values of R, A and N may then be inserted into the relevant equations to give a conservative estimate of the plant performance. Thus the basic geometry of the plant may be formulated.

The choice of the number of stages needed for the flotation unit will be dependant on the balance between construction and operating costs. Tall columns will give a more satisfactory utilisation of the air injected into the system and are thus cheaper to operate. However, it has been shown that the mixing regime in such columns will be less advantageous to purification than those found in baffled channels. Channels therefore represent a more efficient use of the volumetric capacity of a plant.

It has been demonstrated that a low free surfactant concentration combined with a relatively high surfactant adsorption on to the particle surfaces provides ideal conditions for efficient flotation. This consideration will also govern the choice of the number of stages needed.

A low surfactant concentration in the final effluent will usually be required to minimise the amount of further treatment required. Extra plant capacity may be needed in order to ensure this.

Methods of removing the solids concentrate formed in the

foam have not been considered in detail, but the results of one series of tests carried out using the channel have shown that a very high dry solids content can be attained providing the production of foam is kept to a minimum. This consideration will probably limit the air rate used in the unit.

In some applications it may be important that the unit should be capable of coping with shock loadings, either from increases in the hydraulic flow to the unit or from sudden variations in the solids concentration of the influent. It is felt that a multi-stage unit would be preferable in such situations and that a degree of automation could be introduced by allowing the air supply to the unit to be modulated by an impulse from a suitable monitoring device.

One parameter which has not been optimised during the present study is the time needed for adsorption prior to entry into the flotation unit. The adsorption period used in the present study (see Section 3.6) was probably excessively long and could be reduced considerably. However, the results of the preliminary experiments (see Section 4.7.4) indicate that this adsorption period cannot be dispensed with completely. In addition, such a pretreatment capacity would provide a volumetric buffer in which shock loadings could be assimilated.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

5.1 FOAM FLOTATION DESIGN PARAMETERS

The purpose of the research described in this thesis was to formulate a rational method for the design and operation of foam flotation systems. This has been successfully accomplished and the main conclusions regarding the mechanisms of foam flotation and the effects of the process parameters are listed below:

(i) The removal of particles by flotation is due to a process of collision between hydrophobic particles and air bubbles. For clay particles this collision mechanism is first order with respect to time.

(ii) Particle hydrophoby is caused by the adsorption of surfactant molecules on to the surfaces of the particles in the flotation pool. For the system used in the present study the isotherm of this adsorption process is linear.

(iii) Surfactant not adsorbed to particle surfaces (free surfactant) is removed from the flotation pool by adsorption on to the surfaces of the injected air bubbles. The isotherm for the adsorption of the surfactant used in the present study is of exponential form. From this isotherm an equation linking the removal of free surfactant with time has been derived. For the purposes of operational control this equation may be approximated by a zero order relationship above a certain critical free surfactant concentration and a first order relationship below this concentration.

(iv) Flotation efficiency and air flow rate are linearly dependant for both particle and surfactant removal. For the removal of particles the important parameter is the number of bubbles released per unit plan area of flotation cell per unit time. For surfactant removal the total bubble surface area generated per unit cell volume per unit time is the critical factor.

(v) The presence of free surfactant in the flotation pool inhibits the flotation of particles. This is because free surfactant adsorption occurs more rapidly than bubble/particle collision and potential particle collection sites on the bubble surface are filled by adsorbed free surfactant

molecules. At low concentrations of free surfactant this effect is masked by the need to create particle hydrophoby.

(vi) The depth of the flotation pool does not by itself affect the rate of decrease of particle concentration in the flotation cell. The rate of decrease in the free surfactant concentration in a flotation cell is inversely proportional to the depth of the flotation pool.

(vii) The hydraulic regime in a single-stage dispersed air flotation cell approximates closely to complete mixing. The regime in a multi-stage flotation cell approximates to a series of completely mixed cells. In a single-stage cell of the type used in the present study it is not possible to induce an incompletely mixed hydraulic regime by the insertion of packing.

(viii) The performance of single-stage flotation cells under continuous operation may be predicted from the results of batch tests. The performance of multi-stage flotation cells is complicated by variations in the free surfactant concentration in each stage.

(ix) The basic parameter which characterises the treatment capacity of a continuously operated flotation system is its retention time. The volume of flotation plant required for a given influent throughput may be determined from this parameter.

(x) Long shallow flotation channels represent a more efficient utilization of plant capacity since a degree of compartmentalisation can be introduced. Tall narrow flotation columns use plant capacity less efficiently but are more economical in their utilisation of air bubbles.

(xi) If suitable rates are selected for air and surfactant addition, the volume of foam generated by a flotation unit can be reduced to a low level. Under these conditions floated particles can be removed in a highly concentrated form.

(xii) The use of the chemical kinetics approach to describe the purification by flotation of naturally occurring waters appears to have considerable potential.

5.2 THE POTENTIAL OF FOAM FLOTATION AS A WASTEWATER TREATMENT PROCESS

The formulation of a rational design method for foam flotation units enables a greater degree of process optimisation and control to be exercised than was previously possible. A number of the traditional disadvantages of the process (eg high concentrations of surfactant in the effluent and large volumes of generated foam) can be minimised and its potential may be more fully exploited.

The future utilisation of the foam flotation process will probably be concentrated in the field of industrial effluent treatment. The process is particularly suited to applications where the material to be removed is already surface active or can readily be rendered hydrophobic. For example, many effluents produced in petrochemical operations fulfil these criteria and foam flotation or foam fractionation could be combined with other processes to provide an effective treatment system.

The coagulation/dissolved air flotation process is now firmly established as a method for the clarification of waters for potable supply. However, it has been noted (144) that whilst this process is successful in treating low-turbidity reservoir waters, it is not responsive to the heavy and variable solids loadings which can occur when lowland river waters are utilised for potable supply. In contrast foam flotation has been shown to be capable of purifying influents which are heavily laden with suspended solids, and may therefore be attractive in such a situation. The main problem envisaged with this application of the process is that traces of surfactant would not be acceptable in a potable water supply and an additional treatment step (eg activated carbon adsorption) would therefore be required. However, careful process control using the models for surfactant removal developed in the present study should minimise the cost of this additional treatment step.

5.3 RECOMMENDATIONS FOR FURTHER WORK

There is considerable scope for further investigations into the use of chemical reactor theory as an aid to the design and operation of foam flotation systems. In particular a more detailed analysis of the kinetics of surfactant adsorption and desorption on particle surfaces would produce more sophisticated models of the process. This would enable optimisation of the adsorption period prior to flotation to be carried out, and the models formulated in the present study could be extended so as to accurately describe the operation of multi-stage flotation units.

In addition to deriving more comprehensive models of foam flotation systems, there are a number of modifications to the process itself that could be beneficial.

It is probable that decreasing the size of the air bubbles passing through the flotation cell will greatly enhance its performance. There are three main reasons for this. Firstly, the rate of particle removal will be increased because a larger number of bubbles will be produced per unit volume of air injected. Since bubble collision efficiency is virtually independent of bubble size (95) a greater number of particle/bubble collisions will occur. Secondly, surfactant removal is likely to be aided by the increased bubble surface are made available. The work of Sheiham and Pinfold (148) indicates that this increase in surfactant removal rate with decreasing bubble size is eventually limited by the reduced kinetic energy of the smaller bubbles. Finally, the use of smaller bubbles should significantly improve the mixing characteristics of the flotation cell. A combination of foam flotation and dissolved air bubble generation therefore appears attractive. Grieves et al have made preliminary studies of such a system both for water clarification (145) and for industrial waste treatment (147). They report marked improvements in flotation efficiency.

The possibility of partially automating the foam flotation process was introduced in Section 4.7.6. In some applications the ability of a treatment system to react to shock loadings may be critical to its successful operation. The

incorporation of some form of process modulation into foam flotation systems should therefore be investigated. Alternatively, if flotation is used as a pre-treatment step prior to another process (eg filtration) it may only be necessary for the flotation unit to operate intermittently. In this case the speed with which a flotation unit can be brought on stream would facilitate such a mode of operation. The dry solids content of the floated particle agglomerations which can be removed from the top of the foam layer is relatively high. This may be a significant factor for many applications of the foam flotation process, and should be investigated in greater detail.

The next major step in the development of foam flotation as a wastewater treatment process should be a demonstration of its suitability for the purification of a variety of different wastewaters. This could conveniently be carried out using a small portable unit. Data obtained from this unit could then be combined with a suitable kinetic model so as to predict the likely performance of a full-scale system. Suggested areas of application are the treatment of wastewaters from the petrochemicals, paper making and food preparation industries, together with the pre-treatment of turbid river waters for potable supply.

A useful extension to the work described in this thesis would be the formulation of a model of the coagulation/ dissolved air flotation process using a chemical kinetics analogy. The currently accepted method for the design of dissolved air flotation systems (149) is based on a series of empirically derived power relationships between the main process parameters. This method is analogous to that used by Grieves and Bhattacharyya (54) to describe the foam flotation process, and is subject to similar restrictions regarding its use. The adoption of a more fundamental approach to the analysis of the process might therefore be advantageous. It is likely that there will be differences in the kinetics of removal since the collision of particles with bubbles and their subsequent attachment will depend on

mechanisms different from those assumed in the present study. In addition, the hydraulic conditions in dissolved air flotation cells cannot be accurately described by mixing models used for dispersed air cells (150). However, in view of the success of the kinetic approach experienced during the present investigation, it is felt that this would be a particularly promising area for future research.

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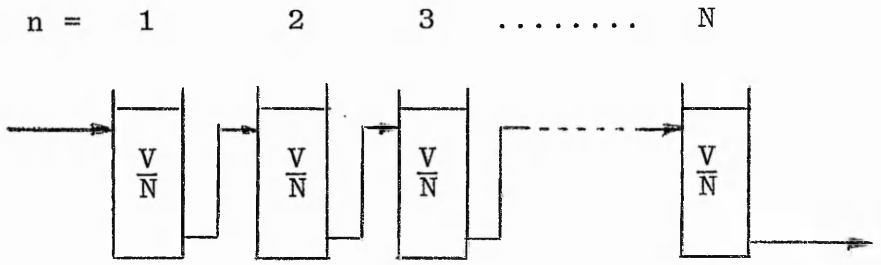
APPENDIX 1

THEORETICAL DERIVATIONS

1.1



n = 1:

$$\frac{dT_1}{dt} = - T_1 \cdot \frac{Nv}{V} = - \frac{NT_1}{R}$$

$$\Rightarrow \frac{T_1}{T_i} = e^{\frac{-Nt}{R}}$$

n = 2:

$$\frac{dT_2}{dt} = - \frac{NT_2}{R} + \frac{NT_1}{R}$$

$$\Rightarrow \frac{dT_2}{dt} = - \frac{NT_2}{R} + \frac{NT_i}{R} e^{\frac{-Nt}{R}}$$

Use Integrating Factor = $e^{\frac{Nt}{R}}$

$$\Rightarrow \frac{dT_2}{dt} e^{\frac{Nt}{R}} + \frac{NT_2}{R} e^{\frac{Nt}{R}} = \frac{NT_i}{R}$$

$$\Rightarrow \frac{d}{dt} \left[T_2 \, e^{\frac{Nt}{R}} \right] = \frac{NT_i}{R}$$

$$\Rightarrow T_2 \, e^{\frac{Nt}{R}} = \frac{NT_i}{R} \int_0^t dt$$

$$\Rightarrow T_2 \, e^{\frac{Nt}{R}} = \frac{NT_i}{R} \left[t \right]_o^t + X$$

where X = constant of Integration

$$\Rightarrow \frac{T_2}{T_i} = \frac{Nt}{R} e^{\frac{-Nt}{R}} + X \, e^{\frac{-Nt}{R}}$$

Boundary Conditions: when $t = 0$, $T_2 = T_i$, $\frac{T_2}{T_i} = 1$

$$\Rightarrow X = T_i \left(-T_i \right)$$

$$\Rightarrow \frac{T_2}{T_i} = \left[1 + \frac{Nt}{R} \right] e^{\frac{-Nt}{R}}$$

n = 3:

$$\frac{dT_3}{dt} = - \frac{NT_3}{R} + \frac{NT_2}{R}$$

$$\Rightarrow \frac{dT_3}{dt} = - \frac{NT_3}{R} + \frac{NT_i}{R} \left[1 + \frac{Nt}{R} \right] e^{\frac{-Nt}{R}}$$

$$\Rightarrow \frac{dT_3}{dt} + \frac{NT_3}{R} = \frac{NT_i}{R} \left[1 + \frac{Nt}{R} \right] e^{\frac{-Nt}{R}}$$

Use Integrating Factor = $e^{\frac{Nt}{R}}$

$$\Rightarrow T_3 \, e^{\frac{Nt}{R}} = \frac{NT_i}{R} \int_o^t \left\{ 1 + \frac{Nt}{R} \right\} dt$$

$$\Rightarrow T_3 \, e^{\frac{Nt}{R}} = \frac{NT_i}{R} \left[t + \frac{Nt^2}{2R} \right]_o^t + X$$

where X = Cosntant of Integration = 1 (as above)

$$\Rightarrow \frac{T_3}{T_i} = \left[1 + \frac{Nt}{R} + \frac{1}{2}\left\{\frac{Nt}{R}\right\}^2 \right] e^{\frac{-Nt}{R}}$$

Thus as n increases stepwise towards its final value of N, the series on the RHS of the equation increases each step by one term. The value of this term is a factor of N/R times the integral of the previous term.

Thus when n = N:

$$\frac{T_N}{T_i} = \left[X \right] e^{\frac{-Nt}{R}}$$

where

$$\left[X \right] = 1 + \frac{Nt}{R} + \frac{1}{2!}\left\{\frac{Nt}{R}\right\}^2 + \ldots.$$

$$\ldots. + \frac{1}{(N-1)!}\left\{\frac{Nt}{R}\right\}^{N-1}$$

The series $\left[X \right]$ has N terms.

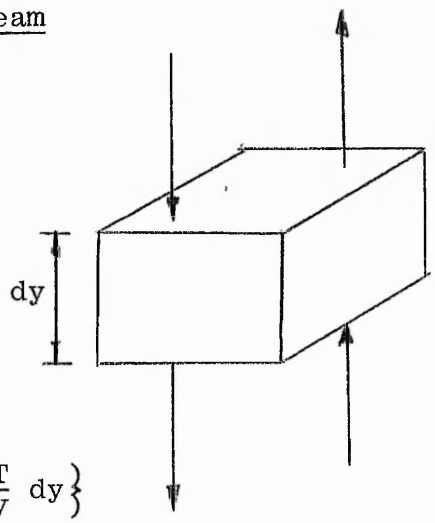
1.2

The basic equation for the loss of tracer from an increment of volume at a distance y from the inlet of the reactor due to the effects of turbulent dispersion alone is as follows:

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial y^2}$$

For a continuously operated tubular reactor (with plan area a and liquid velocity in the y-direction u_L) this equation must be modified to take account of the inputs and outputs of tracer due to the passage of the process stream.

Consider the inputs and outputs of tracer in an incremental volume at a distance y from the inlet of the reactor:



Process Stream

u_L a T

u_L a $\left\{T + \frac{\partial T}{\partial y} dy\right\}$

Turbulent Dispersion

D a $\left(\frac{\partial T}{\partial y}\right)$

D a $\frac{\partial}{\partial y}\left\{T + \frac{\partial T}{\partial y} dy\right\}$

The overall loss of tracer from the incremental volume may be expressed by:

$$a\, dy \frac{\partial T}{\partial t} = u_L\, a\, T - u_L\, a\, (T + \frac{\partial T}{\partial y} dy) - D\, a \frac{\partial T}{\partial y} + D\, a \frac{\partial}{\partial y}\left\{T + \frac{\partial T}{\partial y} dy\right\}$$

$$\Rightarrow \frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial y^2} + u_L \frac{\partial T}{\partial y}$$

1.3

$$\frac{dc}{dt} = - kc + \frac{c_i}{R} - \frac{c}{R}$$

$$\Rightarrow \frac{dc}{dt} + \left[\frac{Rk+1}{R}\right] c = \frac{c_i}{R}$$

Use Integrating Factor $e^{\left\{\frac{(Rk+1)}{R}\right\}t}$

$$\Rightarrow \frac{dc}{dt} \cdot e^{\left\{\frac{(Rk+1)}{R}\right\}t} + \left[\frac{Rk+1}{R}\right] c\, e^{\left\{\frac{(Rk+1)}{R}\right\}t} = \frac{c_i}{R}\, e^{\left\{\frac{(Rk+1)}{R}\right\}t}$$

$$\Rightarrow \frac{d}{dt}\left[c\, e^{\left\{\frac{(Rk+1)}{R}\right\}t}\right] = \frac{c_i}{R}\, e^{\left\{\frac{(Rk+1)}{R}\right\}t}$$

$$\Rightarrow c\, e^{\left\{\frac{(Rk+1)}{R}\right\}t} = \frac{c_i}{R} \int_o^t e^{\left\{\frac{(Rk+1)}{R}\right\}t}\, dt$$

$$\Rightarrow c\, e^{\left\{\frac{(Rk+1)}{R}\right\}t} = \frac{c_i}{R} \cdot \frac{R}{(Rk+1)} \left[e^{\left\{\frac{(Rk+1)}{R}\right\}t} \right]_o^t + X$$

where X = Constant of Integration

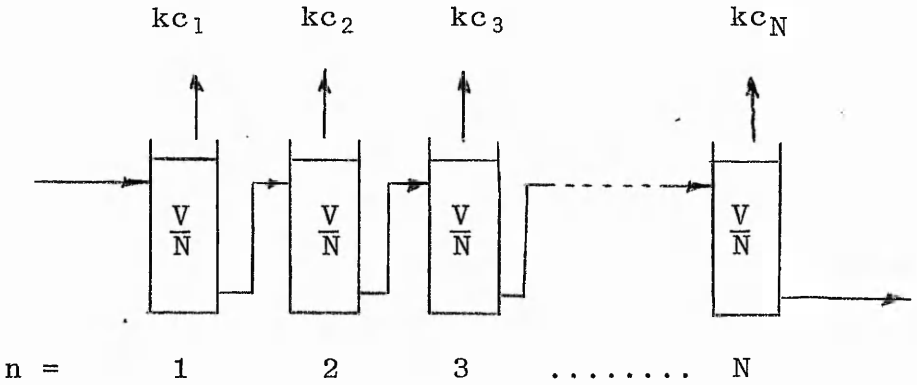
$$\Rightarrow \frac{c}{c_i} = \frac{1}{(Rk+1)} \left[1 - e^{-\left\{\frac{(Rk+1)}{R}\right\}t} \right] + X\, e^{-\left\{\frac{(Rk+1)}{R}\right\}t}$$

Boundary Conditions: when $t = 0$, $c = c_i$, $\frac{c}{c_i} = 1$

$\Rightarrow X = 1$

$$\Rightarrow \frac{c}{c_i} = \left[1 - \frac{1}{(Rk+1)}\right] e^{-\left\{\frac{(Rk+1)}{R}\right\}t} + \frac{1}{(Rk+1)}$$

1.4



n = 1:

$$\frac{dc_1}{dt} = -kc_1 - \frac{N}{R}c_1 + \frac{N}{R}c_i$$

$$\Rightarrow \frac{dc_1}{dt} + \left[\frac{Rk+N}{R}\right]c_1 = \frac{N}{R}c_i$$

Use Integrating Factor $= e^{\left\{\frac{(Rk+N)}{R}\right\}t}$

$$\Rightarrow c_1 e^{\left\{\frac{(Rk+N)}{R}\right\}t} = \frac{N}{R}c_i \int_0^t e^{\left\{\frac{(Rk+N)}{R}\right\}t}\, dt$$

$$\Rightarrow \frac{c_1}{c_i} = \left[1 - \left\{\frac{N}{(Rk+N)}\right\}\right] e^{-\left\{\frac{(Rk+N)}{R}\right\}t} + \frac{N}{(Rk+N)}$$

n = 2:

$$\frac{dc_2}{dt} = -kc_2 - \frac{N}{R}c_2 + \frac{N}{R}c_1$$

$$\Rightarrow \frac{dc_2}{dt} + \left[\frac{Rk+N}{R}\right]c_2 = \frac{N}{R}c_1$$

Use Integrating Factor = $e^{\left\{\frac{(Rk+N)}{R}\right\}t}$

$$\Rightarrow \quad c_2 \, e^{\left\{\frac{(Rk+N)}{R}\right\}t} = \frac{N}{R}\left[1 - \left\{\frac{N}{(Rk+N)}\right\}\right] c_i \int_o^t dt + \frac{N}{R} \cdot \frac{N}{Rk+N} \cdot c_i \int_o^t e^{\left\{\frac{(Rk+N)}{R}\right\}t} \, dt$$

$$\Rightarrow \frac{c_2}{c_i} = \left\{\left[1 - \left\{\frac{N}{(Rk+N)}\right\}^2\right] + \frac{Nt}{R}\left[1 - \left\{\frac{N}{(Rk+N)}\right\}\right]\right\} e^{-\left\{\frac{(Rk+N)}{R}\right\}t} + \left[\frac{N}{Rk+N}\right]^2$$

when n = N:

$$\frac{c_N}{c_i} = \left[Y\right] e^{-\left\{\frac{(Rk+N)}{R}\right\}t} + \left[\frac{N}{Rk+N}\right]^N$$

where

$$\left[Y\right] = \left[1 - \left\{\frac{N}{(Rk+N)}\right\}^N\right] + \frac{Nt}{R}\left[1 - \left\{\frac{N}{(Rk+N)}\right\}^{N-1}\right] + \left[\frac{Nt}{R}\right]^{N-1}\left[1 - \left\{\frac{N}{(Rk+N)}\right\}\right]$$

The series $\left[Y\right]$ has N terms.

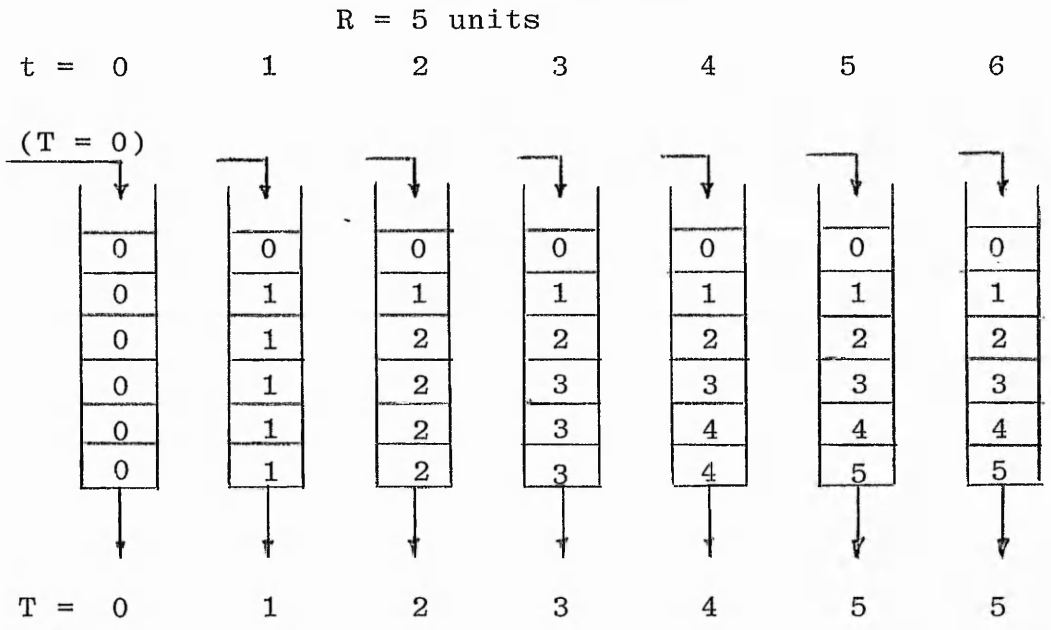
1.5

In a plug flow situation, there is no mixing between individual increments of volume in the reactor.

Since there is no mixing, at the start of a run each new increment of volume arriving at the reactor outlet will have been in the reactor for t units of time.

This situation will persist until t = R. After this each new increment of volume arriving at the reactor will have been in the reactor for a constant amount of time, equal to R.

This concept is illustrated below for a plug flow reactor receiving discrete volumetric increments:



The concentration of substance in individual increments of volume in the reactor will not be affected by the addition of influent or the extraction of effluent, but only by the progress of the chemical reactions taking place. Therefore each increment will undergo what amounts to batch treatment whilst in the reactor, and the relative drop in concentration of an increment of volume due to a first order reaction may be described by the equation:

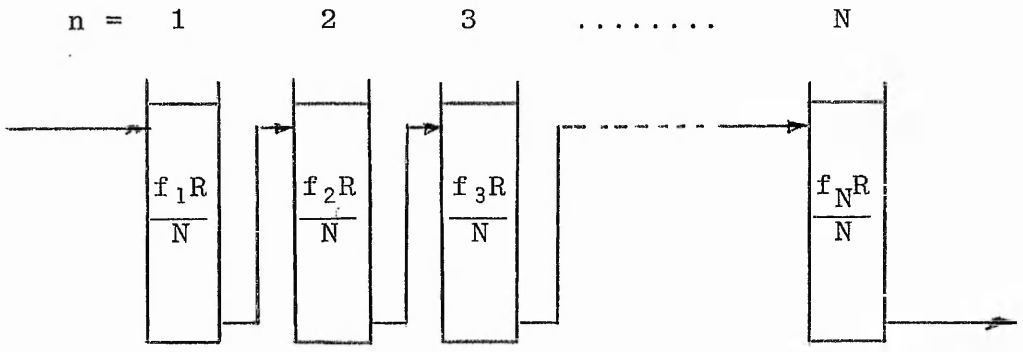
$$\frac{c}{c_i} = e^{-kT}$$

Where T refers to the treatment time for each increment of volume. Therefore the variation of c/c_i with run time, t, is given by:

$$0 < t < R \qquad \frac{c}{c_i} = e^{-kt}$$

$$R < t \qquad \frac{c}{c_i} = e^{-kR}$$

1.6



Total Retention Time, $R = (f_1 + f_2 + f_3 + ... + f_N) \frac{R}{N}$

n = 1:

$$\frac{dT_1}{dt} = - \frac{N}{f_1 R} T_1$$

$$\Rightarrow \frac{T_1}{T_i} = e^{\frac{-Nt}{f_1 R}}$$

n = 2:

$$\frac{dT_2}{dt} = - \frac{N}{f_2 R} T_2 + \frac{N}{f_2 R} T_1$$

$$\Rightarrow \frac{dT_2}{dt} + \frac{N}{f_2 R} T_2 = \frac{N}{f_2 R} T_i \, e^{\frac{-Nt}{f_1 R}}$$

Use Integrating Factor = $e^{\frac{Nt}{f_2 R}}$

$$\Rightarrow T_2 \, e^{\frac{Nt}{f_2 R}} = \frac{N}{f_2 R} T_i \int_0^t e^{\frac{Nt}{R}\left(\frac{1}{f_2} - \frac{1}{f_1}\right)} \, dt$$

$$\Rightarrow \frac{T_2}{T_i} = \frac{1}{1 - (f_2/f_1)} \left[e^{\frac{-Nt}{f_1 R}} - e^{\frac{-Nt}{f_2 R}} \right] + X \, e^{\frac{-Nt}{f_2 R}}$$

where X = Constant of Integration,

Boundary Conditions: when $t = 0$, $T_2/T_i = 1 \Rightarrow X = 1$

$$\Rightarrow \frac{T_2}{T_i} = \left[\frac{1}{1 - (f_2/f_1)} \right] \left[e^{\frac{-Nt}{f_1 R}} \right] + \left[1 - \frac{1}{1 - (f_2/f_1)} \right] \left[e^{\frac{-Nt}{f_2 R}} \right]$$

n = 3:

By a similar approach to the above:

$$\frac{T_3}{T_i} = \left[\frac{1}{1 - (f_3/f_1)} \right] \left[\frac{1}{1 - (f_2/f_1)} \right] \left[e^{\frac{-Nt}{f_1 R}} \right] + \left[\frac{1}{1 - (f_3/f_2)} \right] \left[1 - \frac{1}{1 - (f_2/f_1)} \right] \left[e^{\frac{-Nt}{f_2 R}} \right] + \left\{ \left[1 - \frac{1}{1 - (f_3/f_1)} \right] \left[\frac{1}{1 - (f_2/f_1)} \right] - \left[\frac{1}{1 - (f_3/f_2)} \right] \left[1 - \frac{1}{1 - (f_2/f_1)} \right] \right\} \left[e^{\frac{-Nt}{f_3 R}} \right]$$

It will be seen that this expression for T_3/T_i may be derived from the expression for T_2/T_i by the following procedure:

a. There will be three separate exponential terms, viz:

$$e^{\frac{-Nt}{f_1 R}}$$

$$e^{\frac{-Nt}{f_2 R}}$$

$$e^{\frac{-Nt}{f_3 R}}$$

b. The value of the series preceding each exponential term will be as follows:

$e^{\frac{-Nt}{f_1R}}$ term: Multiply relevant series from T_2/T_i series by

$$\frac{1}{1 - (f_3/f_1)}$$

$e^{\frac{-Nt}{f_2R}}$ term: Multiply relevant series from T_2/T_i series by

$$\frac{1}{1 - (f_3/f_2)}$$

$e^{\frac{-Nt}{f_3R}}$ term: Subtract the sum of the two series derived above from unity.

Thus for n = n:

$$\frac{T_n}{T_i} = \left[\frac{1}{1 - (f_n/f_1)}\right]\left[\begin{array}{l}\text{relevant series in} \\ \text{expression for } T_n\end{array}\right]\left[e^{\frac{-Nt}{f_1R}}\right]$$

$$+ \left[\frac{1}{1 - (f_n/f_2)}\right]\left[\begin{array}{l}\text{relevant series in} \\ \text{expression for } T_n\end{array}\right]\left[e^{\frac{-Nt}{f_1R}}\right]$$

$$+ \cdots\cdots\cdots\cdots$$

$$\vdots$$

$$+ \left[1 - \text{sum of all previous series}\right]\left[e^{\frac{-Nt}{f_nR}}\right]$$

In order to avoid lengthy algebraic expressions, the numerical values for the series preceding each exponential term have been calculated for the particular experimental system used in the research programme.

2-STAGE OPERATION

$f_1 = 1.008 \qquad f_2 = 0.992$

$$\Rightarrow \frac{T_2}{T_i} = 63\left[e^{-1.984\frac{t}{R}}\right] - 62\left[e^{-2.016\frac{t}{R}}\right]$$

Using this equation, values of T_2/T_i have been calculated for various values of t/R. These have been compared with the values of T_2/T_i calculated from equation (XII), Section 2.4.1.3.c., assuming each compartment is of equal volume.

t/R	T_2/T_i (Unequal Volumes)	T_2/T_i (Equal Volumes)
0.0	1.000	1.000
0.2	0.938	0.938
0.4	0.809	0.809
0.6	0.663	0.663
0.8	0.525	0.525
1.0	0.406	0.406
1.5	0.199	0.199
2.0	0.092	0.092
3.0	0.017	0.017

3-STAGE OPERATION

$f_1 = 1.036 \qquad f_2 = 0.970 \qquad f_3 = 0.995$

$$\Rightarrow \frac{T_3}{T_i} = 396.64 \left[e^{-2.896 \frac{t}{R}} \right] + 570.24 \left[e^{-3.093 \frac{t}{R}} \right] - 965.88 \left[e^{-3.015 \frac{t}{R}} \right]$$

From which:

t/R	T_3/T_i (Unequal Volumes)	T_3/T_i (Equal Volumes)
0.0	1.000	1.000
0.2	0.977	0.977
0.4	0.880	0.879
0.6	0.731	0.731
0.8	0.570	0.570
1.0	0.423	0.423
1.5	0.174	0.174
2.0	0.062	0.062
3.0	0.006	0.006

6-STAGE OPERATION

$f_1 = 1.091$ $f_2 = 1.017$ $f_3 = 0.990$

$f_4 = 0.937$ $f_5 = 0.998$ $f_6 = 0.968$

$$\Rightarrow \frac{T_6}{T_i} = 117,398 \left[e^{-5 \cdot 500 \frac{t}{R}}\right] - 7,310,879 \left[e^{-5 \cdot 900 \frac{t}{R}}\right] - 37,386,423 \left[e^{-6 \cdot 061 \frac{t}{R}}\right] - 584,951 \left[e^{-6 \cdot 403 \frac{t}{R}}\right] + 38,271,464 \left[e^{-6 \cdot 012 \frac{t}{R}}\right] + 6,892,392 \left[e^{-6 \cdot 198 \frac{t}{R}}\right]$$

From which:

t/R	T_6/T_i (Unequal Volumes)	T_6/T_i (Equal Volumes)
0.0	1.000	1.000
0.2	0.999	0.998
0.4	0.964	0.964
0.6	0.844	0.844
0.8	0.651	0.651
1.0	0.446	0.446
1.5	0.116	0.116
2.0	0.020	0.020
3.0	0.000	0.000

1.7

The formulation of an expression for c/c_i, when the influent flowrate through the cell (v) varies, follows a similar procedure to that described in Appendix 1.3 for constant flow conditions. The same basic differential equation applies:

$$\frac{dc}{dt} = - kc + \frac{c_i}{R} - \frac{c}{R}$$

In Appendix 1.3 this was shown to produce the expression:

$$\frac{c}{c_i} = \frac{1}{(Rk+1)} \left[1 - e^{-\left\{\frac{(Rk+1)}{R}\right\}t} \right] + X\, e^{-\left\{\frac{(Rk+1)}{R}\right\}t}$$

When a stepwise variation in influent flowrate is applied to the flotation cell, each step will have its own solution to the above equation. The difference between the form of the equation for each step will depend on two factors:

a. Since influent flowrate (v) varies, so too will the cell retention time (R).

b. For each step a new value of the integration constant (X) must be found.

This is illustrated for the case described in Section 4.6.3.

For the whole duration of test the following apply:

$k = 0.116067\ min^{-1}$

$V = 110\ l$

$0 < t < 5$

$v = 2\ l\ min^{-1}$

$\Rightarrow R = 55\ min$

$$\frac{c}{c_i} = 0.1354 \left[1 - e^{-0.1342t} \right] + X\, e^{-0.1342t}$$

Boundary Conditions: when $t = 0$, $c/c_i = 1$

$\Rightarrow X = 1$

$$\Rightarrow \frac{c}{c_i} = 0.8646\ e^{-0.1342t} + 0.1354$$

When $t = 5$, $c/c_i = 0.5773$

$5 < t < 10$

$v = 6\ l\ min^{-1}$

$\Rightarrow R = 18.33\ min$

$$\frac{c}{c_i} = 0.3197\left[1 - e^{-0.1706t}\right] + X\ e^{-0.1706t}$$

Boundary Conditions: when $t = 5$, $c/c_i = 0.5773$

$\Rightarrow X = 0.9242$

$$\Rightarrow \frac{c}{c_i} = 0.6045\ e^{-0.1706t} + 0.3197$$

When $t = 10$, $c/c_i = 0.4295$

The above procedure can be used for each stepwise change in flowrate.

The resulting equations for c/c_i are summarised below:

$0 < t < 5 \quad \frac{c}{c_i} = 0.8646\ e^{-0.1342t} + 0.1354$

$5 < t < 10 \quad \frac{c}{c_i} = 0.6045\ e^{-0.1706t} + 0.3197$

$10 < t < 15 \quad \frac{c}{c_i} = -0.0773\ e^{-0.2070t} + 0.4392$

$15 < t < 25 \quad \frac{c}{c_i} = 2.2496\ e^{-0.1342t} + 0.1354$

$25 < t < 30 \quad \frac{c}{c_i} = -7.5335\ e^{-0.1706t} + 0.3197$

$30 < t < 35 \quad \frac{c}{c_i} = -31.8833\ e^{-0.1888t} + 0.3852$

$$35 < t < 40 \quad \frac{c}{c_i} = 21.5009\, e^{-0.1524t} + 0.2386$$

$$40 < t < 50 \quad \frac{c}{c_i} = 32.5465\, e^{-0.1342t} + 0.1354$$

If appropriate values of t are inserted in these equations a graph of c/c_i vs t for the whole test may be produced (see Figure 40).

1.8

$$-\frac{V}{Ax_2b} \cdot \frac{ds}{dt} = X\,(1 - e^{-Ys})$$

$$\Rightarrow \int_{s_i}^{s} \frac{ds}{1 - e^{-Ys}} = -X \cdot \frac{Ax_2b}{V} \int_{o}^{t} dt$$

Solve by substituion: $I = e^{-Ys}$

$$\Rightarrow \frac{dI}{ds} = -Y\,e^{-Ys} = -YI$$

$$\Rightarrow \int \frac{ds}{1 - e^{-Ys}} = \int \frac{dI}{-YI\,(1 - I)}$$

$$= -\int \frac{dI}{YI} - \int \frac{dI}{Y(1 - I)}$$

$$= -\frac{\ln I}{Y} + \frac{\ln(1 - I)}{Y}$$

$$\Rightarrow \int_{s_i}^{s} \frac{ds}{1 - e^{-Ys}} = -\frac{1}{Y}\left[\ln e^{-Ys}\right]_{s_i}^{s} + \frac{1}{Y}\left[\ln(1 - e^{-Ys})\right]_{s_i}^{s}$$

$$= (s - s_i) + \frac{1}{Y} \ln\left[\frac{(1 - e^{-Ys})}{(1 - e^{-Ysi})}\right]$$

$$\Rightarrow Y\left[s - s_i\right] + \ln\left[\frac{(1 - e^{-Ys})}{(1 - e^{-Ysi})}\right] = -XY \cdot \frac{Ax_2b}{V} \cdot t$$

APPENDIX 2

DETAILS OF EXPERIMENTAL PROGRAMME

2.1 Group P Experiments

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v ($l\ min^{-1}$)	s* ($mg\ l^{-1}$)	N
P1	Continuous test	240	1,000	30	10	2
P2	"	"	"	20	"	"
P3	"	"	"	15	"	"
P4	"	"	"	12	"	"
P5	"	"	"	10	"	"
P6	"	"	"	30	20	"
P7	"	"	"	20	"	"
P8	"	"	"	15	"	"
P9	"	"	"	12	"	"
P10	"	"	"	10	"	"
P11	"	"	"	30	25	"
P12	"	"	"	20	"	"
P13	"	"	"	15	"	"
P14	"	"	"	12	"	"
P15	"	"	"	10	"	"

* Nominal surfactant concentration (see 4.7.4)

2.2 Group A Experiments

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v* ($l\ min^{-1}$)	s** ($mg\ l^{-1}$)	c_i ($mg\ l^{-1}$)	N
A1	Conductivity calibration	–	–	–	–	–	–
A2	Mixing test	25	150	2	–	–	1
A3	"	5	"	"	–	–	"
A4	"	0	"	"	–	–	"
A5	Turbidity calibration	–	–	–	–	–	–
A6	Batch test for clay removal	25	150	2	25 initial	100	1
A7	"	"	"	"	25 nominal	"	"
A8	"	20	"	"	25 initial	"	"
A9	"	"	"	"	25 nominal	"	"
A10	"	15	"	"	25 initial	"	"
A11	"	"	"	"	25 nominal	"	"
A12	"	10	"	"	25 initial	"	"
A13	"	"	"	"	25 nominal	"	"

* In the case of batch tests this value represents the flow rate of the recirculation stream

** This value represents either the initial surfactant concentration (for tests under variable conditions) or the nominal surfactant concentration (for tests under constant conditions)

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v* ($l\ min^{-1}$)	s** ($mg\ l^{-1}$)	c_i ($mg\ l^{-1}$)	N
A14	Batch test for clay removal	5	150	2	25 initial	100	1
A15	Continuous test for clay removal	25	"	8	25 nominal	"	"
A16	"	"	"	6	"	"	"
A17	"	"	"	4	"	"	"
A18	"	"	"	2	"	"	"
A19	"	20	"	8	"	"	"
A20	"	"	"	6	"	"	"
A21	"	"	"	4	"	"	"
A22	"	"	"	2	"	"	"
A23	"	15	"	8	"	"	"
A24	"	"	"	6	"	"	"
A25	"	"	"	4	"	"	"
A26	"	"	"	2	"	"	"
A27	"	10	"	8	"	"	"
A28	"	"	"	6	"	"	"
A29	"	"	"	4	"	"	"
A30	"	"	"	2	"	"	"
A31	Coulter counter analysis of Test A30	-	-	-	-	-	-

2.3 Group B Experiments

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v* ($l\ min^{-1}$)	s** ($mg\ l^{-1}$)	c_i ($mg\ l^{-1}$)	N
B1	Mixing test	5	110	4	-	-	1
B2	Batch test for surfactant removal	25	"	2	45 initial	100	"
B3	"	20	"	"	"	"	"
B4	"	15	"	"	"	"	"
B5	"	10	"	"	"	"	"
B6	"	5	"	"	"	"	"
B7	Batch test for clay removal	25	"	"	35 nominal	"	"
B8	"	"	"	"	25 nominal	"	"
B9	"	"	"	"	15 nominal	"	"
B10	"	"	"	"	7.5 nominal	"	"
B11	"	"	"	"	5 nominal	"	"
B12	"	20	"	"	45 nominal	"	"
B13	"	"	"	"	35 nominal	"	"
B14	"	"	"	"	25 nominal	"	"
B15	"	"	"	"	15 nominal	"	"

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v* ($l\ min^{-1}$)	s** ($mg\ l^{-1}$)	c_i ($mg\ l^{-1}$)	N
B16	Batch test for clay removal	20	110	2	7.5 nominal	100	1
B17	"	"	"	"	5 nominal	"	"
B18	"	15	"	"	35 nominal	"	"
B19	"	"	"	"	25 nominal	"	"
B20	"	"	"	"	15 nominal	"	"
B21	"	"	"	"	7.5 nominal	"	"
B22	"	"	"	"	5 nominal	"	"
B23	"	10	"	"	35 nominal	"	"
B24	"	"	"	"	25 nominal	"	"
B25	"	"	"	"	15 nominal	"	"
B26	"	"	"	"	7.5 nominal	"	"
B27	"	"	"	"	5 nominal	"	"
B28	"	5	"	"	35 nominal	"	"

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v* ($l\ min^{-1}$)	s** ($mg\ l^{-1}$)	c_i ($mg\ l^{-1}$)	N
B29	Batch test for clay removal	5	110	2	25 nominal	100	1
B30	"	"	"	"	15 nominal	"	"
B31	"	"	"	"	7.5 nominal	"	"
B32	"	"	"	"	5 nominal	"	"
B33	Spectrophotometer calibration	-	-	-	-	-	-
B34	Titration standardisation	-	-	-	-	-	-

2.4 Group C Experiments

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v* ($l\ min^{-1}$)	s** ($mg\ l^{-1}$)	c_i ($mg\ l^{-1}$)	N
C1	Mixing tests	30	300	5	-	-	1
C2	"	"	"	"	-	-	2
C3	"	"	"	"	-	-	3
C4	"	"	"	"	-	-	6
C5	Batch test for surfactant removal	"	"	"	45 initial	100	1
C6	"	50	"	"	"	"	"
C7	Batch test for clay removal	30	"	"	7.5 nominal	"	"
C8	"	50	"	"	"	"	"
C9	Continuous test for clay removal	30	"	"	"	"	"
C10	"	"	"	"	"	"	2
C11	"	"	"	"	"	"	3
C12	"	"	"	"	"	"	6
C13	"	50	"	"	"	"	1
C14	"	"	"	"	"	"	2
C15	"	"	"	"	"	"	3
C16	"	"	"	"	"	"	6

2.5 Group D Experiments

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v* ($l\ min^{-1}$)	s** ($mg\ l^{-1}$)	c_i ($mg\ l^{-1}$)	N
D1	Batch test for surfactant removal	25	110	2	45 initial	100	1
D2	"	"	90	"	"	"	"
D3	"	"	70	"	"	"	"
D4	"	"	50	"	"	"	"
D5	"	"	110	"	"	200	"
D6	"	"	"	"	"	0	"
D7	Batch test for surfactant removal using model sediment	"	"	"	"	100	"
D8	Batch test for clay removal	"	"	"	100 nominal	"	"
D9	"	"	"	"	80 nominal	"	"
D10	"	"	"	"	60 nominal	"	"
D11	"	"	"	"	50 nominal	"	"
D12	"	"	"	"	40 nominal	"	"
D13	"	"	"	"	30 nominal	"	"
D14	"	"	"	"	20 nominal	"	"
D15	"	"	"	"	15 nominal	"	"

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v* ($l\ min^{-1}$)	s** ($mg\ l^{-1}$)	c_i ($mg\ l^{-1}$)	N
D16	Batch test for clay removal	25	110	2	10 nominal	100	1
D17	"	"	"	"	7.5 nominal	"	"
D18	"	"	"	"	5 nominal	"	"
D19	"	"	"	"	2.5 nominal	"	"
D20	"	"	"	"	25 nominal	"	"
D21	"	"	90	"	"	"	"
D22	"	"	70	"	"	"	"
D23	"	"	50	"	"	"	"
D24	"	"	110	"	50 nominal	200	"
D25	"	"	"	"	40 nominal	"	"
D26	"	"	"	"	30 nominal	"	"
D27	"	"	"	"	20 nominal	"	"
D28	"	"	"	"	10 nominal	"	"
D29	Continuous test for clay removal	"	"	2 - 10 variable	10 nominal	100	"

Test No.	Comments	A ($l\ min^{-1}$)	V (l)	v* ($l\ min^{-1}$)	s** ($mg\ l^{-1}$)	c_i ($mg\ l^{-1}$)	N
D30	Batch test for model sediment removal	25	110	2	10 nominal	100	1
D31	Continuous test for model sediment removal	"	"	3	"	"	"
D32	Turbidity standardisation of model sediment	-	-	-	-	-	-
D33	Sieve analysis of model sediment	-	-	-	-	-	-
D34	Coulter counter analysis of model sediment	-	-	-	-	-	-
D35	Batch test for clay removal	5	50	2	7.5 nominal	100	1
D36	Mixing test with honeycomb packing	25	110	5	-	-	"
D37	"	5	"	"	-	-	"

APPENDIX 3

RESULTS

TEST P1

t (min.)	τ (FTU)	τ/τ_i
0	34.0	1.00
5	32.0	0.94
15	28.0	0.82
25	24.0	0.71
35	21.0	0.62
45	20.0	0.59
55	19.0	0.56
65	19.0	0.56
75	19.0	0.56

TEST P2

t (min.)	τ (FTU)	τ/τ_i
0	29.8	1.00
2	28.0	0.94
12	22.5	0.76
22	19.0	0.64
32	16.0	0.54
42	14.0	0.47
52	13.0	0.44
62	12.5	0.42
72	12.5	0.42
82	12.5	0.42

TEST P3

t (min.)	τ (FTU)	τ/τ_i
0	9.9	1.00
2	9.6	0.97
12	7.9	0.80
22	6.2	0.63
32	5.2	0.53
42	4.2	0.42
52	3.8	0.38
62	3.8	0.38
72	3.6	0.36
82	3.6	0.36
92	3.6	0.36

TEST P4

t (min.)	τ (FTU)	τ/τ_i
0	10.5	1.00
2	10.5	1.00
12	8.6	0.82
22	7.2	0.69
32	6.2	0.59
42	5.2	0.50
52	4.3	0.41
62	3.9	0.37
72	3.7	0.35
82	3.6	0.34
92	3.6	0.34
102	3.6	0.34

TEST P5

t (min.)	τ (FTU)	τ/τ_i
0	10.5	1.00
8	9.2	0.88
18	7.6	0.72
28	6.6	0.63
38	5.7	0.54
48	4.8	0.46
58	4.5	0.43
68	4.1	0.39
78	4.0	0.38
88	4.0	0.38
98	4.0	0.38

TEST P6

t (min.)	τ (FTU)	τ/τ_i
0	8.5	1.00
5	7.0	0.82
15	5.2	0.61
25	4.6	0.54
35	4.5	0.53
45	4.5	0.53
55	4.5	0.53
65	4.5	0.53

TEST P7

t (min.)	τ (FTU)	τ/τ_i
0	7.5	1.00
3	7.0	0.93
13	5.0	0.67
23	4.0	0.53
33	3.5	0.47
43	3.3	0.44
53	3.0	0.40
63	3.0	0.40
73	3.0	0.40

TEST P8

t (min.)	τ (FTU)	τ/τ_i
0	9.9	1.00
3	9.4	0.95
13	7.0	0.71
23	5.0	0.51
33	4.6	0.47
43	4.0	0.40
53	3.6	0.36
63	3.3	0.33
73	3.0	0.30
83	2.7	0.27
93	2.7	0.27
103	2.7	0.27

TEST P9

t (min.)	τ (FTU)	τ/τ_i
0	8.5	1.00
2	8.3	0.98
12	6.9	0.81
22	4.5	0.53
32	3.2	0.38
42	2.6	0.31
52	2.4	0.28
62	2.2	0.26
72	2.2	0.26
82	2.2	0.26

TEST P10

t (min.)	τ (FTU)	τ/τ_i
0	8.6	1.00
3	8.1	0.94
13	6.5	0.76
23	3.9	0.45
33	3.5	0.41
43	3.3	0.38
53	3.0	0.35
63	2.8	0.33
73	2.5	0.29
83	2.5	0.29
93	2.5	0.29

TEST P11

t (min.)	τ (FTU)	τ/τ_i
0	10.3	1.00
10	8.0	0.78
20	6.0	0.58
30	5.5	0.54
40	5.2	0.50
50	5.0	0.49
60	5.0	0.49
70	5.0	0.49

TEST P12

t (min.)	τ (FTU)	τ/τ_i
0	37.4	1.00
8	31.5	0.84
18	25.5	0.68
28	19.5	0.52
38	16.5	0.44
48	14.5	0.39
58	13.5	0.36
68	12.5	0.33
78	12.0	0.32
88	12.0	0.32
98	12.0	0.32

TEST P13

t (min.)	τ (FTU)	τ/τ_i
0	34.4	1.00
8	32.0	0.93
18	28.5	0.83
28	24.0	0.70
38	21.0	0.61
48	17.0	0.49
58	15.0	0.44
68	13.5	0.39
78	12.0	0.35
88	11.5	0.33
98	10.0	0.29
108	9.4	0.27
118	9.4	0.27
128	9.4	0.27

TEST P14

t (min.)	τ (FTU)	τ/τ_i
0	11.0	1.00
10	7.5	0.68
20	5.0	0.45
30	4.0	0.36
40	3.1	0.28
50	2.6	0.24
60	2.4	0.22
70	2.4	0.22
80	2.4	0.22

TEST P15

t (min.)	τ (FTU)	τ/τ_i
0	19.4	1.00
7	14.0	0.72
17	9.4	0.48
27	7.7	0.40
37	6.6	0.34
47	5.1	0.26
57	4.3	0.22
67	4.1	0.21
77	3.6	0.19
87	3.4	0.18
97	3.4	0.18
107	3.4	0.18

TEST A1

T ($g\ l^{-1}$)	Ω (mmho)	$\log_{10}$ T	$\log_{10}$ Ω
0.000	0.30	$-\infty$	-0.5228
0.433	1.05	-0.3635	0.0212
0.827	1.66	-0.0825	0.2201
1.187	2.18	0.0745	0.3385
1.516	2.65	0.1807	0.4232
1.819	3.00	0.2598	0.4771
2.105	3.32	0.3233	0.5211
2.358	3.62	0.3725	0.5587
2.599	3.90	0.4148	0.5911
2.823	4.11	0.4507	0.6138
3.032	4.30	0.4817	0.6335
3.228	4.50	0.5089	0.6532
3.411	4.70	0.5329	0.6721
3.584	4.85	0.5544	0.6857
3.746	5.00	0.5736	0.6990

Tracer Type: Sodium Chloride

Liquid Medium: Laboratory Tapwater

TEST A2

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i	$\ln(T/T_i)$
0.0	4.15	2.83	1.0000	0.0000
7.5	3.83	2.54	0.8975	-0.1081
15.0	3.54	2.28	0.8057	-0.2161
22.5	3.29	2.06	0.7279	-0.3176
30.0	3.04	1.84	0.6502	-0.4305
37.5	2.82	1.66	0.5866	-0.5335
45.0	2.61	1.48	0.5230	-0.6482
52.5	2.42	1.34	0.4735	-0.7476
60.0	2.24	1.20	0.4240	-0.8580
67.5	2.07	1.07	0.3781	-0.9726
75.0	1.93	0.98	0.3463	-1.0605
82.5	1.79	0.89	0.3145	-1.1568
90.0	1.64	0.79	0.2792	-1.2760
97.5	1.51	0.70	0.2473	-1.3970
105.0	1.40	0.64	0.2261	-1.4866
112.5	1.30	0.57	0.2014	-1.6024
120.0	1.23	0.53	0.1873	-1.6752

TEST A3

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i	$\ln(T/T_i)$
0.0	4.14	2.82	1.0000	0.0000
7.5	3.88	2.58	0.9149	-0.0889
15.0	3.60	2.33	0.8262	-0.1909
22.5	3.32	2.08	0.7376	-0.3044
30.0	3.07	1.84	0.6525	-0.4270
37.5	2.83	1.67	0.5922	-0.5239
45.0	2.61	1.48	0.5248	-0.6447
52.5	2.42	1.34	0.4752	-0.7441
60.0	2.23	1.19	0.4220	-0.8628
67.5	2.07	1.07	0.3794	-0.9691
75.0	1.92	0.97	0.3440	-1.0672
82.5	1.78	0.88	0.3121	-1.1646
90.0	1.64	0.79	0.2801	-1.2725
97.5	1.52	0.71	0.2518	-1.3792
105.0	1.40	0.64	0.2270	-1.4830
112.5	1.31	0.58	0.2057	-1.5815
120.0	1.22	0.52	0.1849	-1.6907

TEST A4

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i
0.00	4.50	3.20	1.0000
7.50	4.50	3.20	1.0000
15.00	4.50	3.20	1.0000
22.50	4.49	3.19	0.9969
30.00	4.48	3.18	0.9938
37.50	4.47	3.17	0.9906
45.00	4.46	3.16	0.9875
52.50	4.46	3.16	0.9875
60.00	4.44	3.14	0.9813
67.50	4.40	3.09	0.9656
75.00	4.37	3.06	0.9563
75.75	4.37	3.06	0.9563
76.50	4.32	2.95	0.9219
77.25	3.83	2.53	0.7906
78.00	3.06	1.84	0.5750
78.75	2.48	1.39	0.4344
79.50	2.03	1.05	0.3281
80.25	1.71	0.84	0.2625
81.00	1.40	0.63	0.1969
81.75	1.17	0.50	0.1563
82.50	0.89	0.32	0.1000
83.25	0.60	0.15	0.0469
84.00	0.48	0.09	0.0281
84.75	0.44	0.06	0.0188
86.25	0.41	0.05	0.0156
90.00	0.38	0.04	0.0125
97.50	0.36	0.03	0.0094
105.00	0.34	0.02	0.0063
112.50	0.34	0.02	0.0063
120.00	0.33	0.01	0.0031

TEST A5

c (mg l^{-1})	τ (FTU)
0.00	1.5
4.93	3.0
9.85	4.3
19.69	8.0
30.29	12.0
40.38	15.0
50.47	18.0
69.62	22.5
89.25	32.0
111.56	37.5
131.25	44.0
150.00	50.0

Clay Type: RLO 1724

Liquid Medium: Laboratory Tapwater

TEST A6

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	31.0	91.2371	1.0000	0.0000
3	22.5	64.9485	0.7119	-0.3398
6	17.5	49.4845	0.5424	-0.6118
9	13.0	35.5670	0.3898	-0.9421
12	10.0	26.2887	0.2881	-1.2444
15	7.9	19.7938	0.2169	-1.5283
18	6.6	15.7732	0.1729	-1.7550
21	5.3	11.7526	0.1288	-2.0495
24	4.5	9.2784	0.1017	-2.2857
27	3.9	7.4227	0.0814	-2.5084
30	3.6	6.4948	0.0712	-2.6430

t (min.)	s/s_i	$\ln(s/s_i)$
0	1.0000	0.0000
3	0.9301	-0.0725
6	0.8598	-0.1511
9	0.8050	-0.2169
12	0.7425	-0.2977
15	0.6956	-0.3629
18	0.6565	-0.4208
21	0.6096	-0.4949
24	0.5706	-0.5611
27	0.5159	-0.6619
30	0.4690	-0.7572

TEST A7

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
3	28.5	83.5052	0.8308	-0.1854
6	22.0	63.4021	0.6308	-0.4608
9	16.5	46.3918	0.4615	-0.7733
12	12.0	32.4742	0.3231	-1.1298
15	10.0	26.2887	0.2615	-1.3413
18	7.9	19.7983	0.1969	-1.6251
21	6.6	15.7732	0.1569	-1.8521
24	5.5	12.3711	0.1231	-2.0948
27	4.9	10.5155	0.1046	-2.2576
30	4.5	9.2784	0.0923	-2.3827

t (min.)	s/s_i
0	1.0000
15	1.1228
30	1.2281

TEST A8

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	31.5	92.7835	1.0000	0.0000
4	24.5	71.1340	0.7667	-0.2657
8	18.5	52.5773	0.5667	-0.5679
12	13.0	35.5670	0.3833	-0.9589
16	9.0	23.1959	0.2500	-1.3863
20	7.5	18.5567	0.2000	-1.6094
24	6.0	13.9175	0.1500	-1.8971
30	5.2	11.4433	0.1233	-2.0931
32	4.7	9.8969	0.1067	-2.2377
36	3.9	7.4227	0.0800	-2.5257

t (min.)	s/s_i	$\ln(s/s_i)$
0	1.0000	0.0000
4	0.9920	-0.0080
8	1.0000	0.0000
12	0.8720	-0.1370
16	0.8160	-0.2033
20	0.7520	-0.2850
24	0.7120	-0.3397
30	0.6720	-0.3975
32	0.6320	-0.4589
36	0.6000	-0.5108

TEST A9

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	32.5	95.8763	1.0000	0.0000
4	26.5	77.3196	0.8065	-0.2151
8	18.5	52.5773	0.5484	-0.6008
12	13.5	37.1134	0.3871	-0.9491
16	10.0	26.2887	0.2742	-1.2939
20	8.1	20.4124	0.2129	-1.5469
24	6.4	15.1546	0.1581	-1.8445
28	5.3	11.7526	0.1226	-2.0988
32	4.3	8.6598	0.0903	-2.4046
36	3.6	6.4948	0.0677	-2.6927

t (min.)	s/s_i
0	1.0000
16	1.0156
36	1.0313

TEST A10

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	31.5	92.7835	1.0000	0.0000
5	25.5	74.2268	0.8000	-0.2231
10	19.0	54.1237	0.5833	-0.5391
15	15.0	41.7526	0.4500	-0.7985
20	11.5	30.9278	0.3333	-1.0987
25	8.9	22.8866	0.2467	-1.3996
30	7.7	19.1753	0.2067	-1.5765
35	6.1	14.2268	0.1533	-1.8754
40	5.4	12.0619	0.1300	-2.0402
45	3.9	7.4227	0.0800	-2.5257

t (min.)	s/s_i	$\ln(s/s_i)$
0	1.0000	0.0000
5	0.8976	-0.1080
10	0.8346	-0.1807
15	0.7953	-0.2291
20	0.7717	-0.2592
25	0.7402	-0.3009
30	0.6850	-0.3783
35	0.6142	-0.4875
40	0.5669	-0.5675
45	0.5354	-0.6247

TEST A11

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	37.0	109.7938	1.0000	0.0000
3	32.0	94.3299	0.8592	-0.1518
6	25.0	72.6804	0.6620	-0.4125
9	22.0	63.4021	0.5775	-0.5490
12	18.0	51.0309	0.4648	-0.7661
15	14.5	40.2062	0.3662	-1.0046
18	12.0	32.4742	0.2958	-1.2181
21	10.0	26.2887	0.2394	-1.4296
24	8.5	21.6495	0.1972	-1.6235
27	7.7	19.1753	0.1746	-1.7453
30	7.4	18.2474	0.1662	-1.7946
33	6.2	14.5361	0.1324	-2.0219

t (min.)	s/s_i
0	1.0000
21	1.0317
33	1.0953

TEST A12

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	26.5	77.3196	1.0000	0.0000
8	19.0	54.1237	0.7000	-0.3567
16	15.0	41.7526	0.5400	-0.6162
26	10.0	26.2887	0.3400	-1.0788
32	7.8	19.4845	0.2520	-1.3783
40	6.3	14.8454	0.1920	-1.6503
48	5.1	11.1340	0.1440	-1.9379
56	3.8	7.1134	0.0920	-2.3860
64	3.3	5.5670	0.0720	-2.6311
72	2.6	3.4021	0.0440	-2.1236

t (min.)	s/s_i	$\ln(s/s_i)$
0	1.0000	0.0000
8	0.9035	-0.1015
16	0.8509	-0.1615
26	0.7982	-0.2253
32	0.7456	-0.2935
40	0.6930	-0.3668
48	0.6228	-0.4735
56	0.5789	-0.5465
64	0.5351	-0.6253
72	0.4825	-0.7289

TEST A13

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	31.0	91.2371	1.0000	0.0000
8	23.0	66.4948	0.7288	-0.3164
16	16.0	44.8454	0.4915	-0.7103
24	10.5	27.8351	0.3051	-1.1871
42	6.3	14.8454	0.1627	-1.8158
48	4.8	10.2062	0.1119	-2.1901
57	4.0	7.7320	0.0847	-2.4686
64	3.7	6.8041	0.0746	-2.5956
72	3.6	6.4948	0.0712	-2.6423

t (min.)	s/s_i
0	1.0000
42	1.0000
72	1.0000

TEST A14

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	32.0	94.3299	1.0000	0.0000
8	32.0	94.3299	1.0000	0.0000
16	29.0	85.0515	0.9016	-0.1035
24	23.0	66.4948	0.7049	-0.3497
32	24.0	69.5876	0.7377	-0.3042
40	17.0	47.9381	0.5082	-0.6789
48	18.0	51.0309	0.5410	-0.6144
56	13.0	35.5670	0.3770	-0.9754
64	10.5	27.8351	0.2951	-1.2205
72	9.5	24.7423	0.2623	-1.3383

t (min.)	s/s_i	$\ln(s/s_i)$
0	1.0000	0.0000
8	0.9661	-0.0345
16	0.9407	-0.0612
24	0.9068	-0.0979
32	0.8898	-0.1167
40	0.8559	-0.1556
48	0.8220	-0.1960
64	0.7542	-0.2820
72	0.7458	-0.2933

TEST A15

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0	33.0	97.4227	1,0000	1.0000
1	33.0	97.4227	1.0000	
2	30.0	88.1443	0.9048	
3	27.0	78.8660	0.8095	
4	25.5	74.2268	0.7619	
5	22.0	63.4021	0.6508	
6	21.0	60.3093	0.6190	
7	20.0	57.2165	0.5873	
8	19.0	54.1237	0.5556	
9	18.0	51.0309	0.5238	
10	17.5	49.4845	0.5079	1.0847
11	17.0	47.9381	0.4921	
12	17.0	47.9381	0.4921	
13	16.0	44.8454	0.4603	
14	16.0	44.8454	0.4603	
15	15.5	43.2990	0.4444	
16	15.0	41.7526	0.4286	
17	15.0	41.7526	0.4286	
18	15.0	41.7526	0.4286	
19	15.0	41.7526	0.4286	
20	15.0	41.7526	0.4286	1.1186

TEST A16

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0.0	33.0	97.4227	1.0000	1.0000
1.5	32.0	94.3299	0.9683	
3.0	29.0	85.0515	0.8730	
4.5	24.0	69.5896	0.7143	
6.0	22.0	63.4021	0.6508	
7.5	19.0	54.1237	0.5556	
9.0	18.0	51.0309	0.5238	
10.5	17.0	47.9381	0.4921	
12.0	17.0	47.9381	0.4921	
13.5	15.0	41.7526	0.4286	
15.0	15.0	41.7526	0.4286	1.1636
16.5	14.0	38.6598	0.3968	
18.0	13.5	37.1134	0.3810	
19.5	13.5	37.1134	0.3810	
21.0	13.5	37.1134	0.3810	
22.5	13.5	37.1134	0.3810	
24.0	13.5	37.1134	0.3810	
25.5	13.0	35.5670	0.3651	
27.0	13.0	35.5670	0.3651	
28.5	13.0	35.5670	0.3651	
30.0	13.0	35.5670	0.3651	1.2364

TEST A17

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0.0	34.0	100.5155	1.0000	1.0000
2.5	32.0	94.3299	0.9385	
5.0	25.0	72.6804	0.7231	
7.5	21.0	60.3093	0.6000	
10.0	17.0	47.9381	0.4769	
12.5	14.5	40.2062	0.4000	
15.0	13.0	35.5670	0.3538	
17.5	12.5	34.0206	0.3385	
20.0	12.0	32.4742	0.3231	
22.5	11.5	30.9278	0.3077	
25.0	11.0	29.3814	0.2923	
27.5	11.0	29.3814	0.2923	
30.0	10.5	27.8351	0.2769	
32.5	10.0	26.2887	0.2615	
35.0	10.0	26.2887	0.2615	
37.5	10.0	26.2887	0.2615	
40.0	10.0	26.2887	0.2615	
42.5	10.0	26.2887	0.2615	
45.0	10.0	26.2887	0.2615	
47.5	10.0	26.2887	0.2615	
50.0	10.0	26.2887	0.2615	1.1270

TEST A18

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0	32.0	94.3299	1.0000	1.0000
3	26.0	75.7732	0.8033	
6	19.0	54.1237	0.5738	
9	15.0	41.7526	0.4426	
12	11.5	30.9278	0.3279	
15	9.4	24.4330	0.2590	
18	8.3	21.0309	0.2230	
21	7.4	18.2474	0.1934	
24	7.2	17.6289	0.1869	1.0149
27	6.9	16.7010	0.1770	
30	6.9	16.7010	0.1770	
33	6.7	16.0825	0.1705	
36	6.7	16.0825	0.1705	
39	6.8	16.3918	0.1738	
42	6.7	16.0825	0.1705	
45	6.8	16.3918	0.1738	
48	6.6	15.7732	0.1672	
51	6.8	16.3918	0.1738	1.0896

TEST A19

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0.0	33.0	97.4227	1.0000	1.0000
1.0	32.0	94.3299	0.9683	
2.0	29.0	85.0515	0.8730	
3.0	27.0	78.8660	0.8095	
4.0	25.0	72.6804	0.7460	
5.0	24.0	69.5876	0.7143	
6.0	22.5	64.9485	0.6667	
7.3	21.0	60.3093	0.6190	
8.0	20.0	57.2165	0.5873	
9.0	19.0	54.1237	0.5556	
10.0	18.5	52.5773	0.5397	
11.0	18.0	51.0309	0.5238	1.0000
12.0	17.5	49.4845	0.5079	
13.0	17.5	49.4845	0.5079	
14.0	17.0	47.9381	0.4921	
15.0	17.0	47.9381	0.4921	
16.0	17.0	47.9381	0.4921	
17.0	17.0	47.9381	0.4921	
18.0	17.0	47.9381	0.4921	
19.0	17.0	47.9381	0.4921	
20.0	17.0	47.9381	0.4921	
21.0	17.0	47.9381	0.4921	
22.0	17.0	47.9381	0.4921	1.0000

TEST A20

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0.0	32.0	94.3299	1.0000	1.0000
1.5	30.0	88.1443	0.9344	
3.0	27.5	80.4124	0.8525	
4.5	24.0	69.5876	0.7377	
6.0	22.0	63.4021	0.6721	
7.5	20.5	58.7629	0.6230	
9.0	18.0	51.0309	0.5410	
10.5	17.5	49.4845	0.5246	
12.0	17.0	47.9381	0.5082	
13.5	16.0	44.8454	0.4754	
15.0	15.5	43.2990	0.4590	1.0328
16.5	15.0	41.7526	0.4426	
18.0	15.0	41.7526	0.4426	
19.5	15.0	41.7526	0.4426	
21.0	14.5	40.2062	0.4262	
22.5	14.5	40.2062	0.4262	
24.0	14.5	40.2062	0.4262	
25.5	14.5	40.2062	0.4262	
27.0	14.0	38.6598	0.4098	
28.5	14.0	38.6598	0.4098	
30.0	14.0	38.6598	0.4098	1.0820

TEST A21

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0.0	35.0	103.6082	1.0000	1.0000
2.5	29.5	86.5979	0.8358	
5.0	23.5	68.0412	0.6567	
7.5	19.5	55.6701	0.5373	
10.0	18.0	51.0309	0.4925	
12.5	16.0	44.8454	0.4328	
15.0	14.5	40.2062	0.3881	
17.5	14.0	38.6598	0.3731	1.1035
20.0	13.0	35.5670	0.3433	
22.5	12.0	32.4742	0.3134	
25.0	12.5	34.0206	0.3284	
27.5	12.5	34.0206	0.3284	
30.0	12.0	32.4742	0.3134	
32.5	12.0	32.4742	0.3134	
35.0	12.0	32.4742	0.3134	1.1035

TEST A22

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0.0	36.0	106.7010	1.0000	1.0000
3.0	30.0	88.1443	0.8261	
6.0	24.0	69.5876	0.6522	
9.0	18.0	51.0309	0.4783	
12.0	15.5	43.2990	0.4058	
15.0	13.5	37.1134	0.3478	
18.0	12.5	34.0206	0.3188	
21.0	11.5	30.9278	0.2899	
24.0	10.0	26.2887	0.2464	
27.0	8.6	21.9588	0.2058	
30.0	8.9	22.8866	0.2145	0.9836
33.0	8.5	21.6495	0.2029	
36.0	8.4	21.3402	0.2000	
39.0	8.4	21.3402	0.2000	
42.0	8.2	20.5670	0.1928	
45.0	7.8	19.3299	0.1812	
48.0	8.0	20.1031	0.1884	
51.0	8.2	20.7216	0.1942	
55.0	7.8	19.4845	0.1826	
57.0	7.9	19.7938	0.1855	
60.0	7.8	19.4845	0.1826	0.9672

TEST A23

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0	33.0	97.4227	1.0000	1.0000
1	32.5	95.8763	0.9841	
2	30.5	89.6907	0.9206	
3	30.0	88.1443	0.9048	
4	28.0	81.9588	0.8413	
5	25.5	74.2268	0.7619	
6	24.0	69.5876	0.7143	
7	23.5	68.0412	0.6984	
8	22.5	64.9485	0.6667	
9	21.5	61.8557	0.6349	
10	20.5	58.7629	0.6032	1.0862
11	19.5	55.6701	0.5714	
12	19.0	54.1237	0.5556	
13	18.5	52.5773	0.5397	
14	18.5	52.5773	0.5397	
15	18.5	52.5773	0.5397	
16	18.0	51.0309	0.5238	
17	17.5	49.4843	0.5079	
18	17.0	47.9381	0.4921	
19	17.0	47.9381	0.4921	
20	17.0	47.9381	0.4921	1.1034

TEST A24

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0.0	36.5	108.2474	1.0000	1.0000
1.5	34.0	100.5155	0.9286	
3.5	30.0	88.1443	0.8143	
4.5	28.0	81.9588	0.7571	
6.0	25.0	72.6804	0.6714	
7.5	24.0	69.5876	0.6429	
9.0	22.0	63.4021	0.5857	
10.5	20.5	58.7629	0.5429	
12.5	20.0	57.2165	0.5143	
13.5	19.5	55.6701	0.5143	
15.0	19.0	54.1237	0.5000	
16.5	18.5	52.5773	0.4857	1.0645
18.0	18.0	51.0309	0.4714	
19.5	18.0	51.0309	0.4714	
21.0	17.5	49.4845	0.4571	
22.5	17.0	47.9381	0.4429	
24.0	17.0	47.9381	0.4429	
25.5	17.0	47.9381	0.4429	
27.0	17.0	47.9381	0.4429	
28.5	17.5	49.4845	0.4571	
30.0	17.0	47.9381	0.4429	1.0806

TEST A25

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0	32.0	94.3299	1.0000	1.0000
3	32.0	94.3299	1.0000	
5	26.0	75.7732	0.8033	
6	23.5	68.0412	0.7213	
8	22.0	63.4021	0.6721	
10	20.0	57.2165	0.6066	
12	18.5	52.5773	0.5574	
14	17.5	49.4845	0.5246	
16	17.0	47.9381	0.5082	
18	16.5	46.3918	0.4918	1.0609
20	15.5	43.2990	0.4590	
22	15.0	41.7526	0.4426	
24	14.5	40.2062	0.4262	
26	14.0	38.6598	0.4098	
28	13.5	37.1134	0.3934	
30	13.0	35.5670	0.3770	
32	13.0	35.5670	0.3770	
34	13.0	35.5670	0.3770	
36	13.0	35.5670	0.3770	
38	12.5	34.0206	0.3607	
40	13.0	35.5670	0.3770	1.0957

TEST A26

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0	34.0	100.5155	1.0000	1.0000
4	28.0	81.9588	0.8754	
8	24.0	69.5876	0.6923	
12	19.0	54.1237	0.5385	
16	15.0	41.7526	0.4154	1.3085
20	13.0	35.5670	0.3538	
24	11.5	30.9278	0.3077	
28	9.3	24.1237	0.2400	
32	8.9	22.8866	0.2277	
36	8.5	21.6495	0.2154	1.3191
40	7.9	19.7938	0.1969	
46	7.6	18.8660	0.1877	
50	7.6	18.8660	0.1877	
52	7.5	18.5567	0.1846	
56	7.6	18.8660	0.1877	1.3298
60	7.5	18.5567	0.1846	
64	7.5	18.5567	0.1846	
68	7.5	18.5567	0.1846	
72	7.7	19.1753	0.1908	
76	7.7	19.1753	0.1908	1.3404
80	7.9	19.7938	0.1969	
84	7.8	19.4845	0.1938	
88	7.7	19.1753	0.1908	
92	7.6	18.6600	0.1877	
96	7.9	19.7938	0.1969	1.3830
100	7.8	19.4845	0.1938	
104	7.7	19.1753	0.1908	
108	7.8	19.4845	0.1938	
112	7.9	19.7938	0.1969	
116	7.7	19.1753	0.1908	1.3830

TEST A27

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0	33.0	97.4227	1.0000	1.0000
2	31.5	92.7835	0.9524	
4	29.0	85.0515	0.8730	
6	27.0	78.8660	0.8095	
8	25.5	74.2268	0.7619	
10	25.0	72.6804	0.7460	
12	23.5	68.0412	0.6984	
14	22.5	64.9485	0.6667	
16	22.0	63.4021	0.6508	
18	22.0	63.4021	0.6508	
20	21.5	61.8557	0.6349	1.0909
22	21.5	61.8557	0.6349	
24	21.5	61.8557	0.6349	
26	21.0	60.3093	0.6190	
28	20.5	58.7629	0.6032	
30	21.0	60.3093	0.6190	
32	20.5	58.7629	0.6032	
34	20.5	58.7629	0.6032	
36	20.5	58.7629	0.6032	
38	20.5	58.7629	0.6032	
40	20.5	58.7629	0.6032	1.1091

TEST A28

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0	34.0	100.5155	1.0000	1.0000
3	31.5	92.7835	0.9231	
6	28.0	81.9588	0.8154	
9	24.0	69.5876	0.6923	
12	22.0	63.4021	0.6308	
15	20.0	57.2165	0.5692	
18	19.0	54.1237	0.5385	
21	19.0	54.1237	0.5385	0.9677
24	18.5	52.5773	0.5231	
27	18.5	52.5773	0.5231	
30	18.0	51.0309	0.5077	
33	18.0	51.0309	0.5077	
36	18.0	51.0309	0.5077	
39	18.5	52.5773	0.5231	
42	18.5	52.5773	0.5231	1.0161

TEST A29

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0	36.0	106.7010	1.0000	1.0000
4	32.0	94.3299	0.8841	
8	26.5	77.3196	0.7246	
12	22.5	64.9485	0.6087	
16	20.5	58.7629	0.5507	
20	18.5	52.5773	0.4928	
24	17.5	49.4845	0.4638	
28	17.0	47.9381	0.4493	
32	16.5	46.3918	0.4348	1.0667
36	16.5	46.3918	0.4348	
40	16.5	46.3918	0.4348	
44	16.5	46.3918	0.4348	
48	16.0	44.8454	0.4203	
52	16.0	44.8454	0.4203	
56	16.5	46.3918	0.4348	
60	16.5	46.3918	0.4348	1.1111

TEST A30

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	s/s_i
0	32.5	95.8763	1.0000	1.0000
5	30.5	89.6907	0.9355	
12	26.0	75.7732	0.7903	
15	22.0	63.4021	0.6613	
20	18.0	51.0309	0.5323	
25	17.0	47.9381	0,5000	
30	15.0	41.7526	0.4355	
35	13.5	37.1134	0.3871	
40	12.5	34.0206	0.3548	
45	12.5	34.0206	0.3548	
50	12.0	32.4742	0.3387	
55	11.5	30.9278	0.3226	1.0426
60	11.5	30.9278	0.3226	
65	11.5	30.9278	0.3226	
70	11.0	29.3814	0.3065	
75	11.0	29.3814	0.3065	
80	11.0	29.3814	0.3065	
85	11.0	29.3814	0.3065	
90	10.5	27.8351	0.2903	
100	11.0	29.3814	0.3065	1.1148

TEST A31

Particle Size Range (μm)	Concentration (mg l^{-1})				
1.75 - 2.20	1.2738	0.6653	0.9327	0.1119	0.9355
2.20 - 2.78	2.8873	1.5966	2.0430	0.2612	1.4968
2.78 - 3.50	5.6897	3.1267	3.8640	0.3731	1.9022
3.50 - 4.41	9.3414	5.3221	5.1964	0.5597	1.9645
4.41 - 5.56	15.2009	7.9831	5.6849	0.7462	2.5258
5.56 - 7.00	18.8526	8.5153	4.0416	0.7462	3.5860
7.00 - 8.82	16.8144	4.5903	1.8209	0.3731	3.2430
8.82 - 11.1	10.7001	1.9293	1.3768	0.3731	1.3097
11.1 - 14.0	5.0953	1.0644	0.8439	0.2985	0.6237
14.0 - 17.6	2.5476	1.3970	1.3324	0.5597	0.8108
17.6 - 22.3	1.6135	1.0734	1.5545	0.6343	1.5591
22.3 - 28.0	1.0191	1.9958	1.3768	1.4925	3.4613
28.0 - 35.3	0.8492	5.1890	4.5746	3.3581	5.3947
35.3 - 44.5	1.8683	10.6442	6.7064	6.7162	4.6774
44.5 - 56.0	2.1230	20.2239	9.6821	25.1486	0.5301
t (min.)	0	12	20	30	40

TEST A31 (Continued)

Particle Size Range (μm)	Concentration (mg l^{-1})				
1.75 - 2.20	0.2640	0.4399	0.2652	0.4635	0.3556
2.20 - 2.78	0.4694	0.7972	0.5304	0.7468	0.6165
2.78 - 3.50	0.6160	1.0997	0.7955	1.0300	0.9484
3.50 - 4.41	0.7627	1.0997	0.9811	1.1588	1.0906
4.41 - 5.56	0.8801	1.1271	1.1933	1.3133	1.1381
5.56 - 7.00	1.2027	1.4021	1.0872	1.4163	0.9721
7.00 - 8.82	0.8801	1.0997	0.5569	1.0043	0.4742
8.82 - 11.1	0.3227	0.5223	0.2652	1.0300	0.2371
11.1 - 14.0	0.1760	0.2474	0.1326	0.7210	0.2371
14.0 - 17.6	0.2934	0.2199	0.2121	1.0558	0.2371
17.6 - 22.3	0.5867	0.5223	0.4773	1.2618	0.3082
22.3 - 28.0	1.2908	0.9622	1.0607	1.1330	0.7824
28.0 - 35.3	3.4909	3.3814	2.4131	2.1888	2.8452
35.3 - 44.5	5.3684	5.0034	4.5345	3.2961	4.2914
44.5 - 56.0	15.8704	13.0034	14.8763	11.5620	13.3011
t (min.)	50	60	70	80	90

TEST B1

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i	$\ln(T/T_i)$
0.00	3.50	2.24	1.0000	0.0000
2.75	3.17	1.95	0.8705	-0.1386
5.50	2.95	1.75	0.7813	-0.2469
8.25	2.75	1.60	0.7143	-0.3365
11.00	2.56	1.43	0.6384	-0.4488
13.75	2.37	1.30	0.5804	-0.5441
16.50	2.21	1.18	0.5268	-0.6410
19.25	2.05	1.06	0.4732	-0.7482
22.00	1.91	0.96	0.4286	-0.8473
24.75	1.78	0.89	0.3973	-0.9230
27.50	1.66	0.80	0.3571	-1.0296
30.25	1.55	0.73	0.3259	-1.1212
33.00	1.44	0.66	0.2946	-1.2220
35.75	1.35	0.60	0.2679	-1.3173
38.50	1.26	0.54	0.2411	-1.4227
41.25	1.18	0.50	0.2232	-1.4996
44.00	1.10	0.45	0.2009	-1.6050
46.75	1.03	0.42	0.1875	-1.6740
49.50	0.97	0.38	0.1696	-1.7741
52.25	0.91	0.34	0.1518	-1.8853
55.00	0.85	0.31	0.1384	-1.9777
57.75	0.79	0.27	0.1205	-2.1158

TEST B2

t (min.)	s (mg l^{-1})	s/s_i	$\ln(s/s_i)$
0	33.7507	1.0000	0.0000
8	29.7602	0.8818	-0.1258
16	25.3263	0.7504	-0.2872
24	20.7446	0.6146	-0.4867
32	19.4144	0.5752	-0.5530
40	15.7194	0.4658	-0.7641
48	10.9899	0.3256	-1.1220
56	6.8516	0.2030	-1.5945
64	4.6346	0.1373	-1.9855
72	2.4177	0.0716	-2.6362
80	0.3485	0.0103	-4.5731

TEST B3

t (min.)	s (mg l^{-1})	s/s_i	$\ln(s/s_i)$
0	38.9111	1.0000	0.0000
10	32.6853	0.8400	-0,1744
20	28.8153	0.7405	-0.3004
30	23.7673	0.6108	-0.4930
40	20.4021	0.5243	-0.6456
50	15.8589	0.4076	-0.8975
60	11.6523	0.2995	-1.2058
70	8.6236	0.2216	-1.5068
80	5.7631	0.1481	-1.9098
90	4.4170	0.1135	-2.1758
100	3.5757	0.0919	-2.3871
110	2.3978	0.0616	-2.7867
120	1.2200	0.0314	-3.4624
130	0.5469	0.0141	-4.2648
144	0.2104	0.0054	-5.2200
150	0.0000	0.0000	$-\infty$

TEST B4

t (min.)	s (mg l^{-1})	s/s_i	$\ln(s/s_i)$
0	34.7045	1.0000	0.0000
12	30.4979	0.8788	-0.1292
24	27.4691	0.7915	-0.2338
36	23.7673	0.6848	-0.3786
48	21.0751	0.6073	-0.4988
61	17.0386	0.4909	-0.7115
72	13.3350	0.3842	-0.9565
84	9.9697	0.2873	-1.2473
96	7.4457	0.2145	-1.5392
108	4.9218	0.1418	-1.9532
120	2.9026	0.0836	-2.4813
132	1.5565	0.0449	-3.1044
144	0.8834	0.0255	-3.6708
156	0.0421	0.0012	-6.7146
168	0.0000	0.0000	$-\infty$
180	0.0000	0.0000	$-\infty$

TEST B5

t (min.)	s (mg l^{-1})	s/s_i	$\ln(s/s_i)$
0	35.2093	1.0000	0.0000
18	31.3392	0.8901	-0.1164
36	27.6374	0.7849	-0.2421
54	25.1134	0.7133	-0.3379
72	21.2434	0.6033	-0.5053
90	18.0464	0.5125	-0.6684
110	13.1667	0.3740	-0.9836
126	10.8110	0.3070	-1.1807
146	7.7823	0.2210	-1.5095
162	4.7535	0.1350	-2.0024
180	2.7343	0.0777	-2.5554
198	1.7247	0.0490	-3.0163
221	0.8834	0.0251	-3.6853
234	0.5469	0.0155	-4.1648
252	0.2104	0.0060	-5.1201
270	0.0421	0.0012	-6.7290

TEST B6

t (min.)	s (mg l^{-1})	s/s_i	$\ln(s/s_i)$
0	34.3680	1.0000	0.0000
36	31.3392	0.9119	-0.0923
72	27.1326	0.7895	-0.2364
122	20.9068	0.6083	-0.4971
144	17.0368	0.4957	-0.7018
180	13.6715	0.3978	-0.9218
216	9.1284	0.2656	-1.3257
252	6.0996	0.1775	-1.7289
288	3.5757	0.1040	-2.2630
325	1.5565	0.0453	-3.0947
362	1.0517	0.0306	-3.4867
396	0.2104	0.0061	-5.0959

TEST B7

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.5	98.9691	1.0000	0.0000
2.4	29.0	85.0515	0.8594	-0.1515
4.8	24.0	69.5876	0.7031	-0.3522
7.8	19.0	54.1237	0.5469	-0.6035
9.6	17.0	47.9381	0.4844	-0.7249
12.0	14.0	38.6598	0.3906	-0.9400
14.4	12.5	34.0206	0.3437	-1.0678
16.8	9.7	25.3608	0.2562	-1.3616
19.2	8.1	20.4124	0.2062	-1.5787
21.6	6.6	15.7732	0.1594	-1.8365
24.0	6.0	13.9175	0.1406	-1.9617

t (min.)	s (mg l^{-1})
0.0	24.7506
7.8	24.3402
16.8	22.6988
24.0	20.7495

TEST B8

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	32.5	95.8763	1.0000	0.0000
2.4	28.0	81.9588	0.8548	-0.1568
4.8	23.0	66.4948	0.6935	-0.3659
7.2	18.0	51.0309	0.5323	-0.6306
9.6	14.0	38.6598	0.4032	-0.9083
12.0	12.0	32.4742	0.3387	-1.0826
14.4	10.0	26.2887	0.2742	-1.2939
16.8	8.3	21.0309	0.2194	-1.5171
19.2	7.1	17.3196	0.1806	-1.7112
21.6	5.9	13.6082	0.1419	-1.9524
24.0	5.3	11.7526	0.1226	-2.0990

t (min.)	s (mg l^{-1})
0.0	15.9276
7.2	17.6717
19.2	16.5432
24.0	15.9276

TEST B9

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	32.5	95.8763	1.0000	0.0000
2.4	27.5	80.4124	0.8387	-0.1759
4.8	21.5	61.8557	0.6452	-0.4383
7.2	16.5	46.3918	0.4839	-0.7259
9.6	13.0	35.5670	0.3710	-0.9915
12.0	10.5	27.8351	0.2903	-1.2368
14.4	8.4	21.3402	0.2226	-1.5025
16.8	6.7	16.0825	0.1677	-1.7853
19.2	5.6	12.6804	0.1323	-2.0230
21.6	4.8	10.2062	0.1065	-2.2401
24.0	4.1	8.0412	0.0839	-2.4785

t (min.)	s (mg l^{-1})
0.0	9.6694
7.2	10.1824
16.8	10.1824
24.0	9.6694

TEST B10

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.4	27.0	78.8660	0.8095	-0.2113
4.8	21.0	60.3093	0.6190	-0.4796
7.2	16.5	46.3918	0.4762	-0.7419
9.6	12.0	32.4742	0.3333	-1.0986
12.0	9.0	23.1959	0.2381	-1.4351
14.4	7.2	17.6289	0.1810	-1.7095
16.8	6.4	15.1546	0.1556	-1.8608
19.2	5.0	10.8247	0.1111	-2.1972
22.0	4.0	7.7320	0.0794	-2.5337
24.0	3.5	6.1856	0.0635	-2.7568

t (min.)	s (mg l^{-1})
0.0	3.2317
7.2	2.5688
16.8	1.9050
24.0	2.0164

TEST B11

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.4	28.0	81.9588	0.8413	-0.1728
4.8	22.5	64.9485	0.6667	-0.4055
7.2	17.5	49.4845	0.5079	-0.6774
9.6	14.0	38.6598	0.3968	-0.9243
12.0	11.0	29.3814	0.3016	-1.1987
14.4	8.9	22.8866	0.2349	-1.4485
16.8	6.8	16.3918	0.1683	-1.7823
19.5	5.7	12.9897	0.1333	-2.0149
21.6	4.8	10.2062	0.1048	-2.2561
24.0	3.9	7.4227	0.0762	-2.5745

t (min.)	s (mg l^{-1})
0.0	1.7954
7.2	1.2430
16.8	0.9115
24.0	0.6906

TEST B12

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
3	28.5	83.5052	0.8308	-0.1854
6	25.5	74.2268	0.7385	-0.3032
9	21.0	60.3093	0.6000	-0.5108
12	19.0	54.1237	0.5385	-0.6190
15	17.0	47.9381	0.4769	-0.7404
18	15.0	41.7526	0.4154	-0.8786
21	13.0	35.5670	0.3538	-1.0389
24	10.5	27.8351	0.2769	-1.2840
27	9.0	23.1959	0.2308	-1.4663
30	7.6	18.8660	0.1877	-1.6730

t (min.)	c_s (mg l^{-1})
0	37.8246
9	35.2710
21	33.9942
30	32.0791

TEST B13

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
3	27.0	78.8660	0.7846	-0.2476
6	22.0	63.4021	0.6308	-0.4608
9	18.5	52.5773	0.5231	-0.6480
12	15.0	41.7526	0.4154	-0.8786
15	12.0	32.4742	0.3231	-1.1299
18	10.0	26.2887	0.2615	-1.3412
21	8.2	20.7216	0.2062	-1.5791
24	7.1	17.3196	0.1723	-1.7585
27	5.8	13.2990	0.1323	-2.0226
30	5.0	10.8247	0.1077	-2.2285

t (min.)	s (mg l^{-1})
0	26.7166
9	25.6952
21	24.4184
30	23.0139

TEST B14

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
3	28.0	81.9588	0.8413	-0.1728
6	22.0	63.4021	0.6508	-0.4296
9	17.5	49.4845	0.5079	-0.6774
12	14.0	38.6598	0.3968	-0.9243
15	11.0	29.3814	0.3016	-1.1987
18	8.5	21.6495	0.2222	-1.5041
21	7.0	17.0103	0.1746	-1.7452
25	5.2	11.4433	0.1175	-2.1417
27	4.7	9.8969	0.1016	-2.2868
30	4.2	8.3505	0.0857	-2.4567

t (min.)	s (mg l^{-1})
0	19.8220
9	19.0559
21	17.9068
30	17.1408

TEST B15

t (min..)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
3	27.5	80.4124	0.8254	-0.1919
6	21.0	60.3093	0.6190	-0.4796
9	17.0	47.9381	0.4921	-0.7091
12	13.5	37.1134	0.3810	-0.9651
15	10.5	27.8351	0.2857	-1.2528
18	8.1	20.4124	0.2095	-1.5629
21	6.6	15.7732	0.1619	-1.8207
24	5.6	12.6804	0.1302	-2.0390
27	4.8	10.2062	0.1048	-2.2561
30	4.1	8.0412	0.0825	-2.4945

t (min.)	s (mg l^{-1})
0	11.6506
9	11.7783
21	11.5229
30	12.2890

TEST B16

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
3	26.5	77.3196	0.7937	-0.2311
6	21.0	60.3093	0.6190	-0.4796
9	15.5	43.2990	0.4444	-0.8109
12	12.0	32.4742	0.3333	-1.0986
15	8.7	22.2680	0.2286	-1.4759
18	6.4	15.1546	0.1556	-1.8608
21	5.4	12.0619	0.1238	-2.0890
24	4.7	9.8969	0.1016	-2.2868
27	3.8	7.1134	0.0730	-2.6171
30	3.0	4.6392	0.0476	-3.0445

t (min.)	s (mg l^{-1})
0	6.1605
6	5.7774
12	5.5221
18	5.7774
24	6.0328
30	6.4158

TEST B17

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
3	27.5	80.4124	0.8254	-0.1919
6	21.5	61.8557	0.6349	-0.4543
9	16.5	46.3918	0.4762	-0.7419
12	13.0	35.5670	0.3651	-1.0076
15	10.0	26.2887	0.2698	-1.3099
18	7.7	19.1753	0.1968	-1.6254
21	6.0	13.9175	0.1429	-1.9459
24	5.1	11.1340	0.1143	-2.1691
27	4.1	8.0412	0.0825	-2.4945
30	3.3	5.5670	0.0571	-2.8622

t (min.)	s (mg l^{-1})
0	4.1176
6	3.8623
12	3.4792
18	3.8623
24	3.8623
30	3.7346

TEST B18

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	32.0	94.3299	1.0000	0.0000
4	25.0	72.6804	0.7705	-0.2607
8	21.0	60.3093	0.6393	-0.4473
12	17.5	49.4845	0.5246	-0.6451
16	15.0	41.7526	0.4426	-0.8150
20	13.0	35.5670	0.3770	-0.9754
24	11.0	29.3814	0.3115	-1.1664
28	9.3	24.1237	0.2557	-1.3636
32	8.0	20.1031	0.2131	-1.5459
36	7.3	17.9381	0.1902	-1.6599
40	6.6	15.7732	0.1672	-1.7885

t (min.)	s (mg l^{-1})
0	22.8013
12	25.5714
28	24.7506
40	23.9299

TEST B19

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
4	26.0	75.7732	0.7778	-0.2513
8	20.0	57.2165	0.5873	-0.5322
12	15.0	41.7526	0.4286	-0.8473
16	12.0	32.4742	0.3333	-1.0986
20	9.2	23.8144	0.2444	-1.4088
24	7.6	18.8660	0.1937	-1.6417
28	6.0	13.9175	0.1429	-1.9459
32	4.9	10.5155	0.1079	-2.2262
36	4.5	9.2784	0.0952	-2.3514
40	3.8	7.1134	0.0730	-2.6171

t (min.)	s (mg l^{-1})
0	17.0561
12	16.6458
28	16.2354
40	15.4146

TEST B20

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
4	24.5	71.1340	0.7302	-0.3145
8	18.5	52.5773	0.5397	-0.6168
12	14.0	38.6598	0.3968	-0.9243
16	10.5	27.8351	0.2857	-1.2528
20	8.7	22.2680	0.2286	-1.4759
24	6.8	16.3918	0.1683	-1.7823
28	5.3	11.7526	0.1206	-2.1150
32	4.8	10.2062	0.1048	-2.2561
36	4.0	7.7320	0.0794	-2.5337
40	3.5	6.1856	0.0635	-2.7568

t (min.)	s (mg l^{-1})
0	10.0798
12	10.1824
28	10.2850
40	9.9772

TEST B21

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
4	27.5	80.4124	0.8000	-0.2231
8	21.0	60.3093	0.6000	-0.5108
12	16.0	44.8454	0.4462	-0.8071
16	12.0	32.4742	0.3231	-1.1299
20	9.0	23.1959	0.2308	-1.4663
24	6.9	16.7010	0.1662	-1.7948
28	5.3	11.7526	0.1169	-2.1462
32	4.3	8.6598	0.0862	-2.4516
36	3.7	6.8041	0.0677	-2.6928
40	3.3	5.5670	0.0554	-2.8935

t (min.)	s (mg l^{-1})
0	5.1553
12	5.1553
28	5.1553
40	5.1553

TEST B22

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
4	28.5	83.5052	0.8571	-0.1542
8	21.0	60.3093	0.6190	-0.4796
12	17.0	47.9381	0.4921	-0.7091
16	13.0	35.5670	0.3651	-1.0076
20	10.5	27.8351	0.2857	-1.2528
24	8.0	20.1031	0.2063	-1.5782
28	6.4	15.1546	0.1556	-1.8608
32	5.0	10.8247	0.1111	-2.1972
36	4.1	8.0412	0.0825	-2.4945
40	3.5	6.1856	0.0635	-2.7568

t (min.)	s (mg l^{-1})
0	3.0009
12	3.4112
28	3.8216
40	4.2320

TEST B23

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
6	28.0	81.9588	0.8413	-0.1728
12	22.5	64.9485	0.6667	-0.4055
18	17.0	47.9381	0.4921	-0.7091
24	15.0	41.7526	0.4286	-0.8473
30	12.0	32.4742	0.3333	-1.0986
36	10.0	26.2887	0.2698	-1.3099
42	8.2	20.7216	0.2127	-1.5479
48	7.5	18.5567	0.1905	-1.6582
54	6.9	16.7010	0.1714	-1.7636
60	6.4	15.1546	0.1556	-1.8608

t (min.)	s (mg l^{-1})
0	23.0065
18	25.4688
42	24.8532
60	23.2117

TEST B24

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	32.5	95.8763	1.0000	0.0000
6	26.5	77.3196	0.8065	-0.2151
12	19.5	55.6701	0.5806	-0.5436
18	15.5	43.2990	0.4516	-0.7949
24	12.0	32.4742	0.3387	-1.0826
30	9.4	24.4330	0.2548	-1.3671
36	7.7	19.1753	0.2000	-1.6094
42	6.6	15.7732	0.1645	-1.8047
48	6.1	14.2268	0.1484	-1.9079
54	5.1	11.1340	0.1161	-2.1531
60	4.6	9.5876	0.1000	-2.3026

t (min.)	s (mg l^{-1})
0	15.6198
18	16.6458
42	16.3380
60	15.6198

TEST B25

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
6	27.5	80.4124	0.8000	-0.2231
12	21.5	61.8557	0.6154	-0.4855
18	16.5	46.3918	0.4615	-0.7732
24	12.5	34.0206	0.3385	-1.0833
30	9.6	25.0515	0.2492	-1.3894
36	7.2	17.6289	0.1754	-1.7408
42	5.8	13.2990	0.1323	-2.0226
48	4.9	10.5155	0.1046	-2.2575
54	4.3	8.6598	0.0862	-2.4516
60	4.0	7.7320	0.0769	-2.5649

t (min.)	s (mg l^{-1})
0	10.8552
18	10.6342
42	9.5293
60	9.5293

TEST B26

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	32.5	95.8763	1.0000	0.0000
6	27.5	80.4124	0.8387	-0.1759
12	20.0	57.2165	0.5968	-0.5162
18	15.5	43.2990	0.4516	-0.7949
24	12.0	32.4742	0.3387	-1.0826
30	8.6	21.9588	0.2290	-1.4739
36	6.7	16.0825	0.1677	-1.7853
42	5.5	12.3711	0.1290	-2.0477
48	4.6	9.5876	0.1000	-2.3026
54	3.8	7.1134	0.0742	-2.6011
60	3.5	6.1856	0.0645	-2.7408

t (min.)	s (mg l^{-1})
0	4.2261
18	4.3366
42	4.3366
60	4.3366

TEST B27

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
6	27.0	78.8660	0.7846	-0.2426
12	20.5	58.7629	0.5846	-0.5368
18	17.5	49.4845	0.4923	-0.7087
24	13.5	37.1134	0.3692	-0.9963
30	10.5	27.8351	0.2769	-1.2840
38	7.3	17.9381	0.1785	-1.7234
42	6.1	14.2268	0.1415	-1.9552
48	5.0	10.8247	0.1077	-2.2285
54	4.3	8.6598	0.0862	-2.4516

t (min.)	s (mg l^{-1})
0	3.1212
42	0.6906
60	2.5688

TEST B28

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	32.0	94.3299	1.0000	0.0000
12	26.0	75.7732	0.8033	-0.2191
24	19.0	54.1237	0.5738	-0.5555
36	15.0	41.7526	0.4426	-0.8150
48	13.0	35.5670	0.3770	-0.9754
60	10.0	26.2887	0.2787	-1.2777
72	8.0	20.1031	0.2131	-1.5459
84	7.1	17.3196	0.1836	-1.6950
96	6.2	14.5361	0.1541	-1.8702
108	5.4	12.0619	0.1279	-2.0568
120	4.7	9.8969	0.1049	-2.2546

t (min.)	s (mg l^{-1})
0	26.6545
36	26.3231
84	24.2238
120	23.3400

TEST B29

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
12	25.0	72.6804	0.7460	-0.2930
24	19.0	54.1237	0.5556	-0.5878
36	15.0	41.7526	0.4286	-0.8473
48	12.0	32.4742	0.3333	-1.0986
60	8.8	22.5773	0.2317	-1.4621
72	7.3	17.9381	0.1841	-1.6921
84	6.4	15.1546	0.1556	-1.8608
96	5.6	12.6804	0.1302	-2.0390
108	5.1	11.1340	0.1143	-2.1691
120	4.7	9.8969	0.1016	-2.2868

t (min.)	s (mg l^{-1})
0	18.9206
36	19.1415
84	17.9262
120	18.1472

TEST B30

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
12	25.5	74.2268	0.7385	-0.3032
24	18.5	52.5773	0.5231	-0.6480
36	13.5	37.1134	0.3692	-0.9963
48	10.0	26.2887	0.2615	-1.3412
60	7.1	17.3196	0.1723	-1.7585
72	5.6	12.6804	0.1262	-2.0703
84	4.4	8.9691	0.0892	-2.4165
96	4.0	7.7320	0.0769	-2.5649
108	3.2	5.2577	0.0523	-2.9506
120	2.7	3.7113	0.0369	-3.2989

t (min.)	s (mg l^{-1})
0	9.9713
36	9.3084
84	8.3140
120	7.7616

TEST B31

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
12	25.0	72.6804	0.7231	-0.3242
24	17.5	49.4845	0.4923	-0.7087
36	12.0	32.4742	0.3231	-1.1299
48	8.5	21.6495	0.2154	-1.5353
60	5.8	13.2990	0.1323	-2.0226
72	4.5	9.2784	0.0923	-2.3826
84	3.5	6.1856	0.0615	-2.7881
96	2.9	4.3299	0.0431	-3.1448
108	2.6	3.4021	0.0338	-3.3859
120	2.3	2.4742	0.0246	-3.7044

t (min.)	s (mg l^{-1})
0	3.3422
36	3.2317
84	3.5632
120	4.0051

TEST B32

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
12	26.0	75.7732	0.7538	-0.2826
24	18.0	51.0309	0.5077	-0.6779
36	13.5	37.1134	0.3692	-0.9963
48	10.0	26.2887	0.2615	-1.3412
60	7.1	17.3196	0.1723	-1.7585
72	5.9	13.6082	0.1354	-1.9996
84	4.3	8.6598	0.0862	-2.4516
96	3.6	6.4948	0.0646	-2.7393
108	2.8	4.0206	0.0400	-3.2189
120	2.5	3.0928	0.0308	-3.4812

t (min.)	s (mg l^{-1})
0	1.7954
36	1.3535
84	2.2373
120	2.4583

TEST B33

s ($mg\ l^{-1}$)	Absorbance
0	0.002
1	0.093
2	0.213
3	0.343
4	0.504
5	0.655
6	0.777
7	0.833
8	0.985
9	1.174
10	1.235

TEST B34

Concentrations of solutions used (mg l^{-1})		Combination of volumes required to reach end-point (ml)		Combination of masses required to reach end-point (mg)	
CTAB	NaLS	CTAB	NaLS	CTAB	NaLS
599.6	381.6	40.0	48.1	23.984	18.355
		30.0	36.1	17.988	13.778
		20.0	24.2	11.992	9.235
		10.0	12.2	5.996	4.655
		0.0	0.1	0.000	0.038
119.92	76.32	40.0	51.0	4.784	3.892
		30.0	38.0	3.588	2.900
		20.0	25.5	2.392	1.946
		10.0	13.0	1.196	0.992
		0.0	0.5	0.000	0.038
23.98	15.26	40.0	51.0	0.959	0.778
		30.0	38.0	0.719	0.580
		20.0	25.5	0.480	0.389
		10.0	13.3	0.240	0.203
		0.0	1.5	0.000	0.023
86.60	51.20	75.0	106.0	6.495	5.427
		50.0	71.8	4.330	3.676
		40.0	56.5	3.464	2.893
		35.0	51.2	3.031	2.621
		32.0	46.3	2.771	2.371
		25.0	37.1	2.165	1.900
		20.0	30.3	1.732	1.551
		15.0	23.2	1.299	1.188
		10.0	16.1	0.866	0.824
		7.5	12.5	0.650	0.640
		5.0	9.0	0.433	0.461
		3.0	6.1	0.260	0.312
		2.0	4.7	0.173	0.241
		1.0	3.2	0.087	0.164
		0.0	2.0	0.000	0.102
307.80	261.00	42.0	39.6	12.928	10.336
		37.0	34.7	11.389	9.057
		31.0	29.4	9.542	7.673
		25.0	23.6	7.695	6.160
		20.0	19.0	6.156	4.959
		15.0	14.4	4.617	3.758
		10.0	9.8	3.078	2.558
		7.5	7.4	2.309	1.931
		5.0	5.1	1.539	1.331
		0.5	0.9	0.154	0.235

TEST B34 (Continued)

Concentrations of solutions used (mg l^{-1})		Combination of volumes required to reach end-point (ml)		Combination of masses required to reach end-point (mg)	
CTAB	NaLS	CTAB	NaLS	CTAB	NaLS
86.60	52.20	35.0	47.6	3.031	2.485
		25.0	34.5	2.165	1.801
		15.0	21.0	1.299	1.096
		5.0	8.0	0.433	0.418

CTAB = Cetyltrimethylammonium Bromide

NaLS = Sodium Lauryl Sulphate

TEST C1

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i
0	3.55	2.314	1.000
6	3.42	2.198	0.950
12	3.16	1.971	0.852
18	2.91	1.760	0.761
24	2.67	1.563	0.675
30	2.45	1.389	0.600
36	2.24	1.228	0.531
42	2.06	1.094	0.473
48	1.90	0.979	0.423
54	1.75	0.874	0.378
60	1.61	0.779	0.337
78	1.26	0.556	0.240
84	1.16	0.496	0.214
90	1.08	0.450	0.194
96	1.01	0.410	0.177

Dimensions of Unit:

Single Stage only: 1.908 x 0.306 x 0.500 m

TEST C2

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i
0	2.55	1.467	1.000
6	2.52	1.444	0.984
12	2.43	1.373	0.936
18	2.31	1.281	0.873
24	2.18	1.183	0.806
30	2.01	1.057	0.721
36	1.85	0.943	0.643
42	1.70	0.840	0.572
48	1.56	0.746	0.509
54	1.40	0.643	0.438
60	1.27	0.562	0.383
66	1.16	0.496	0.338
72	1.04	0.427	0.291
78	0.95	0.377	0.257
84	0.87	0.329	0.224
90	0.80	0.289	0.197
96	0.73	0.248	0.169
102	0.67	0.214	0.146
108	0.62	0.185	0.126
114	0.57	0.156	0.106
120	0.54	0.139	0.094

Dimensions of Unit:

First Stage: 0.948 x 0.306 x 0.504 m

Second Stage: 0.948 x 0.306 x 0.496 m

TEST C3

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i
0	2.93	1.777	1.000
6	2.89	1.740	0.979
12	2.82	1.686	0.949
18	2.73	1.608	0.905
24	2.59	1.499	0.844
30	2.42	1.368	0.770
36	2.22	1.215	0.684
42	2.00	1.053	0.593
48	1.80	0.910	0.512
54	1.60	0.771	0.434
60	1.42	0.656	0.369
66	1.24	0.544	0.306
72	1.09	0.453	0.255
78	0.95	0.379	0.213
84	0.84	0.319	0.179
90	0.74	0.266	0.150
96	0.65	0.224	0.126
102	0.58	0.191	0.108
108	0.52	0.164	0.092
114	0.47	0.145	0.081
120	0.43	0.126	0.071

Dimensions of Unit:

First Stage: 0.641 x 0.306 x 0.505 m
Second Stage: 0.606 x 0.306 x 0.500 m
Third Stage: 0.637 x 0.306 x 0.488 m

TEST C4

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i
0	3.190	1.989	1.000
6	3.187	1.986	0.999
12	3.174	1.975	0.993
18	3.139	1.943	0.977
24	3.036	1.851	0.931
30	2.866	1.703	0.856
36	2.639	1.508	0.758
42	2.360	1.313	0.660
48	2.058	1.103	0.555
54	1.747	0.887	0.446
60	1.459	0.697	0.351
66	1.215	0.540	0.271
72	0.994	0.401	0.201
78	0.802	0.290	0.146
84	0.651	0.203	0.102
90	0.542	0.139	0.070
96	0.452	0.088	0.044
102	0.391	0.053	0.026
108	0.343	0.025	0.013
114	0.311	0.006	0.003
120	0.289	0.000	0.000

Dimensions of Unit:

First Stage: 0.324 x 0.306 x 0.510 m
Second Stage: 0.305 x 0.306 x 0.505 m
Third Stage: 0.303 x 0.306 x 0.495 m
Fourth Stage: 0.291 x 0.306 m 0.488 m
Fifth Stage: 0.313 x 0.306 x 0.483 m
Sixth Stage: 0.312 x 0.306 x 0.470 m

TEST C5

t (min.)	s (mg l^{-1})	s/s_i	$\ln(s/s_i)$
0	37.3507	1.0000	0.0000
36	28.1338	0.7532	-0.2834
72	18.6721	0.4999	-0.6933
108	12.1469	0.3252	-1.1233
144	6.3557	0.1702	-1.7710
180	2.9299	0.0784	-2.5454
216	1.5433	0.0413	-3.1864
252	0.5645	0.0151	-4.1922
288	0.2382	0.0064	-5.0550

Dimensions of Unit:

Single Stage only: 1.908 x 0.306 x 0.500 m

TEST C6

t (min.)	s (mg l^{-1})	s/s_i	$\ln(s/s_i)$
0	39.6013	1.0000	0.0000
25	28.2506	0.7134	-0.3377
50	18.6836	0.4718	-0.7512
75	9.2787	0.2343	-1.4511
100	3.6033	0.0910	-2.3970
125	1.0089	0.0255	-3.6700
150	0.0359	0.0009	-7.0059

Dimensions of Unit:

Single Stage only: 1.908 x 0.306 x 0.500 m

TEST C7

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	34.0	100.5155	1.0000	0.0000
12	27.5	80.4124	0.8000	-0.2231
24	21.5	61.8557	0.6154	-0.4855
36	16.0	44.8454	0.4462	-0.8071
48	11.5	30.9278	0.3077	-1.1787
60	9.0	23.1959	0.2308	-1.4663
72	6.9	16.7010	0.1662	-1.7948
84	5.3	11.7526	0.1169	-2.1462
96	4.6	9.5876	0.0954	-2.3498
108	4.0	7.7320	0.0769	-2.5649
120	3.4	5.8763	0.0585	-2.8394

t (min.)	s (mg l^{-1})
0	2.9547
36	2.0273
84	2.4053
120	2.7293

Dimensions of Unit:

Single Stage only: 1.908 x 0.306 x 0.500 m

TEST C8

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
7.5	27.0	78.8660	0.8095	-0.2113
15.0	21.0	60.3093	0.6190	-0.4796
22.5	15.0	41.7526	0.4286	-0.8473
30.0	12.0	32.4742	0.3333	-1.0986
37.5	9.2	23.8144	0.2444	-1.4088
45.0	7.2	17.6289	0.1810	-1.7095
52.5	5.8	13.2990	0.1365	-1.9914
60.0	4.4	8.9691	0.0921	-2.3853
67.5	3.7	6.8041	0.0698	-2.6615
75.0	3.1	4.9485	0.0508	-2.9800

t (min.)	s (mg l^{-1})
0.0	5.3870
22.5	3.1169
52.5	3.7655
75.0	4.2519

Dimensions of Unit:

Single Stage only: 1.908 x 0.306 m 0.500 m

TEST C9

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i
0	33.0	97.4227	1.0000
12	28.0	81.9588	0.8413
24	24.5	71.1340	0.7302
36	20.5	58.7629	0.6032
48	18.0	51.0309	0.5238
60	17.0	47.9381	0.4921
72	17.0	47.9381	0.4921
84	16.5	46.3918	0.4762
90	16.0	44.8454	0.4603
96	15.5	43.2990	0.4444
102	15.5	43.2990	0.4444
108	15.0	41.7526	0.4286
114	15.0	41.7526	0.4286
120	15.5	43.2990	0.4444

t (min.)	s (mg l^{-1})
0	4.9005
30	5.2248
84	5.2248
120	5.5492

Dimensions of Unit:

Single Stage only: 1.908 x 0.306 . 0.500 m

TEST C10

t (min.)	n	τ (FTU)	c (mg l^{-1})	c/c_i
0	1 & 2	32.0	94.3299	1.0000
6	1	28.5	83.5052	0.8852
12	2	23.0	66.4948	0.7049
18	1	22.0	63.4021	0.6721
24	2	18.0	51.0309	0.5410
30	1	23.0	66.4948	0.7049
36	2	15.0	41.7526	0.4426
42	1	22.0	63.4021	0.6721
48	2	14.5	40.2062	0.4262
54	1	22.0	63.4021	0.6721
60	2	13.5	37.1134	0.3934
66	1	22.0	63.4021	0.6721
72	2	13.0	35.5670	0.3770
78	1	22.5	64.9485	0.6885
84	2	13.0	35.5670	0.3770
90	1	21.5	61.8557	0.6557
96	2	13.0	35.5670	0.3770
102	1	23.0	66.4948	0.7049
108	2	12.5	34.0206	0.3607
114	1	22.5	64.9485	0.6885
120	2	12.0	32.4742	0.3443

TEST C10 (Continued)

t (min.)	n	s (mg l^{-1})
0	1 & 2	5.8735
18	1	5.3870
36	2	3.9276
54	1	5.3870
72	2	3.9276
90	1	5.7113
108	2	4.5762
120	2	4.9005

Dimensions of Unit:

First Stage: 0.948 x 0.306 x 0.504 m

Second Stage: 0.948 x 0.306 x 0.496 m

TEST C11

t (min.)	n	τ (FTU)	c (mg l^{-1})	c/c_i
0	1 - 3	34.0	100.5155	1.0000
4	1	28.0	81.9588	0.8154
8	2	32.0	94.3299	0.9385
12	3	27.5	80.4124	0.8000
16	1	30.0	88.1443	0.8769
20	2	23.5	68.0412	0.6769
24	3	20.0	57.2165	0.5692
28	1	23.5	68.0412	0.6769
32	2	19.0	54.1237	0.5385
36	3	17.0	47.9381	0.4769
40	1	23.5	68.0412	0.6769
44	2	18.0	51.0309	0.5077
48	3	14.5	40.2062	0.4000
52	1	23.0	66.4948	0.6615
56	2	16.5	46.3918	0.4615
60	3	13.5	37.1134	0.3692
64	1	24.0	69.5876	0.6923
68	2	16.5	46.3918	0.4615
72	3	11.5	30.9278	0.3077
76	1	23.0	66.4948	0.6615
80	2	16.5	46.3918	0.4615
84	3	10.5	27.8351	0.2769
88	1	21.0	60.3093	0.6000
92	2	16.0	44.8454	0.4462
96	3	10.5	27.8351	0.2769
100	1	22.0	63.4021	0.6308
104	2	17.0	47.9381	0.4769
108	3	11.0	29.3814	0.2923
112	1	27.0	78.8660	0.7846
116	2	20.0	57.2165	0.5692
120	3	11.0	29.3814	0.2923

TEST C11 (Continued)

t (min.)	n	s (mg l^{-1})
0	1 - 3	3.5759
12	3	2.0004
28	1	3.8624
44	2	2.5733
60	3	1.4275
64	1	5.4379
80	2	3.5759
84	3	1.8572
92	2	3.4327
100	1	5.4379
108	3	2.5733
112	1	6.2973
116	2	3.7191

Dimensions of Unit:

First Stage: 0.641 x 0.306 x 0.505 m
Second Stage: 0.606 x 0.306 x 0.500 m
Third Stage: 0.637 x 0.306 x 0.488 m

Dry Solids Determination:

mass of container = 4.54 g
mass of container + contents = 12.03 g
mass of container + contents after drying = 9.54 g

TEST C12

t (min.)	n	τ (FTU)	c (mg l^{-1})	c/c_i
0	1 - 6	34.0	100.5155	1.0000
6	1	27.0	78.8660	0.7846
8	2	26.5	77.3196	0.7692
10	3	25.0	72.6804	0.7231
12	4	24.0	69.5876	0.6923
14	5	22.5	64.9485	0.6462
16	6	22.0	63.4021	0.6308
18	1	26.0	75.7732	0.7538
20	2	24.0	69.5876	0.6923
22	3	21.0	60.3093	0.6000
24	4	19.5	55.6701	0.5538
26	5	19.0	54.1237	0.5385
28	6	17.0	47.9381	0.4769
30	1	26.0	75.7732	0.7538
32	2	21.5	61.8557	0.6154
34	3	18.5	52.5773	0.5231
36	4	17.0	47.9381	0.4769
38	5	15.0	41.7526	0.4154
40	6	13.0	35.5670	0.3538
42	1	27.0	78.8660	0.7846
44	2	22.0	63.4021	0.6308
46	3	27.0	78.8660	0.7846
48	4	17.5	49.4845	0.4923
50	5	13.5	37.1134	0.3692
52	6	11.5	30.9278	0.3077
54	1	28.0	81.9588	0.8154
56	2	23.0	66.4948	0.6615
58	3	19.5	55.6701	0.5538
60	4	16.5	46.3918	0.4615
62	5	13.5	37.1134	0.3692
64	6	11.0	29.3814	0.2923

TEST C12 (Continued)

t (min.)	n	τ (FTU)	c (mg l^{-1})	c/c_i
66	1	28.0	81.9588	0.8154
68	2	24.5	71.1340	0.7077
70	3	20.0	57.2165	0.5692
74	5	15.5	43.2990	0.4308
76	6	11.5	30.9278	0.3077
78	1	32.0	94.3299	0.9385
80	2	23.0	66.4948	0.6615
82	3	24.0	69.5876	0.6923
84	4	18.0	51.0309	0.5077
86	5	13.0	35.5670	0.3538
88	6	10.0	26.2887	0.2615
90	1	31.0	91.2371	0.9077
92	2	25.5	74.2268	0.7385
94	3	19.5	55.6701	0.5538
96	4	16.5	46.3918	0.4615
98	5	13.0	35.5670	0.3538
100	6	10.0	26.2887	0.2615
102	1	29.0	85.0515	0.8462
104	2	23.5	68.0412	0.6769
106	3	18.5	52.5773	0.5231
108	4	16.0	44.8454	0.4462
110	5	13.0	35.5670	0.3538
112	6	10.0	26.2887	0.2615
114	1	32.0	94.3299	0.9385
116	2	28.5	83.5052	0.8308
118	3	21.0	60.3093	0.6000
120	4	17.0	47.9381	0.4769
122	5	13.0	35.5670	0.3538
124	6	10.0	26.2887	0.2615

TEST C12 (Continued)

t (min.)	n	s (mg l^{-1})
0	1 - 6	4.2382
54	1	8.6917
56	2	7.8010
58	3	7.2072
60	4	4.5351
62	5	3.3475
64	6	3.1991
102	1	8.3948
104	2	7.2072
106	3	6.4650
108	4	5.4258
110	5	4.9805
112	6	3.1991

Dimensions of Unit:

First Stage: 0.324 x 0.306 x 0.510 m
Second Stage: 0.305 x 0.306 x 0.505 m
Third Stage: 0.303 x 0.306 x 0.495 m
Fourth Stage: 0.291 x 0.306 x 0.488 m
Fifth Stage: 0.313 x 0.306 x 0.483 m
Sixth Stage: 0.312 x 0.306 x 0.470 m

TEST C13

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i
0.0	34.0	100.5155	1.0000
7.5	25.5	74.2268	0.7385
15.0	19.0	54.1237	0.5385
22.5	14.5	40.2062	0.4000
30.0	13.0	35.5670	0.3538
37.5	11.0	29.3814	0.2923
45.0	10.0	26.2887	0.2615
52.5	10.0	26.2887	0.2615
60.0	9.3	24.1237	0.2400
67.5	9.4	24.4330	0.2431
75.0	9.4	24.4330	0.2431

t (min.)	s (mg l^{-1})
0.0	4.2288
22.5	3.3263
52.5	3.9279
75.0	3.9279

Dimensions of Unit:

Single Stage only: 1.908 x 0.306 x 0.500 m

TEST C14

t (min.)	n	τ (FTU)	c (mg l^{-1})	c/c_i
0.00	1 & 2	34.0	100.5155	1.0000
3.75	1	31.0	91.2371	0.9077
7.50	2	22.5	64.9485	0.6462
11.25	1	27.5	80.4124	0.8000
15.00	2	15.0	41.7526	0.4154
18.75	1	25.0	72.6804	0.7231
22.50	2	12.0	32.4742	0.3231
26.25	1	18.0	51.0309	0.5077
30.00	2	10.0	26.2887	0.2615
33.75	1	18.0	51.0309	0.5077
37.50	2	8.9	22.8866	0.2277
41.25	1	18.0	51.0309	0.5077
45.00	2	7.8	19.4845	0.1938
48.75	1	17.0	47.9381	0.4769
52.50	2	7.0	17.0103	0.1692
56.25	1	16.5	46.3918	0.4615
60.00	2	6.8	16.3918	0.1631
63.75	1	17.0	47.9381	0.4769
67.50	2	7.0	17.0103	0.1692
71.25	1	16.5	46.3918	0.4615
75.00	2	7.0	17.0103	0.1692

TEST C14 (Continued)

t (min.)	n	s (mg l^{-1})
0.00	1 & 2	4.3792
11.25	1	5.8832
22.50	2	1.6718
33.75	1	7.3873
45.00	2	2.2735
56.25	1	7.3873
67.50	2	2.5743
71.25	1	8.2898

Dimensions of Unit:

First Stage: 0.948 x 0.306 x 0.504 m

Second Stage: 0.948 x 0.306 x 0.496 m

TEST C15

t (min.)	n	τ (FTU)	c (mg l^{-1})	c/c_i
0.0	1 - 3	34.0	100.5155	1.0000
2.4	1	32.5	95.8763	0.9538
4.8	2	18.0	51.0309	0.5077
7.2	3	24.0	69.5876	0.6923
9.6	1	26.0	75.7732	0.7538
12.0	2	23.0	66.4948	0.6615
14.4	3	17.0	47.9381	0.4769
16.8	1	25.5	74.2268	0.7385
19.2	2	16.0	44.8454	0.4462
21.6	3	12.5	34.0206	0.3385
24.0	1	20.5	58.7629	0.5846
26.4	2	15.5	43.2990	0.4308
28.8	3	10.0	26.2887	0.2615
33.6	2	13.5	37.1134	0.3692
36.0	3	8.0	20.1031	0.2000
38.4	1	20.0	57.2165	0.5692
40.8	2	13.0	35.5670	0.3538
43.2	3	6.9	16.7010	0.1662
45.6	1	19.0	54.1237	0.5385
48.0	2	12.5	34.0206	0.3385
50.4	3	6.5	15.4639	0.1538
52.8	1	20.0	57.2165	0.5692
55.2	2	13.0	35.5670	0.3538
57.6	3	5.9	13.6082	0.1354
60.0	1	20.0	57.2165	0.5692
62.4	2	12.0	32.4742	0.3231
64.8	3	5.6	12.6804	0.1262
67.2	1	19.5	55.6701	0.5538
69.6	2	12.0	32.4742	0.3231
72.0	3	5.6	12.6804	0.1262

TEST C15 (Continued)

t (min.)	n	s (mg l^{-1})
0.0	1 - 3	1.5707
7.2	3	2.4301
16.8	1	6.5837
26.4	2	3.2895
36.0	3	0.8545
38.4	1	9.1619
48.0	2	5.0082
50.4	3	1.1410
55.2	2	4.5785
60.0	1	9.1619
64.8	3	1.2842
67.2	1	10.3077
69.6	2	5.2947

Dimensions of Unit:

First Stage: 0.641 x 0.306 x 0.505 m
Second Stage: 0.606 x 0.306 x 0.500 m
Third Stage: 0.637 x 0.306 x 0.488 m

TEST C16

t (min.)	n	τ (FTU)	c (mg l^{-1})	c/c_i
0.0	1 - 6	34.0	100.5155	1.0000
7.5	1	24.0	69.5876	0.6923
7.5	2	23.5	68.0412	0.6769
12.5	5	21.5	61.8557	0.6154
12.5	6	24.0	69.5876	0.6923
15.0	1	21.0	60.3093	0.6000
15.0	2	17.0	47.9381	0.4769
17.5	3	15.0	41.7526	0.4154
17.5	4	17.0	47.9381	0.4769
20.0	5	15.0	41.7526	0.4154
20.0	6	17.0	47.9381	0.4769
22.5	1	23.0	66.4948	0.6615
22.5	2	15.0	41.7526	0.4154
25.0	3	12.0	32.4742	0.3231
25.0	4	12.5	34.0206	0.3385
27.5	5	12.0	32.4742	0.3231
27.5	6	13.5	37.1134	0.3692
30.0	1	23.5	68.0412	0.6769
30.0	2	14.0	38.6598	0.3846
32.5	3	10.0	26.2887	0.2615
32.5	4	8.7	22.9680	0.2215
35.0	5	10.5	27.8351	0.2769
35.0	6	10.0	26.2887	0.2615
37.5	1	23.5	68.0412	0.6769
37.5	2	15.0	41.7526	0.4154
40.0	3	9.2	23.8144	0.2369
40.0	4	7.4	18.2474	0.1815
42.5	5	7.2	17.6289	0.1754
42.5	6	7.6	18.8660	0.1877
45.0	1	24.0	69.5876	0.6923
45.0	2	15.5	43.2990	0.4308

TEST C16 (Continued)

t (min.)	n	τ (FTU)	c (mg l^{-1})	c/c_i
47.5	3	9.6	25.0515	0.2492
47.5	4	7.2	17.6289	0.1754
50.0	5	5.9	13.6082	0.1354
50.0	6	5.8	13.2990	0.1323
52.5	1	24.0	69.5876	0.6923
52.5	2	15.5	43.2990	0.4308
55.0	3	10.0	26.2887	0.2615
55.0	4	7.1	17.3196	0.1723
57.5	5	5.4	12.0619	0.1200
57.5	6	5.0	10.8247	0.1077
60.0	1	25.0	72.6804	0.7231
60.0	2	15.5	43.2990	0.4308
62.5	3	10.5	27.8351	0.2769
62.5	4	7.5	18.5567	0.1846
65.0	5	5.1	11.1340	0.1108
65.0	6	4.6	9.5876	0.0954
67.5	1	25.0	72.6804	0.7231
67.5	2	15.5	43.2990	0.4308
70.0	3	10.5	27.8351	0.2769
70.0	4	7.5	18.5567	0.1846
72.5	5	5.4	12.0619	0.1200
72.5	6	4.2	8.3505	0.0831

TEST C16 (Continued)

t (min.)	n	s (mg l^{-1})
0.0	1 - 6	3.6263
30.0	1	8.9617
30.0	2	5.6916
32.5	3	4.6590
32.5	4	1.2168
35.0	5	1.0446
35.0	6	0.8725
67.5	1	12.4039
67.5	2	9.8223
70.0	3	8.6175
70.0	4	6.3801
72.5	5	5.0032
72.5	6	3.4542

Dimensions of Unit:

First Stage: 0.324 x 0.306 x 0.510 m
Second Stage: 0.305 x 0.306 x 0.505 m
Third Stage: 0.303 x 0.306 x 0.495 m
Fourth Stage: 0.291 x 0.306 x 0.488 m
Fifth Stage: 0.313 x 0.306 x 0.483 m
Sixth Stage: 0.312 x 0.306 x 0.470 m

TEST D1

t (min.)	s (mg l^{-1})
0	38.2337
10	32.0660
20	26.6692
30	21.2725
40	16.1327
50	11.5069
60	7.5524
70	4.4685
80	2.6696
90	1.6416
100	1.6084

TEST D2

t (min.)	s (mg l^{-1})
0	37.1931
10	29.2290
20	22.9126
30	17.4201
40	11.3784
50	7.0623
60	3.9041
70	1.9818
80	1.2952
90	1.1579

TEST D3

t (min.)	s (mg l^{-1})
0.0	37.4677
7.5	31.1514
15.0	24.2858
22.5	18.2440
30.0	12.4769
37.5	8.3575
45.0	5.4146
55.0	2.5310
60.0	1.9818
67.5	1.5698
75.0	1.2952

TEST D4

t (min.)	s (mg l^{-1})
0	36.9185
5	30.0529
10	23.7365
15	17.9694
20	12.4769
25	8.4354
30	5.4146
35	3.3549
40	2.1191
45	1.4325
50	1.4325
55	1.1579
60	1.1579

TEST D5

t (min.)	s (mg l^{-1})
0	37.1049
11	30.5700
20	25.6035
30	20.6369
40	15.9318
50	11.2266
60	7.0510
70	3.9142
80	2.8686
90	2.2151
100	1.9537

TEST D6

t (min.)	s (mg l^{-1})
0	41.0259
10	35.0138
20	29.2630
30	23.2509
40	17.7615
50	13.0564
61	8.2273
70	5.2212
80	3.2607
90	2.0844
100	1.6923

TEST D7

t (min.)	s (mg l^{-1})
0	36.9810
10	30.0472
20	24.8193
30	19.8527
40	14.8862
50	10.7038
60	6.6589
70	3.9142
80	2.4765
90	1.6923

TEST D8

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	33.0	97.4227	1.0000	0.0000
5.0	32.5	95.8763	0.9841	-0.0160
7.5	32.5	95.8763	0.9841	-0.0160
10.0	32.0	94.3299	0.9683	-0.0323
12.5	31.5	92.7835	0.9524	-0.0488
15.0	30.5	89.6907	0.9206	-0.0827
17.5	30.5	89.6907	0.9206	-0.0827
20.0	30.0	88.1443	0.9048	-0.1001
22.5	30.0	88.1443	0.9048	-0.1001
25.0	29.0	85.0515	0.8730	-0.1358
27.5	29.0	85.0515	0.8730	-0.1358
30.0	29.0	85.0515	0.8730	-0.1358

t (min.)	s (mg l^{-1})
0.0	87.8324
15.0	82.6926
30.0	79.6088

TEST D9

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	32.5	95.8763	0.9841	-0.0160
5.0	31.5	92.7835	0.9524	-0.0488
7.5	31.5	92.7835	0.9524	-0.0488
10.0	32.0	94.3299	0.9683	-0.0323
12.5	30.5	89.6907	0.9206	-0.0827
15.0	29.5	86.5979	0.8889	-0.1178
17.5	29.5	86.5979	0.8889	-0.1178
20.0	28.5	83.5052	0.8571	-0.1542
22.5	28.0	81.9588	0.8413	-0.1728
25.0	27.5	80.4124	0.8254	-0.1919
27.5	27.5	80.4124	0.8254	-0.1919
30.0	27.5	80.4124	0.8254	-0.1919

t (min.)	s (mg l^{-1})
0.0	70.3572
15.0	67.2733
30.0	67.0163

TEST D10

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	32.0	94.3299	0.9683	-0.0323
5.0	30.5	89.6907	0.9206	-0.0827
7.5	31.0	91.2371	0.9365	-0.0656
10.0	29.5	86.5979	0.8889	-0.1178
12.5	28.5	83.5052	0.8571	-0.1542
15.0	27.0	78.8660	0.8095	-0.2113
17.5	27.0	78.8660	0.8095	-0.2113
20.0	26.5	77.3196	0.7937	-0.2311
22.5	25.0	72.6804	0.7460	-0.2930
25.0	24.0	69.5876	0.7143	-0.3365
27.5	23.0	66.4948	0.6825	-0.3819
30.0	23.0	66.4948	0.6825	-0.3819

t (min.)	s (mg l^{-1})
0.0	52.6250
15.0	51.8540
30.0	50.0551

TEST D11

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	31.0	91.2371	0.9365	-0.0656
5.0	30.0	88.1443	0.9048	-0.1001
7.5	28.0	81.9588	0.8413	-0.1728
10.0	28.0	81.9588	0.8413	-0.1728
12.5	26.0	75.7732	0.7778	-0.2513
15.0	24.5	71.1340	0.7302	-0.3145
17.5	22.5	64.9485	0.6667	-0.4055
20.0	22.0	63.4021	0.6508	-0.4296
22.5	20.5	58.7629	0.6032	-0.5055
25.0	19.5	55.6701	0.5714	-0.5596
27.5	17.5	49.4845	0.5079	-0.6774
30.0	17.0	47.9381	0.4921	-0.7091

t (min.)	s (mg l^{-1})
0.0	43.3734
15.0	41.3175
30.0	41.3175

TEST D12

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	31.0	91.2371	0.9365	-0.0656
5.0	27.5	80.4124	0.8254	-0.1919
7.5	26.0	75.7732	0.7778	-0.2513
10.0	23.5	68.0412	0.6984	-0.3589
12.5	22.0	63.4021	0.6508	-0.4296
15.0	19.0	54.1237	0.5556	-0.5878
17.5	17.0	47.9381	0.4921	-0.7091
20.0	16.0	44.8454	0.4603	-0.7758
22.5	15.0	41.7526	0.4286	-0.8473
25.0	13.5	37.1134	0.3810	-0.9651

t (min.)	s (mg l^{-1})
0.0	34.1219
15.0	32.8369
25.0	33.6079

TEST D13

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	29.0	85.0515	0.8730	-0.1358
5.0	25.5	74.2268	0.7619	-0.2719
7.5	22.0	63.4021	0.6508	-0.4296
10.0	19.0	54.1237	0.5556	-0.5878
12.5	16.0	44.8454	0.4603	-0.7758
15.0	15.0	41.7526	0.4286	-0.8473
17.5	13.0	35.5670	0.3651	-1.0076
20.0	11.0	29.3814	0.3016	-1.1987
22.5	10.0	26.2887	0.2698	-1.3099
25.0	9.3	24.1237	0.2476	-1.3959

t (min.)	s (mg l^{-1})
0.0	25.6413
15.0	25.1273
25.0	25.3843

TEST D14

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	27.0	78.8660	0.8095	-0.2113
5.0	23.0	66.4948	0.6825	-0.3819
7.5	18.0	51.0309	0.5238	-0.6466
10.0	14.5	40.2062	0.4127	-0.8850
12.0	13.0	35.5670	0.3651	-1.0076
15.0	10.0	26.2887	0.2698	-1.3099
17.5	8.5	21.6495	0.2222	-1.5041
20.0	7.0	17.0103	0.1746	-1.7452
22.5	6.0	13.9175	0.1429	-1.9459
25.0	5.4	12.0619	0.1238	-2.0890

t (min.)	s (mg l^{-1})
0.0	16.6467
15.0	16.9037
25.0	18.1886

TEST D15

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	26.0	75.7732	0.7778	-0.2513
5.0	20.5	58.7629	0.6032	-0.5055
7.5	16.5	46.3918	0.4762	-0.7419
10.0	12.5	34.0206	0.3492	-1.0521
12.5	9.9	25.9794	0.2667	-1.3218
15.0	7.8	19.4845	0.2000	-1.6094
17.5	6.9	16.7010	0.1714	-1.7636
20.0	6.0	13.9175	0.1429	-1.9459
22.5	5.1	11.1340	0.1143	-2.1691
25.0	4.5	9.2784	0.0952	-2.3514

t (min.)	s (mg l^{-1})
0.0	12.4351
15.0	13.2061
25.0	14.3626

TEST D16

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	25.5	74.2268	0.7619	-0.2719
5.0	19.5	55.6701	0.5714	-0.5596
7.5	15.5	43.2990	0.4444	-0.8109
10.0	11.5	30.9278	0.3175	-1.1474
12.5	8.9	22.8866	0.2349	-1.4486
15.0	6.9	16.7010	0.1714	-1.7636
17.5	5.5	12.3711	0.1270	-2.0637
20.0	4.5	9.2784	0.0952	-2.3514
22.5	3.8	7.1134	0.0730	-2.6171
25.0	3.4	5.8763	0.0603	-2.8081

t (min.)	s (mg l^{-1})
0.0	8.4518
15.0	6.2674
25.0	6.7386

TEST D17

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	25.5	74.2268	0.7619	-0.2719
5.0	20.0	57.2165	0.5873	-0.5322
7.5	16.5	46.3918	0.4762	-0.7419
10.0	13.5	37.1134	0.3810	-0.9651
12.5	10.5	27.8351	0.2857	-1.2528
15.0	8.4	21.3402	0.2190	-1.5185
17.5	7.0	17.0103	0.1746	-1.7452
20.0	5.6	12.6804	0.1302	-2.0390
22.5	4.7	9.8969	0.1016	-2.2868
25.0	4.0	7.7320	0.0794	-2.5337

t (min.)	s (mg l^{-1})
0.0	5.2684
15.0	4.3677
25.0	4.2292

TEST D18

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	27.0	78.8660	0.8095	-0.2113
5.0	21.5	61.8557	0.6349	-0.4543
7.5	17.0	47.9381	0.4921	-0.7091
10.0	14.0	38.6598	0.3968	-0.9243
12.5	11.5	30.9278	0.3175	-1.1474
15.0	8.8	22.5773	0.2317	-1.4621
17.5	7.0	17.0103	0.1746	-1.7452
20.0	6.0	13.9175	0.1429	-1.9459
22.5	5.0	10.8247	0.1111	-2.1972
25.0	4.0	7.7320	0.0794	-2.5337

t (min.)	s (mg l^{-1})
0.0	4.0906
15.0	2.8434
25.0	2.3584

TEST D19

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	33.0	97.4227	1.0000	0.0000
2.5	28.0	81.9588	0.8413	-0.1728
5.0	23.0	66.4948	0.6825	-0.3819
7.5	18.5	52.5773	0.5397	-0.6168
10.0	15.5	43.2990	0.4444	-0.8109
12.5	14.0	38.6598	0.3968	-0.9243
15.0	13.0	35.5670	0.3651	-1.0076
17.5	11.0	29.3814	0.3016	-1.1987
20.0	8.8	22.5773	0.2317	-1.4621
22.5	8.2	20.7216	0.2127	-1.5479

t (min.)	s (mg l^{-1})
0.0	1.8734
15.0	1.3191
25.0	1.1806

TEST D20

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	32.0	94.3299	1.0000	0.0000
2.5	30.0	88.1443	0.9344	-0.0678
5.0	25.0	72.6804	0.7705	-0.2607
7.5	22.5	64.9485	0.6885	-0.3732
10.0	18.0	51.0309	0.5410	-0.6144
12.5	15.0	41.7526	0.4426	-0.8150
15.0	13.0	35.5670	0.3770	-0.9754
17.5	12.0	32.4742	0.3443	-1.0664
20.0	10.0	26.2887	0.2787	-1.2777
22.5	8.1	20.4124	0.2164	-1.5307

TEST D21

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	32.5	95.8763	1.0000	0.0000
2.5	30.0	88.1443	0.9194	-0.0841
5.0	25.5	74.2268	0.7742	-0.2559
7.5	22.0	63.4021	0.6613	-0.4136
10.0	18.0	51.0309	0.5323	-0.6306
12.5	15.5	43.2990	0.4516	-0.7949
15.0	13.0	35.5670	0.3710	-0.9916
17.5	12.0	32.4742	0.3387	-1.0826
20.0	10.5	27.8351	0.2903	-1.2368
22.5	9.0	23.1959	0.2419	-1.4191
25.0	7.9	19.7938	0.2065	-1.5777

t (min.)	s (mg l^{-1})
0.0	20.5189
12.5	18.0473
25.0	17.7727

TEST D22

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	32.0	94.3299	1.0000	0.0000
2.5	29.0	85.0515	0.9016	-0.1035
5.0	25.0	72.6804	0.7705	-0.2607
7.5	22.5	64.9485	0.6885	-0.3732
10.0	18.5	52.5773	0.5574	-0.5845
12.5	15.5	43.2990	0.4590	-0.7787
15.0	14.0	38.6598	0.4098	-0.8920
17.5	12.5	34.0206	0.3607	-1.0198
20.0	10.5	27.8351	0.2951	-1.2205
22.5	10.0	26.2887	0.2787	-1.2777

t (min.)	s (mg l^{-1})
0.0	20.6562
12.5	19.0085
22.5	18.7339

TEST D23

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	32.0	94.3299	1.0000	0.0000
2.5	27.5	80.4124	0.8525	-0.1596
5.0	25.0	72.6804	0.7705	-0.2607
7.5	21.0	60.3093	0.6393	-0.4473
10.0	18.5	52.5773	0.5574	-0.5845
12.5	15.5	43.2990	0.4590	-0.7787
15.0	14.0	38.6598	0.4098	-0.8920
17.5	12.0	32.4742	0.3443	-1.0664
20.0	10.5	27.8351	0.2951	-1.2205
22.5	9.3	24.1237	0.2557	-1.3636
25.0	8.0	20.1031	0.2131	-1.5459

t (min.)	s (mg l^{-1})
0.0	19.8324
12.5	17.6354
25.0	17.9100

TEST D24

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	67.5	204.1237	1.0000	0.0000
2.5	67.5	204.1237	1.0000	0.0000
5.0	59.5	179.3814	0.8788	-0.1292
7.5	55.0	165.4639	0.8106	-0.2100
10.0	50.5	151.5464	0.7424	-0.2978
12.5	45.0	134.5361	0.6591	-0.4169
15.0	40.0	119.0722	0.5833	-0.5390
17.5	36.5	108.2472	0.5303	-0.6343
20.0	32.0	94.3299	0.4621	-0.7719
22.5	28.0	81.9588	0.4015	-0.9125

t (min.)	s (mg l^{-1})
0.0	41.8101
12.5	38.6733
22.5	38.9347

TEST D25

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	67.0	202.5773	1.0000	0.0000
2.5	59.5	179.3814	0.8855	-0.1216
5.0	54.0	162.3711	0.8015	-0.2212
7.5	49.0	146.9072	0.7252	-0.3213
10.0	40.0	119.0722	0.5878	-0.5314
12.5	32.0	94.3299	0.4656	-0.7643
15.0	29.0	85.0515	0.4198	-0.8679
17.5	25.0	72.6804	0.3588	-1.0250
20.0	20.5	58.7629	0.2901	-1.2376
22.5	18.5	52.5773	0.2595	-1.3488

t (min.)	s (mg l^{-1})
0.0	33.9682
12.5	31.0928
22.5	30.8314

TEST D26

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	68.0	205.6701	1.0000	0.0000
2.5	57.5	173.1959	0.8421	-0.1719
5.0	44.5	132.9897	0.6466	-0.4360
7.5	32.5	95.8763	0.4662	-0.7632
10.0	28.0	81.9588	0.3985	-0.9201
12.5	22.5	64.9485	0.3158	-1.1527
15.0	17.5	49.4845	0.2406	-1.4246
17.5	14.0	38.6598	0.1880	-1.6715
20.0	12.0	32.4742	0.1579	-1.8458
22.5	10.5	27.8351	0.1353	-2.0000

t (min.)	s (mg l^{-1})
0.0	23.9500
12.5	23.3391
22.5	22.4226

TEST D27

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	68.0	205.6701	1.0000	0.0000
2.5	53.5	160.8247	0.7820	-0.2460
5.0	41.0	122.1649	0.5940	-0.5209
7.5	31.0	91.2371	0.4436	-0.8128
10.0	23.0	66.4948	0.3233	-1.1291
12.5	17.0	47.9381	0.2331	-1.4564
15.0	14.0	38.6598	0.1880	-1.6715
17.5	11.0	29.3814	0.1429	-1.9459
20.0	8.2	20.7216	0.1008	-2.2951
22.5	7.1	17.3196	0.0842	-2.4744

t (min.)	s (mg l^{-1})
0.0	16.0073
12.5	14.7854
22.5	14.4799

TEST D28

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	67.0	202.5773	1.0000	0.0000
2.5	52.0	156.1856	0.7710	-0.2601
5.0	39.0	115.9794	0.5725	-0.5577
7.5	27.0	78.8660	0.3893	-0.9434
10.0	19.5	55.6701	0.2748	-1.2917
12.5	15.0	41.7526	0.2061	-1.5794
15.0	11.0	29.3814	0.1450	-1.9308
17.5	8.0	20.1031	0.0992	-2.3102
20.0	6.6	15.7732	0.0779	-2.5528
22.5	5.5	12.3711	0.0611	-2.7958

t (min.)	s (mg l^{-1})
0.0	7.4537
12.5	8.0646
22.5	9.2866

TEST D29

t (min.)	v (l min^{-1})	τ (FTU)	c (mg l^{-1})	c/c_i
0	2	33.0	97.4227	1.0000
2		29.5	86.5979	0.8889
4		26.0	75.7732	0.7778
5	6			
6		23.0	66.4948	0.6825
8		20.5	58.7629	0.6032
10	10	19.0	54.1237	0.5556
12		18.5	52.5773	0.5397
14		18.0	51.0309	0.5238
15	2			
16		17.0	47.9381	0.4921
18		14.5	40.2062	0.4127
20		13.0	35.5670	0.3651
22		10.5	27.8351	0.2857
24		9.2	23.8144	0.2444
25	6			
26		9.7	25.3608	0.2603
28		11.5	30.9278	0.3175
30	8	12.0	32.4742	0.3333
32		14.0	38.6592	0.3968
34		14.5	40.2062	0.4127
35	4			
36		14.0	38.6598	0.3968
38		12.5	34.0206	0.3492
40	2	12.0	32.4742	0.3333
42		11.0	29.3814	0.3016
44		9.4	24.4330	0.2508
46		8.2	20.7216	0.2127
48		7.4	18.2474	0.1873
50		6.9	16.7010	0.1714

TEST D29 (Continued)

t (min.)	s (mg l^{-1})
0	7.3943
10	7.1455
20	7.6431
30	8.0163
40	8.2651

TEST D30

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0.0	29.5	107.4006	1.0000	0.0000
2.5	29.5	107.4006	1.0000	0.0000
5.0	24.5	88.1929	0.8212	-0.1970
7.5	21.0	74.7474	0.6960	-0.3625
10.0	17.0	59.3813	0.5529	-0.5926
12.5	15.0	51.6982	0.4814	-0.7311
15.0	12.5	42.0943	0.3919	-0.9367
17.5	11.0	36.3320	0.3383	-1.0839
20.0	8.6	27.1123	0.2524	-1.3766
22.5	7.2	21.7341	0.2024	-1.5977
25.0	6.4	18.6609	0.1738	-1.7501
27.5	5.7	15.9718	0.1487	-1.9057
30.0	4.8	12.5144	0.1165	-2.1497
35.0	4.1	9.8253	0.0915	-2.3916
40.0	3.4	7.1362	0.0664	-2.7114
45.0	2.9	5.2155	0.0486	-3.0249

TEST D31

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i
0.0	26.0	93.9552	1.0000
2.5	17.0	59.3813	0.6320
5.0	15.5	53.6189	0.5707
7.5	13.5	45.9358	0.4889
10.0	12.5	42.0943	0.4480
12.5	11.0	38.2528	0.4071
15.0	10.5	34.4112	0.3663
17.5	10.0	32.4904	0.3458
20.0	9.5	30.5697	0.3254
22.5	9.2	29.4172	0.3131
25.0	8.7	27.4964	0.2927
27.5	8.7	27.4964	0.2927
30.0	8.4	26.3440	0.2804
32.5	8.4	26.3440	0.2804
35.0	8.5	26.7281	0.2845
37.5	8.4	26.3440	0.2804
40.0	8.4	26.3440	0.2804
42.5	8.4	26.3440	0.2804
45.0	8.3	25.9598	0.2763
47.5	8.0	24.8073	0.2640
50.0	8.1	25.1915	0.2681
52.5	8.1	25.1915	0.2681
55.0	8.1	25.1915	0.2681
57.5	8.3	25.9598	0.2763
60.0	8.4	26.3440	0.2804

TEST D32

C (mg l^{-1})	τ (FTU)
3.06	1.8
6.12	2.8
8.75	3.5
12.49	4.6
16.66	6.1
22.21	7.5
27.76	8.8
34.71	11.0
40.83	12.5
48.04	14.5
56.51	17.0
64.58	18.5
73.81	20.5
82.01	22.5
91.13	25.5
101.25	27.0
112.50	31.0

Clay Type: Model Sediment

Liquid Medium: Laboratory Tapwater

TEST D33

Sieve Size (μm)	Cumulative Wt. Percentage (%)	Differential Wt. Percentage (%)
2,000	5.81	5.81
1,000	21.68	15.86
600	41.60	19.92
300	81.55	39.96
150	95.35	13.80
90	97.70	2.35
75	98.42	0.72
	100.00	1.58

TEST D34

Mean Spherical Diameter (μm)	Cumulative Wt. Percentage (%)	Differential Wt. Percentage (%)
67.50		
	6.50	6.50
53.60		
	15.99	9.49
42.50		
	27.83	11.83
33.80		
	37.71	9.88
27.10		
	46.03	8.32
21.70		
	54.78	8.76
17.20		
	61.98	7.19
13.80		
	68.21	6.23
10.90		
	74.47	6.25
8.68		
	80.54	6.07
6.89		
	85.77	5.23
5.63		
	91.09	5.32
4.67		
	95.79	4.69
3.99		
	100.00	4.21
3.17		

TEST D35

t (min.)	τ (FTU)	c (mg l^{-1})	c/c_i	$\ln(c/c_i)$
0	33.0	97.4227	1.0000	0.0000
12	23.0	66.4948	0.6825	-0.3819
24	18.5	52.5773	0.5397	-0.6168
36	15.0	41.7526	0.4286	-0.8473
48	12.0	32.4742	0.3333	-1.0986
60	10.0	26.2887	0.2698	-1.3099
72	7.2	17.6289	0.1810	-1.7095
84	6.1	14.2268	0.1460	-1.9239
96	5.1	11.1340	0.1143	-2.1691
108	4.4	8.9691	0.0921	-2.3853
120	3.6	6.4948	0.0667	-2.7081

t (min.)	s (mg l^{-1})
0	4.4104
60	2.2291
120	1.4592

TEST D36

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i	$\ln(T/T_i)$
0	3.50	2.27	1.0000	0.0000
6	2.73	1.61	0.7100	-0.3424
12	2.10	1.12	0.4948	-0.7036
18	1.65	0.81	0.3550	-1.0355
24	1.30	0.58	0.2557	-1.3637
30	1.05	0.43	0.1906	-1.6577
36	0.88	0.33	0.1475	-1.9138
42	0.75	0.26	0.1144	-2.1676
48	0.66	0.21	0.0916	-2.3908
54	0.58	0.16	0.0712	-2.6421
60	0.53	0.13	0.0585	-2.8388

TEST D37

t (min.)	Ω (mmho)	T (g l^{-1})	T/T_i	$\ln(T/T_i)$
0	1.80	0.9085	1.0000	0.0000
3	1.62	0.7858	0.8650	-0.1450
6	1.44	0.6682	0.7355	-0.3071
9	1.28	0.5670	0.6241	-0.4714
12	1.13	0.4810	0.5294	-0.6360
15	1.01	0.4090	0.4502	-0.7981
18	0.93	0.3620	0.3984	-0.9202
21	0.85	0.3152	0.3470	-1.0585
24	0.77	0.2737	0.3012	-1.1999
27	0.71	0.2352	0.2589	-1.3513
30	0.66	0.2061	0.2269	-1.4834

APPENDIX 4

COPY OF A PAPER PRESENTED AT THE JOINT I.CHEM.E/BPBIF SYMPOSIUM "WATER AND EFFLUENT TREATMENT AS IT AFFECTS THE PAPER INDUSTRY"

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FOAM FLOTATION DESIGN PARAMETERS

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Synopsis

An investigation into the use of the foam flotation process for wastewater treatment is described, the main aim being to formulate a suitable method for the design and process optimisation of flotation units. The established theories of mineral flotation kinetics were adapted for use in this application, and the theoretical relationships derived were confirmed experimentally using $0.15m^3$ and $0.3m^3$ pilot plants. A suspension of china clay in tapwater was used to represent the wastewater feed to the flotation units and a quarternary ammonium salt was used as a surface-active agent (surfactant). The effects of various operating parameters were examined, including feed rate, plant dimensions, air flow rate and surfactant concentration. The results of the investigation showed that the clay suspension could be rapidly clarified at low surfactant dose rates and that the floated clay particles could be collected as a sludge of high dry solids content.

1. INTRODUCTION

The primary treatment step in the purification of the majority of raw waters and waste liquors is the removal of suspended material, or turbidity. This consists of finely divided solids of geological, industrial or municipal origin; if a high quality finished water is to be obtained then turbidity must be eliminated.

In the wastewater treatment industry the most widely accepted method for removing suspended matter from its surrounding aqueous medium is by sedimentation. For relatively large particle sizes this process is both inexpensive and efficient, but as the size of the suspended particles approaches the colloidal range the simple settlement process becomes so slow as to be impractical as a treatment method. The traditional solution to this problem is to promote agglomeration of the particles by the addition of coagulating agents. This increases the size (and therefore the settling velocity) of the suspended particles to a point where rapid settlement can take place.

An alternative method for the clarification of wastewaters which has gained wide acceptance in recent years is flotation. Wastewater flotation processes have evolved from the methods used in the mineral processing industry for the separation of valuable ores from their associated guange materials (1). In mineral flotation the particles to be separated are first rendered hydrophobic by the action of surface-active agents and then selectively absorbed

on to the surfaces of air bubbles, causing them to float. The resultant concentration of floated particles at the surface of the flotation pool is then removed and a mineral-rich concentrate is obtained. Air bubbles are usually produced by a dispersed-air method, either by vigorous agitation of the pool or by the diffusion of compressed air through a porous frit.

A number of wastewater treatment processes have been developed from the original concepts of mineral flotation (2). The two most commonly adopted methods are foam flotation and foam fractionation. Both methods rely on the action of surface-active agents, or surfactants. In foam flotation the surfactant is absorbed on to the surfaces of particle species, rendering them amenable to removal by air bubbles. The action of the surfactant also causes foaming at the surface of the flotation pool and the floated particles are trapped in this foam and may subsequently be removed. Foam fractionation is a process used for the removal of soluble pollutants which are themselves surface-active. Air bubbles are blown through the pool and the resultant foam is a highly concentrated stream of the surface-active pollutant.

The use of foam flotation for water treatment was first suggested by Hopper (3), who later showed that clay particles and bacterial cells could be removed from river waters using a cationic surfactant of the quaternary ammonium type (4). More extensive studies have been carried out by Grieves et al (5 to 9), who have examined the use of the process for the removal of a variety of suspended impurities.

Foam fractionation was the subject of considerable interest prior to the introduction of biodegradable detergents since it represented a relatively inexpensive method of removing "hard" detergents from sewage effluents (10). Other surface-active soluble pollutants, for example those arising in petrochemical wastes (11), have been concentrated in a similar manner.

In recent years the development of the foam flotation and foam fractionation processes has been overshadowed by the success of the dissolved air flotation process. This system involves a conventional coagulation stage followed by flotation using microscopically small air bubbles. The attachment of air bubbles to particles in dissolved air flotation is due predominantly to a process of mechanical entrapment of the bubbles in the flocculent structure of the suspended particles. Surface adsorption effects are not significant in the operation of this process and surfactants are not usually employed. The main disadvantages of foam flotation are mostly related to the use of surfactants (eg the creation of large volumes of unwanted foam) and are therefore not encountered in dissolved air flotation. This has led to a wider acceptance of dissolved air flotation processes and a corresponding decline in the interest shown in surface-active flotation methods.

The Water Resources Group at Trent Polytechnic have a long-standing interest in foam flotation and have shown it to be a viable process for the removal of a variety of pollutants including precipitates from plating wastes, viruses and river

sediments. It was felt that whilst coagulation followed by dissolved air flotation might have significant advantages in certain cases, there were some treatment situations in which foam flotation might prove to be the superior process. For example, it would be particularly applicable where the particles to be removed could readily be rendered hydrophobic or where the presence of surfactant might itself have beneficial effects (12).

In order to fully assess the potential of the process a method was required for the design and control of the foam flotation process. The investigation described in this paper was initiated in order to develop such a method by an assessment of the effects of the major process parameters.

2. METHOD OF APPROACH

A schematic diagram of a continuously operated foam flotation unit is shown in Figure 1. Influent and surfactant are mixed for a period of time to allow adsorption of surfactant on to the particle surfaces and the development of particle hydrophoby. The treated influent is then passed to the flotation cell where it is aerated with dispersed air bubbles and flotation takes place. Purified effluent flows from the flotation cell and the resultant foam is removed from the surface of the flotation pool.

The parameters affecting the performance of a flotation system are divided for convenience into two broad groups:

a. Characteristics of the Liquid Undergoing Treatment

This group covers the properties of both the material to be removed and its surrounding liquid medium. Factors influencing the former include the physical state of the material (eg the nature of its surface), the methods by which it can be rendered hydrophobic, and its size and concentration. The characteristics of the latter are those which may affect the surface activity of the material to be removed, eg the presence of dissolved substances which may inhibit or promote flotation.

b. Characteristics of the Treatment System

The main characteristics considered to be of importance are listed below:

Adsorption period.
Type and dose of surfactant.
Feed rate of influent.
Flotation cell size and geometry.
Air rate and bubble size.
Method of removal of resultant foam.

Optimisation of the foam flotation process has to be achieved by manipulation of the second group of parameters since control of the first group of parameters is not possible in most practical wastewater treatment situations. Therefore the present investigation concentrated mainly on the effects of variations in the characteristics of the treatment system.

Having established the basic field of study it was necessary to evaluate a theoretical basis for the investigation. A method which has been used by previous workers in the field of wastewater flotation is an analysis based on an empirical model linking the removal of hydrophobic pollutants to the main process variables (12, 13). The main disadvantage of this approach is that the empirical relationships derived can only be used to describe the steady-state condition and are therefore unsuitable for systems which are subject to varying feed conditions. A review of mineral flotation research revealed that a considerable degree of success had been obtained using a method based on the well-established theories of chemical reactor kinetics. It was felt that this approach had potential for the analysis of wastewater flotation since it enabled the effects of the process parameters to be analysed from a more fundamental standpoint.

The use of chemical reactor kinetics to describe the processes occurring in mineral flotation has been reviewed extensively by Arbiter and Harris (14). The main assumption made in this approach is that the kinetics of removal of particles in a batch operated flotation cell are analogous to a first-order chemical reaction and may be represented by the differential equation:

$$\frac{dc}{dt} = -kc \qquad (I)$$

Equation (I) may be integrated between suitable limits to give:

$$\frac{c}{c_i} = e^{-kt} \qquad (II)$$

The value of the rate constant, k, is dependant on the various process parameters. For continuously-operated flotation cells, equation (I) must be combined with a suitable model for the hydraulic regime in the cell. For example, the following equation describes the removal of particles in a single-stage flotation cell where complete mixing prevails:

$$\frac{dc}{dt} = -kc + \frac{v}{V} c_i - \frac{v}{V} c$$

$$= -kc + \frac{c_i}{R} - \frac{c}{R} \qquad (III)$$

Integration of equation (III) between suitable limits gives:

$$\frac{c}{c_i} = \left[1 - \frac{1}{(Rk + 1)} \right] e^{-\left(\frac{Rk+1}{R}\right)t} + \left[\frac{1}{Rk + 1} \right] \qquad (IV)$$

Examination of equation (IV) reveals that as time, t, increases the first term on the RHS of the equation tends to zero. Therefore under steady-state conditions the relative particle concentration in the effluent stream, c/c_i, becomes:

$$\text{as } t \to \infty, \frac{c}{c_i} \to \frac{1}{(Rk+1)} \qquad (V)$$

Provided that the flowrate through the flotation unit (which governs the retention time, R) and the various process parameters (which determine the value of k) do not vary, this value of c/ci will remain constant. A change in either R or k will cause a variation in c/c_i until another steady-state condition is reached.

The theoretical treatment described above provides a useful means of characterising the effects of process parameters on the performance of flotation cells. In particular, the effects of the majority of process parameters may be investigated in simple batch tests. The values found from the tests for the rate constant, k, can then be incorporated into a relationship such as that described in equation (IV) so that the performance of a continuously-operated cell may be predicted.

Previous to the investigation described in this paper the use of the kinetic approach for the analysis of wastewater flotation systems does not appear to have been the subject of extensive research. A preliminary study was therefore mounted on the treatment of river water by foam flotation. This revealed promising indications that the kinetic approach had potential as a method for characterising the process. In view of this success, a more extensive investigation was initiated.

3. EXPERIMENTAL

Experience gained during the preliminary study indicated that precise process control was necessary if the theoretical model described in Section 2 was to be accurately tested. It was considered that this degree of control would not be possible using an influent such as river water, which was subject to variations in quality. A synthetic influent was therefore used which would allow adequate experimental control whilst maintaining the basic characteristics of a naturally occurring influent. The eventual choice of influent was a refined china clay which was available in powder form. This could be mixed with tapwater to produce suspensions of known consistency.

The surfactant used during the experiments was cationic quaternary ammonium salt, cetyltrimethylammonium bromide (CTAB). This was also available in powder form and solutions of accurate concentration could therefore be prepared.

The layout of the experimental apparatus used during batch and continuous tests is shown in Figures 2 and 3.

For batch runs the flotation cell was filled with a clay suspension of the desired initial concentration (c_i) together with

the required surfactant dose. This was then recirculated for a period of time to allow adequate surfactant/particle adsorption to take place. A stream of air bubbles was then injected into the cell via the air diffuser and the particle concentration in the cell sampled at various time intervals. In this way the removal of particles with time could be monitored and the particle removal rate constant (k) determined. The concentration of surfactant in the cell was maintained at a constant level by the injection of surfactant concentrate into the recirculating liquid stream (see next section). The foam produced by the flotation process was extruded through an opening at the top of the flotation cell.

When the flotation cell was required to operate in the continuous mode, influent was pumped to the flotation cell from a stirred reservoir in which surfactant/particle adsorption had already been allowed to take place. Once in the flotation cell the influent was treated with a stream of air bubbles as before and discharged from the base of the cell as effluent. Samples of effluent were analysed for particle concentration to give an assessment of the performance of the flotation cell. The surfactant concentration in the cell was maintained by the injection of surfactant concentrate.

In order to compare the effect of cell dimensions two experimental flotation cells were constructed. The first had a plan area of $0.1m^2$ and its depth could be varied from 0.5m to 1.5m. This resulted in a variable cell capacity from 50 l to 150 l. The second cell had a plan area of $0.6m^2$ and a fixed pool depth of 0.5m, giving a total capacity of 300 l.

Particle removal performance during both batch and continuous flotation was assessed mainly by the measurement of turbidity, although suspended solids and particle size distribution analyses were also carried out intermittently. Surfactant concentrations were measured using a two-phase titration technique.

In addition to the flotation experiments, a number of tests were carried out to determine the mixing characteristics of the flotation cells. A tracer dispersion technique was employed for this purpose using sodium chloride as the tracing material.

4. RESULTS AND DISCUSSION

a. Mixing Experiments

A sample of the results of the tests carried out to determine the mixing regime prevalent in the flotation cells under continuous operation is illustrated in Figure 4. It was found that at all practical air rates complete mixing prevailed in the cells; this was shown by the characteristic negative exponential curve produced by the tracer dispersion technique. Thus the assumption of complete mixing made in the development of equation (IV) was justified.

b. Linked Batch and Continuous Runs

A number of flotation experiments were carried out to compare the particle removal behaviour of cells when operated in the batch and continuous mode. Each pair of linked batch and continuous tests was run under identical conditions of air rate and surfactant concentration.

A typical example of particle removal in a batch operated flotation cell is shown in Figure 5a. The particle concentration in the cell falls from its initial value, c_i, in exponential fashion. This type of removal conforms with the predictions of equation (II), and a value for the removal rate constant, k, can be found from a plot of ln (c/c_i) vs t. For an exponential decrease such a plot will produce a straight line passing through the origin which has a gradiant of -k.

The value for the particle removal rate constant found from a batch test at a particular air rate and surfactant concentration may be inserted in equation (IV) to predict the behaviour of a continuous cell of retention time R operated under indentical conditions. Predicted removal curves calculated from a value of k derived from Figure 5a and various values of R are shown in Figure 5b. The experimental data points found from continuous runs have been superimposed on these predicted curves. There is generally an excellent degree of correlation between experimental and predicted values and a statistical analysis of a total of 16 continuous runs has shown that the predictions made from batch data combined with equation (IV) are correct to a level of 99% significance.

c. Surfactant Removal and Control

Published accounts of foam flotation investigations indicate that the most difficult parameter to control during the course of flotation experiments is the concentration of surfactant in the flotation cell. It was realised at an early stage of the present research that in order to make an accurate comparison between batch and continuous results a method was required for maintaining the surfactant concentration in the flotation cell at a given level. An account of the difficulty of making such a comparison without accurate surfactant control is contained in the work of Grieves and Schwarz (7).

The main problem encountered in surfactant control during foam flotation is that at any time only a fraction of the total mass of surfactant present in the flotation cell is adsorbed on to the particle surfaces. The remainder is present in solution in molecular form and is removed by direct adsorption on to the surfaces of the bubbles passing through the pool. Thus the foam flotation of particles is invariably accompanied by a simultaneous process of foam fractionation of surfactant not adsorbed on to particle surfaces. In this paper unadsorbed surfactant is termed

"free" surfactant and is represented by s.

If the free surfactant concentration in a flotation cell is not adjusted during the course of a run it gradually decreases. Any value for the particle removal rate constant derived under such conditions cannot therefore be linked to a specific value of surfactant concentration.

A possible solution to the problem of surfactant control was suggested by the realisation that the kinetics of free surfactant removal could be analysed by a similar theoretical treatment to that used to describe the removal of particles. Figure 6 illustrates a typical surfactant removal curve during a batch flotation test. During the adsorption period, prior to flotation, the free surfactant concentration in the cell decreases as the surfactant/particle adsorption process takes place. At the end of the adsorption period a free surfactant concentration of s_i is recorded. After the onset of flotation the concentration of free surfactant in the pool decreases as foam fractionation takes place. Above a certain critical concentration s_c this decrease is linear with respect to time, whilst below s_c the decrease is exponential. The removal of free surfactant in a batch flotation cell may therefore be expressed by a combination of zero order and first order kinetics:

$$\frac{ds}{dt} = -m_o \qquad s_i > s > s_c \qquad \text{(VI)}$$

$$\frac{ds}{dt} = -m_1 s \qquad s_c > s \qquad \text{(VII)}$$

m_o and m_1 are respectively the zero order and first order surfactant removal rate constants. The maintenance of a constant free surfactant concentration during a flotation test may be achieved by continually dosing the flotation cell with surfactant concentrate. If the mass of surfactant added to the cell per unit time is S, then for a batch flotation cell of volume V equations (VI) and (VII) are converted to:

$$\frac{ds}{dt} = -m_o + \frac{S}{V} \qquad s_i > s > s_c \qquad \text{(VIII)}$$

$$\frac{ds}{dt} = -m_1 s + \frac{S}{V} \qquad s_c > s \qquad \text{(IX)}$$

If the free surfactant concentration in the cell remains constant at its initial value s_i, then the rate of change in surfactant concentration is zero, ie:

$$\frac{ds}{dt} = 0 \qquad , s = s_i \qquad \text{(X)}$$

Combining equations (VIII), (IX) and (X):

$$S = V m_o \qquad s_i > s_c \qquad \text{(XI)}$$

$$S = V m_1 s_i \qquad s_i < s_c \qquad \text{(XII)}$$

Thus the rate of addition of surfactant concentrate required to be added to retain a steady free surfactant concentration of s_i may be computed from equation (X) or (XI), provided values for the rate constants m_o and m_1 are known.

Equations (VIII) and (XI) may be adapted for use with a continuously operated flotation cell by insertion of an appropriate mixing term. The technique described above therefore enables the surfactant concentration in a flotation cell to be accurately controlled and allows for direct comparison between batch and continuous flotation. The development of this technique was instrumental in the aquisition of accurate data.

d. Batch Experiments

A number of batch experiments were carried out in order to examine the effects of the main process parameters on the operation of the foam flotation and foam fractionation processes. A more sophisticated theoretical model was developed based on an examination of the various sub-processes which combine to produce surfactant and particle removal (15). For the sake of brevity, this model is not included in the present account but the general conslusions drawn are discussed below together with the results of corroborative experimental tests.

(i) The mass of surfactant adsorbed on to the surfaces of particles during the initial adsorption period is directly proportional to the prevailing free surfactant concentration. This is illustrated in Figure 7 using experimental data related to the mass of surfactant adsorbed after a period of 30 minutes. The time dependence of the surfactant/particle adsorption process proved difficult to measure with any accuracy, but it is considered that complete adsorption had probably taken place after a period of approximately 15 minutes. It is therefore likely that the adsorption isotherm illustrated in Figure 7 represents an equilibrium condition.

(ii) The magnitude of the free surfactant removal rate constants, m_o and m_1 is governed by the total bubble surface area available per unit volume of the flotation pool. For a constant bubble size distribution m_o and m_1 are therefore directly proportional to air flow rate, A, and inversely proportional to cell volume, V. Figures 8 and 8b demonstrate this prediction to be accurate for the experimental system used. It is likely that a decrease in bubble size would increase the efficiency of air utilisation since a greater area of bubble surface would be generated per unit volume of air injected into the cell.

(iii) The magnitude of the particle removal rate constant, k, depends on the number of bubbles produced per unit plan area of flotation cell. For a constant bubble size distribution, k is therefore proportional to the ratio of the air flow rate to cell plan area, A/a. This is illustrated in Figure 9 using experimental data from both flotation cells. Once again it should be noted that a decrease in bubble size would effect a more efficient use of air.

(iv) The process of adsorption of free surfactant on to air bubbles is a far more rapid process than particle/bubble collision. The rate constants m_o and m_1 are therefore largely independent of the particle concentration in the flotation cell. This is demonstrated in Figure 10a which shows the values obtained for m_o and m_1 in runs where the initial particle concentration, c_i, varied from zero to 200 mg/l. A significant difference between the magnitudes of m_o and m_1 for different experiments was not observed.

(v) The presence of the surfactant in the flotation pool can seriously inhibit the removal of particles. This is because the rapid adsorption of free surfactant on the surface of a newly formed bubble reduces the number of sites on the bubble which are available for the collection of particles. This inhibiting effect may be expressed by the relationship:

$$k = We^{-Ys} \qquad \text{(XIII)}$$

The factor Y is constant at all values of s and is related to the surfactant removal rate constants. The parameter W is constant above a certain critical free surfactant concentration and represents the hypothetical value of k which would be attained if no free surfactant was present in the flotation cell. However, in practice the absence of free surfactant implies the absence of particle-adsorbed surfactant and a consequent lack of particle hydrophoby. Thus at very low surfactant concentrations particles cannot be removed despite the relatively high availability of bubble collection sites.

The experimentally determined relationship between k and s is illustrated in Figure 10b. It will be seen that equation (XIII) accurately describes the relationship above a free surfactant concentration of approximately 7.5 mg/l. Below this level the effects of reduced particle hydrophoby are significant.

(vi) The effects on the removal of particles of the method of foam removal from the cell could not be predicted by the theoretical model developed. Experimental observation indicated that effluent quality was not affected by changes in foam removal parameters (eg the height to which the foam layer was allowed to develop before removal). However, one significant phenomenon was observed. At low values of free surfactant concentration the rate of foam production appeared to equal the rate of foam collapse. This resulted in the growth of a layer of floated particles on the upper surface of the foam, and particles could be removed at dry solids concentrations of over 60%. This effect, combined with the obvious economic considerations and the fact that a maximum value of k is achieved at low values of s suggests strongly that the prevailing surfactant concentration in flotation cells should be kept as low as the limits of particle hydrophoby development permit.

5. CONCLUSIONS

It has been shown that the operation of wastewater foam flotation units can be aided by rational process control based on kinetic models similar to those used in mineral flotation. The application of these models enables many of the traditional disadvantages of foam flotation to be minimised and it is possible that the process may become more attractive as a method of clarification. For example, the removal and recovery of china clay from wastewater streams is significant to effluent treatment in the paper industry since considerable quantities of such materials are used as fillers in the paper-making process. However, the work described in this paper is of a fundamentally theoretical nature and the applicability of the process to specific effluent treatment problems will await further investigation.

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NOMENCLATURE

c	Particle concentration in the flotation cell
c_i	Initial particle concentration in the flotation cell
t	Time from start of the flotation process
k	Particle removal first order rate constant
V	Volume of flotation cell
v	Liquid flowrate through flotation cell
R	Retention time of flotation cell = V/v
s	Free surfactant concentration in the flotation cell
s_i	Initial free surfactant concentration in the flotation cell
s_c	Critical free surfactant concentration
m_o	Surfactant removal zero order rate constant
m_1	Surfactant removal first order rate constant
S	Rate of addition of surfactant concentrate mass
W) Y)	Constants: See equation (XIII)

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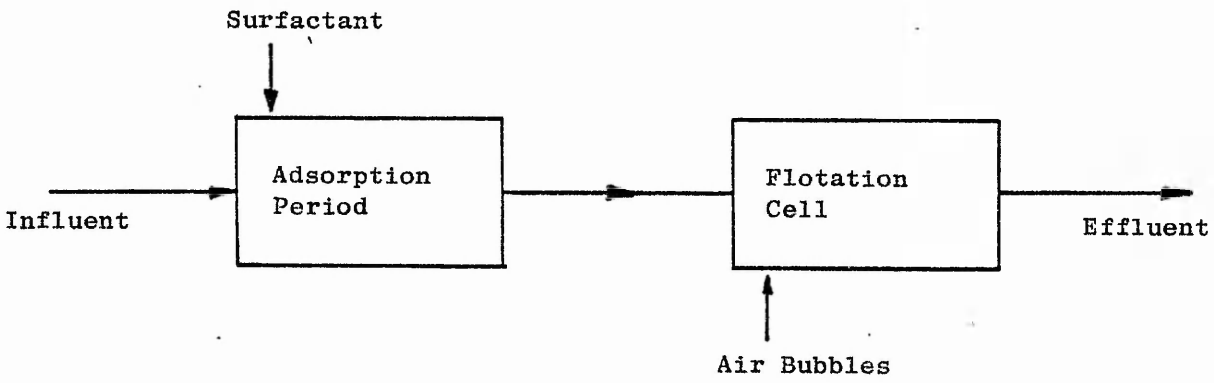
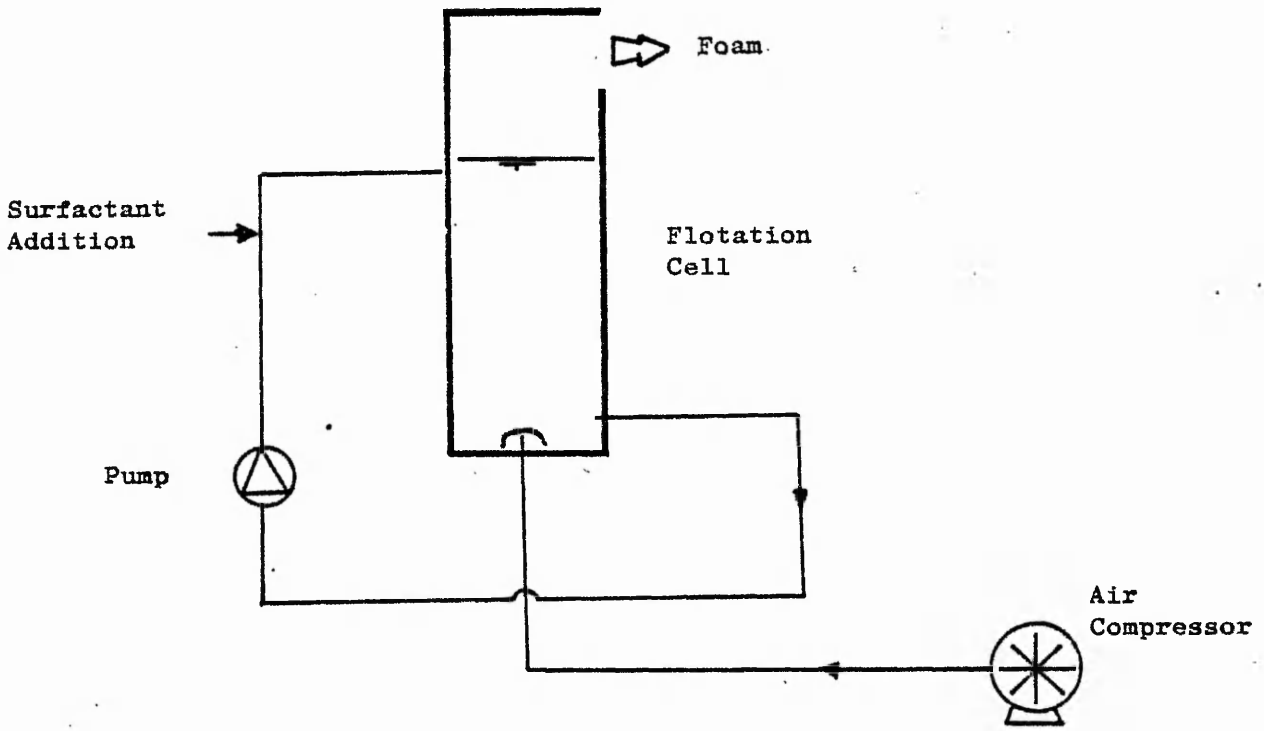


FIGURE 1: Schematic Diagram of a Continuously Operated Foam Flotation Unit



IGURE 2: Experimental Layout for Batch Flotation Tests

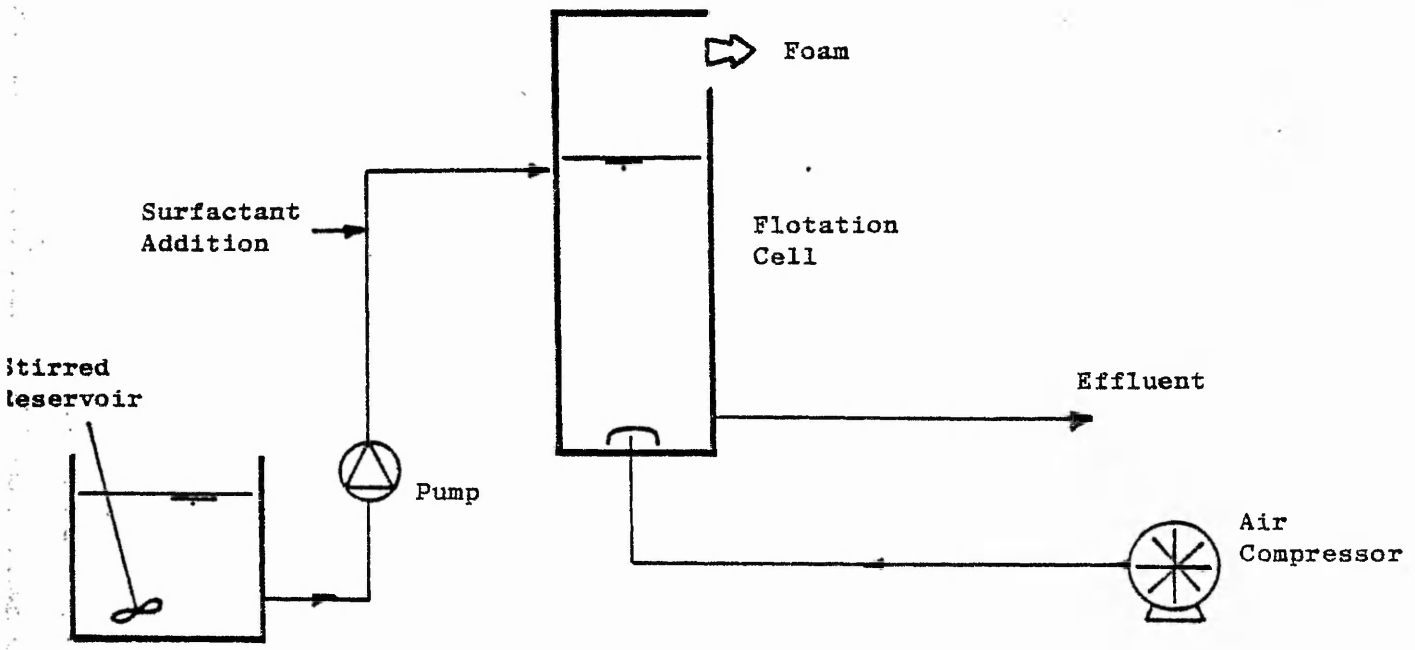


FIGURE 3: Experimental Layout for Continuous Flotation Tests

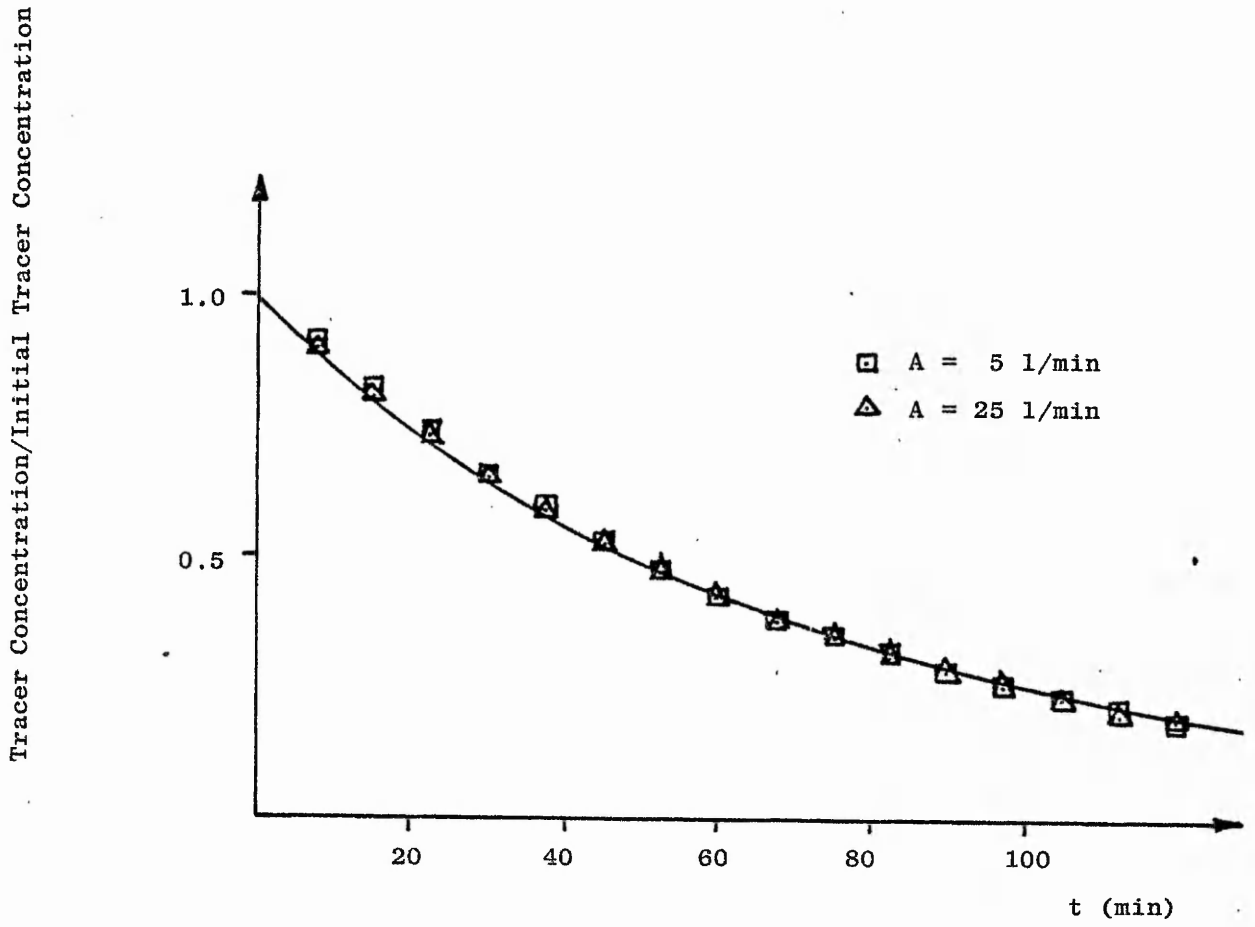


FIGURE 4: Mixing Tests

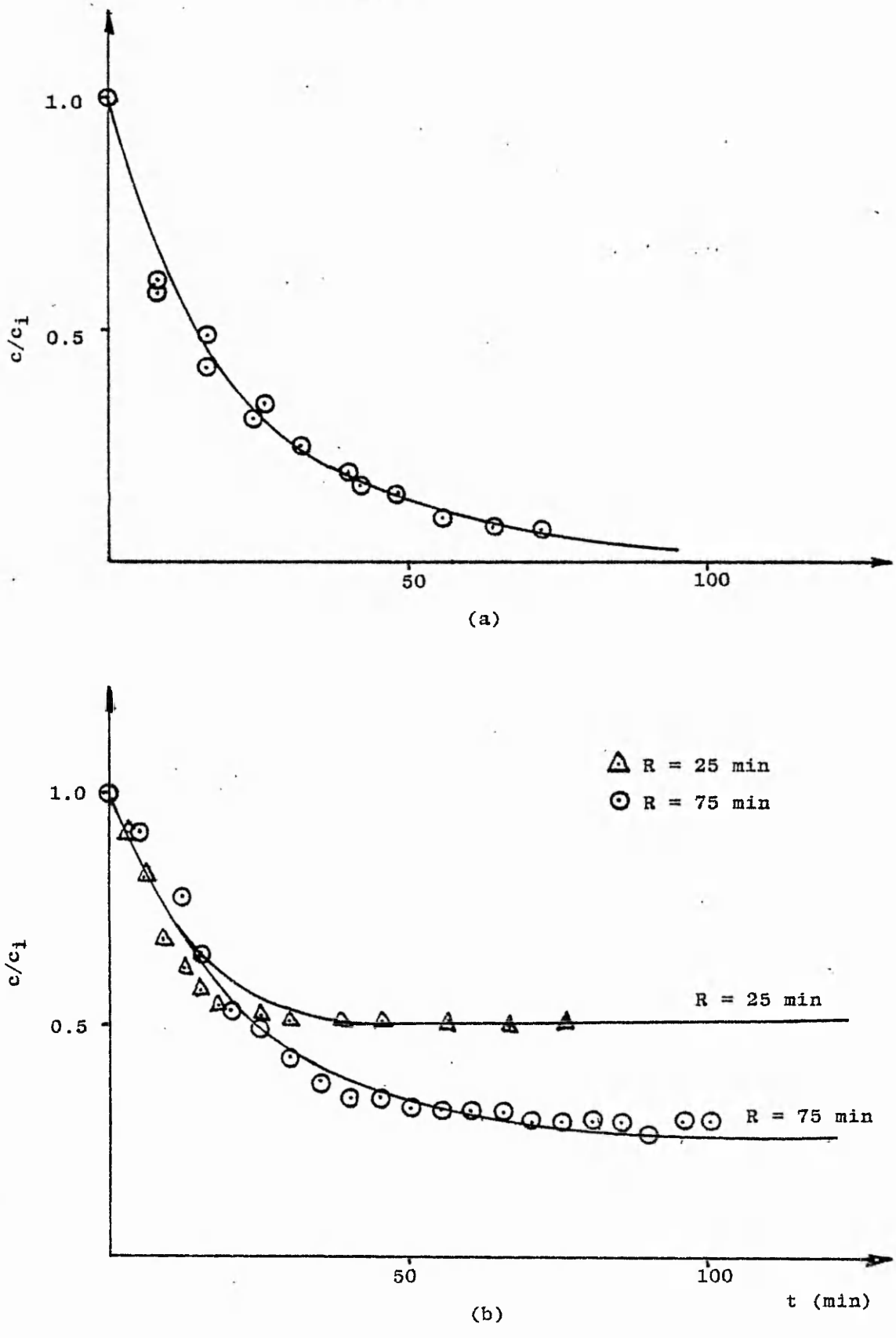


FIGURE 5: Typical Results from Batch and Continuous Flotation Tests

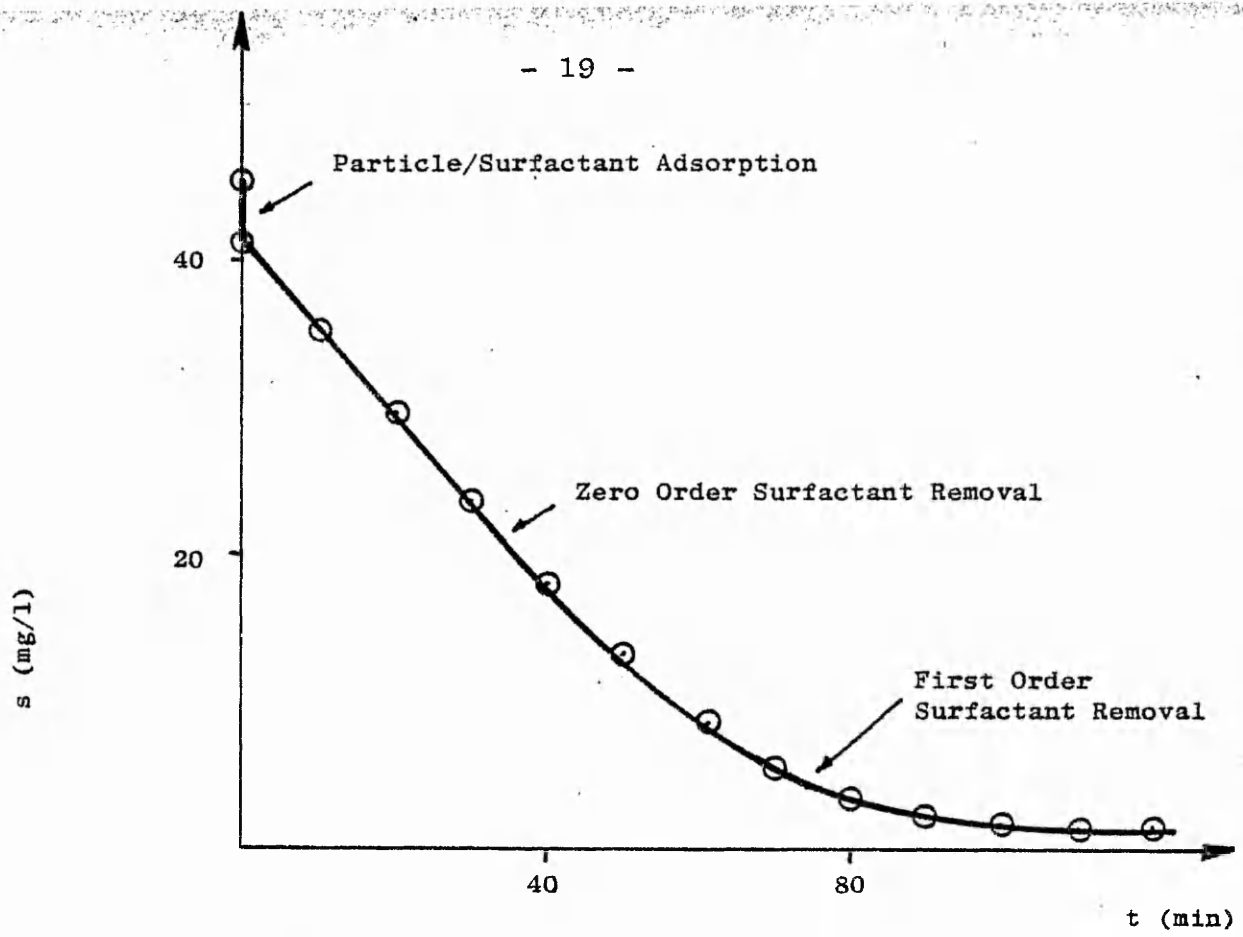


FIGURE 6: Typical Surfactant Removal during Batch Flotation

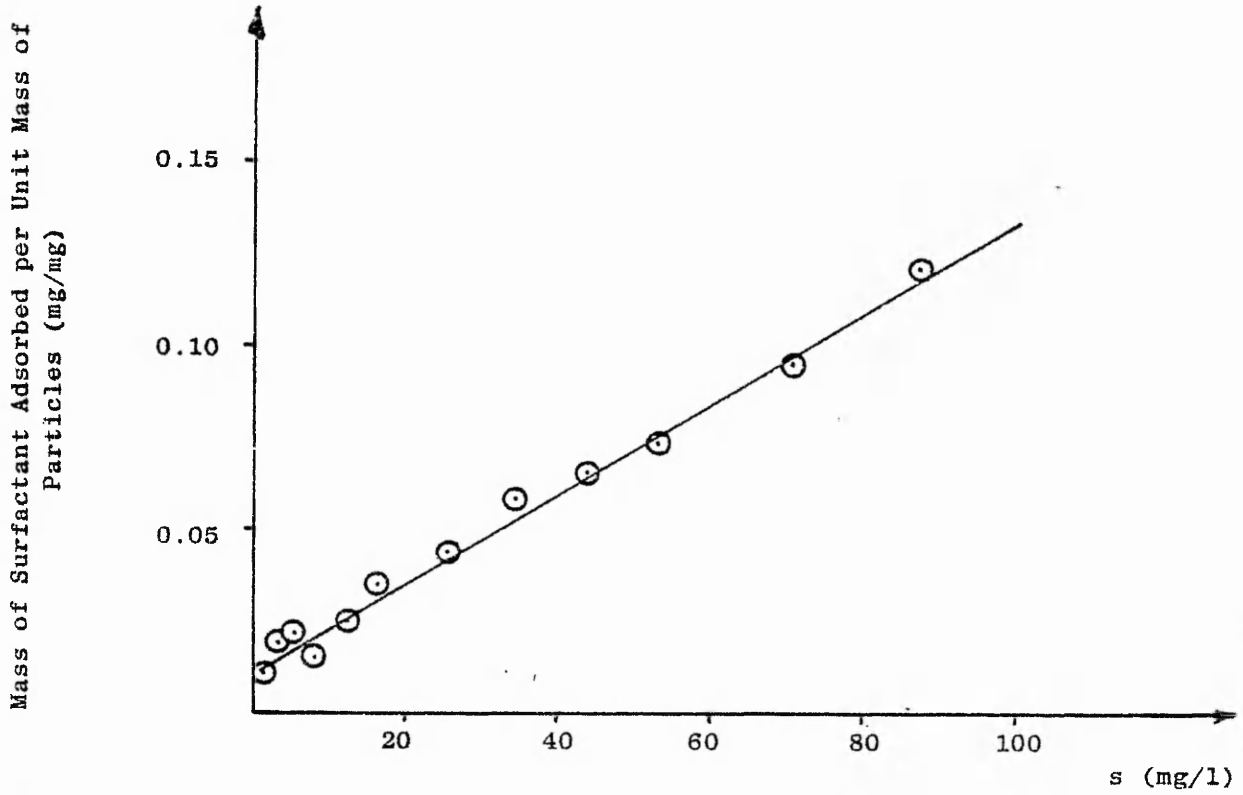


FIGURE 7: Adsorption Isotherm for Surfactant on Particles

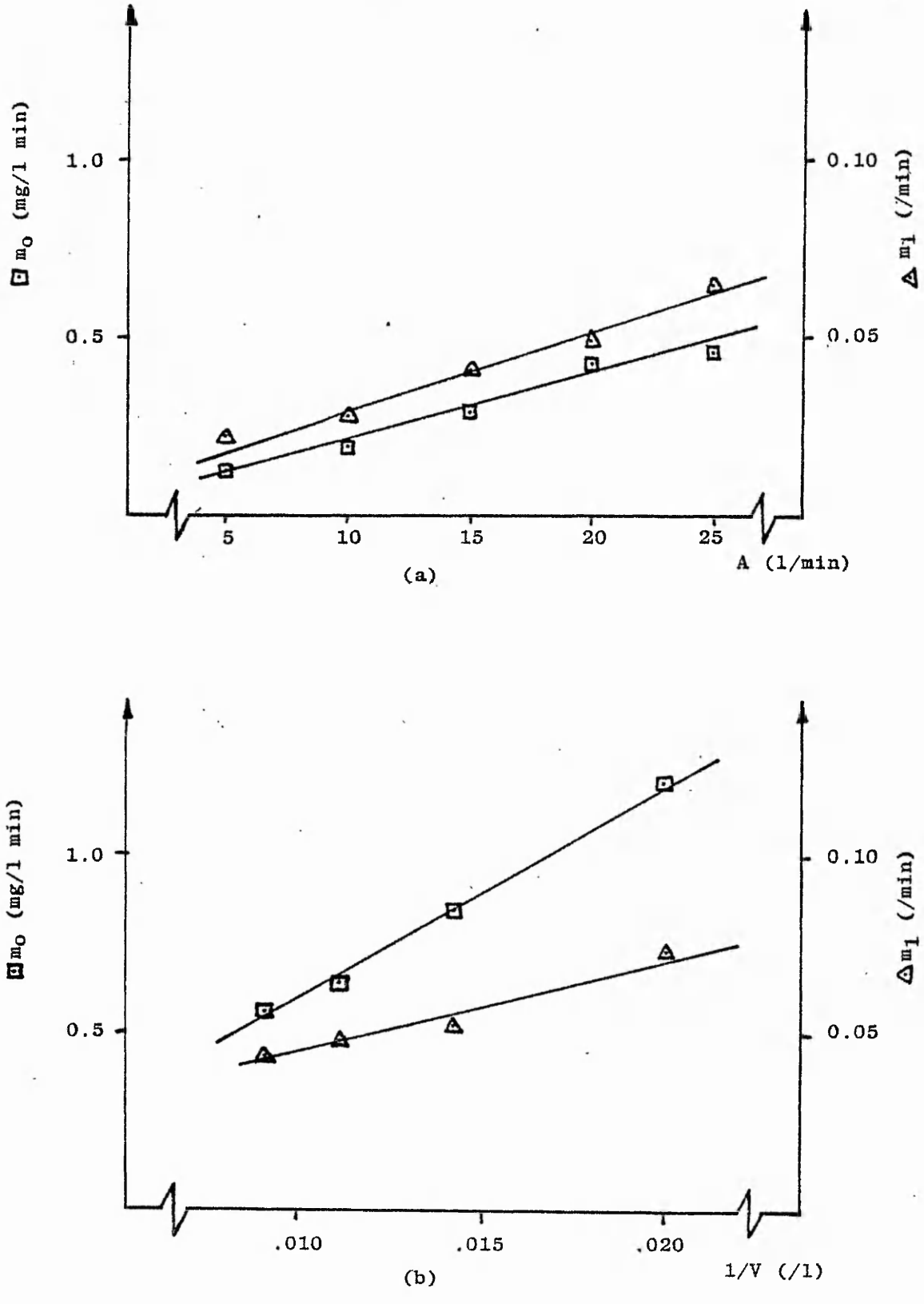


FIGURE 8: Dependence of Surfactant Removal Rate Constants on Process Parameters

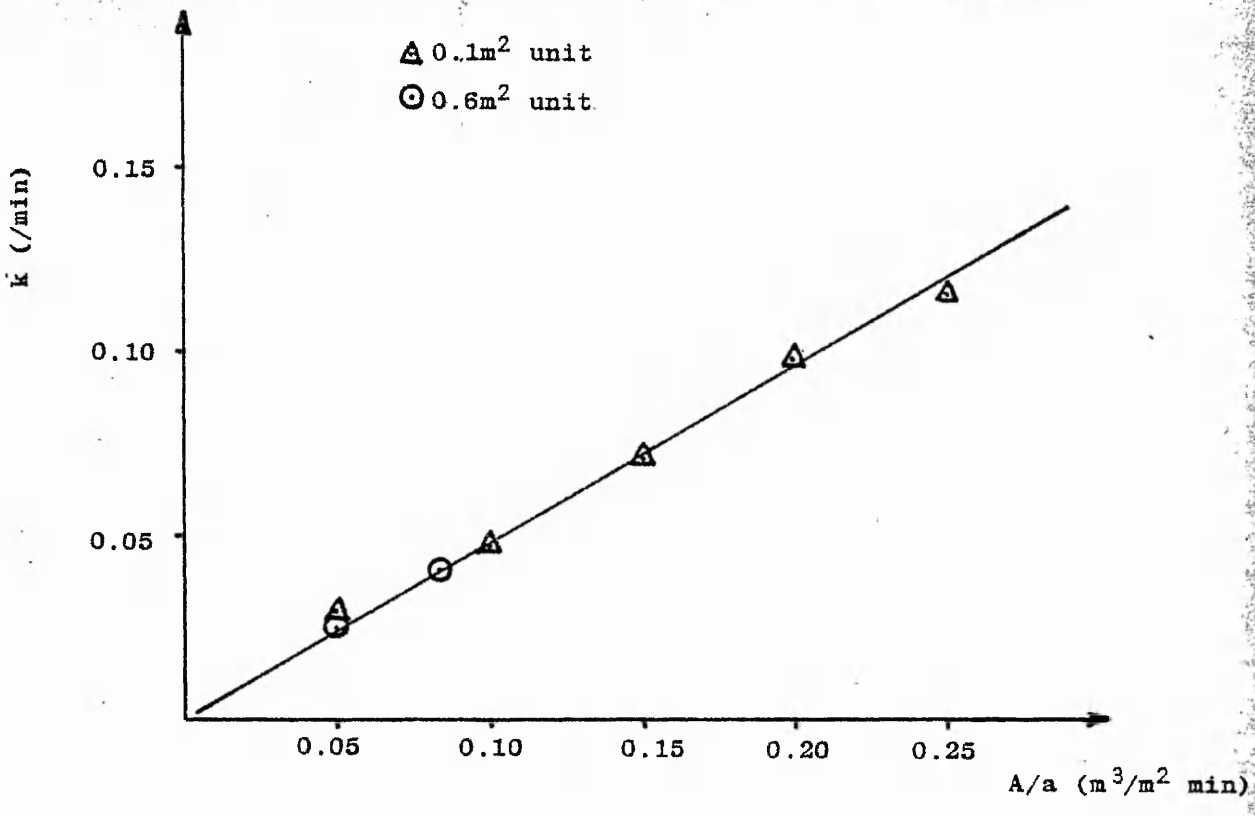


FIGURE 9: Dependence of Particle Removal Rate Constant on Process Parameters

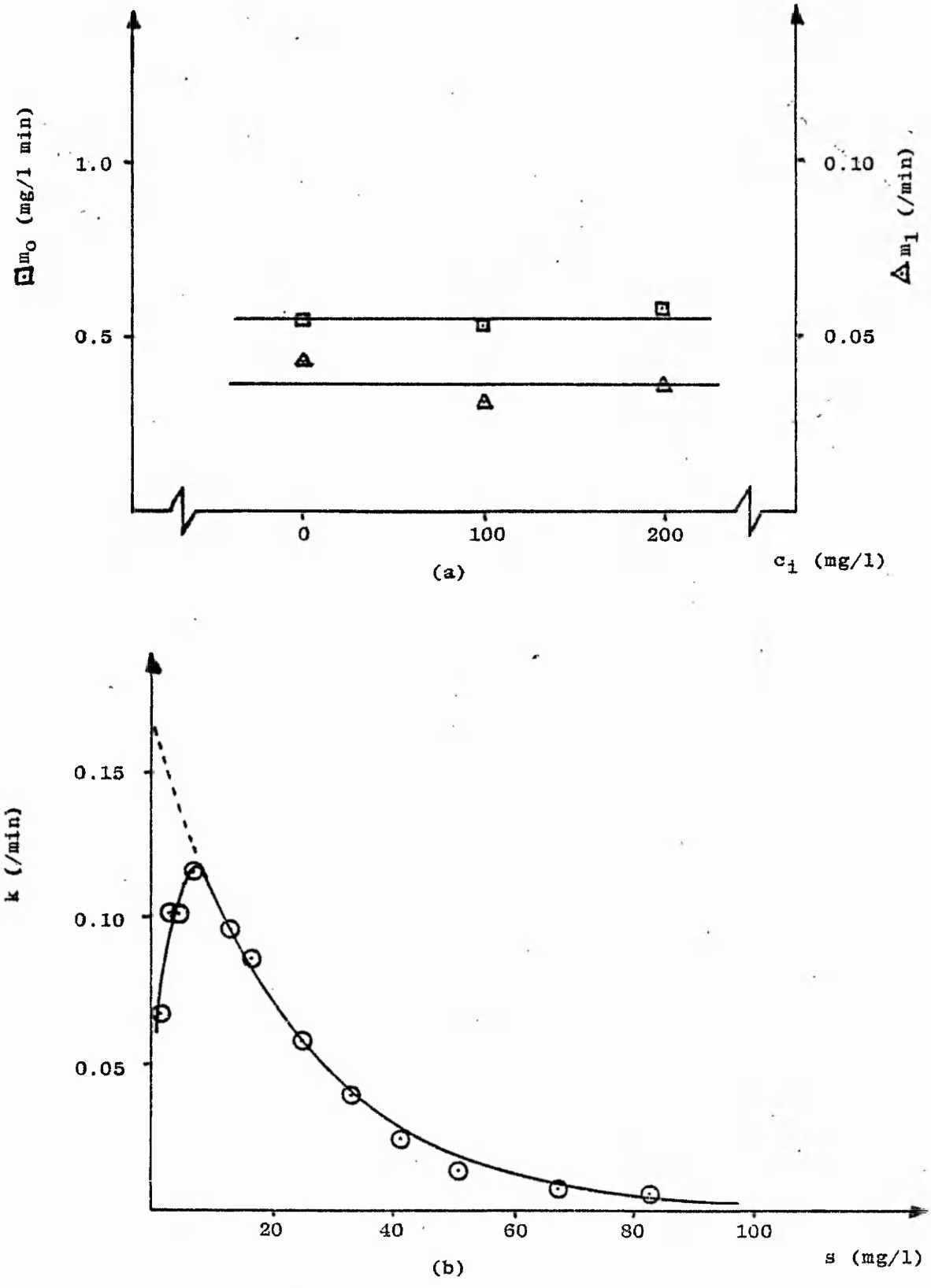


FIGURE 10: Interdependence of Surfactant and Particle Removal Rate Constants