RESIDENCE TIME METHODS FOR MODELLING AND ASSESSING THE PERFORMANCE OF WATER TREATMENT PROCESSES

Jacqueline Lisa Barnett

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SUMMARY

The objective of this study was to provide a technique, based on the residence time distribution of a process, for modelling, assessing and improving flow in the processes of water and waste water treatment works. The technique should be accessible to the staff managing and operating the works.

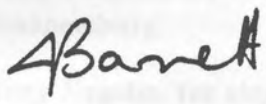
From a review of the literature, a preference was given for the experimental method used for determination of the tracer response, including choice of tracer and tracer addition and monitoring. Data analysis techniques were reviewed, and the method of time domain fitting was developed into a computer program, IMPULSE. IMPULSE provided a tool for analysis of residence time data, and removed the constraint of numerical complexity. Using the building blocks of IMPULSE, a realistic flow model can be constructed from tracer data and evaluated. IMPULSE allows a quantitative comparison of models proposed for a process, and provides the parameters of the models. These parameters quantify the non-idealities in a process. A knowledge of the non-idealities provides a basis for decision-making when modifying a process.

The results of tracer experiments performed on some water and waste water treatment processes were analysed using IMPULSE. The results showed that collection of good experimental data was critical to the success of the analysis.

It is proposed that a guide be produced which draws out the main points raised in the study, including collection of tracer data and use of IMPULSE. The guide should be accessible and easily understandable to the staff managing and operating water and waste water treatment works.

DECLARATION

I hereby declare that this thesis is my own work, unless stated to the contrary in the text, and that it has not been submitted for a degree to any other University or Institution.



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NOMENCLATURE

A	area under a response
a_n	a Fourier coefficient
b_n	a Fourier coefficient
$C(t)$	concentration-time response
C_i	concentration of stream i
D	axial dispersion coefficient
E	anaerobic process efficiency
$f(t)$	any traceable property
I	integer number of stirred tanks of equal volume
k	reaction constant
k_p	first order rate decay constant
L	length of process
N	integer number of stirred tanks of equal volume
n	the number of a moment
M	amount of tracer added
m	flow of tracer added in units/time
p	fractional bypass
Pe	axial Peclet number
q	volumetric flow
r	reaction rate / specific rate of particle solubilisation
S	biodegradable substrate concentration / COD
S_0	influent COD
SSE	sum of squared errors between experimental and model data
T	half the time duration of one experiment
t	time
$\bar{t}$	mean residence time
$\bar{u}$	average fluid velocity
V	the volume of the process
V_i	volume of zone i
V_{mi}	volume of active mixing zone i
V_p	volume of plug flow
x'	dimensionless axial coordinate
z	axial coordinate or axial displacement

β	a fractional number of stirred tanks
τ	dimensionless residence time / delay of ideal plug flow vessel
Θ	elapsed time
θ_i	mean residence time of active mixing zone i

CHAPTER

ONE

Introduction

1.1 Background

Water is essential to life, to social development and to economic progress.
(Department of Water Affairs, 1986)

1.1.1 Provision of water

The provision of an adequate quantity of water of adequate quality is one of the keys to development and progress in any country (Schalekamp, 1990). In South Africa, the national water management strategy is aimed at this provision (Department of Water Affairs and Forestry, 1991). In addition, provision of sanitation is seen as crucial to improving quality of life, and the provision of water without proper sanitation may cause more disease due to an increase in waste water (Wurzel, 1993). In South Africa, it is estimated that 10 million people (25 % of the population) lack access to a safe water supply, and 19 million people (50 %) lack access to adequate sanitation (Palmer Development Group, 1993). There are, however, constraints on the provision of water and sanitation in South Africa. South Africa is a water-deficient country and water sources are increasingly limited. Water is of deteriorating quality as sources become more polluted, and the need to maintain water quality is as important as developing water sources. Thus the use of waste water as a source of water will become more important (Department of Water Affairs, 1986). The Water Research Commission (WRC) is focussing research in waste water treatment on the production of adequate quality effluents for direct or indirect reuse (WRC, 1991).

Therefore, in order to provide water to unserved communities and to meet the needs of a growing population, greater volumes of adequate water are needed, from sources of lower quality. The provision of sanitation, which must occur with the provision of water, means that there will be a greater volume of waste water to treat.

Although treatment of more water and waste water, and treatment of lower quality water, is technologically possible it is costly, as more sophisticated treatment works will be required, and existing works will have to be extended and upgraded. Non-conventional treatment processes are being researched (WRC, 1992), but conventional treatment processes will still predominate. The capital used to build and extend treatment works is the major portion of the cost of providing water : 46,7 % of the *total water supply account* for Umgeni Water in 1991 (Umgeni Water, 1992). The majority of the people for whom adequate water and sanitation is not presently available are limited in their ability to pay for these services.

One approach to reducing the price of services is to delay building or extending treatment works by improving the performance of unit processes. Increasing the capacity and efficiency of a works without major capital expenditure will significantly reduce the cost of treatment. Although purification costs will increase as more treatment chemicals will be needed, this cost is insignificant compared to the capital charges : for Umgeni Water in 1991, this cost was only 3,25 % of the *total water supply account* (Umgeni Water, 1992).

1.1.2 Improving performance

One way to improve the performance of treatment works is to improve the flow through the processes of the works. If the flow through a process is poor, for example, it does not use the entire volume of the process, or it bypasses part of the process, then the performance will be impaired. The flow must therefore be understood and assessed. For this, it is necessary to model the process flow. A model of flow patterns, or a flow model, will allow possible improvements for more efficient operation and process intensification to be postulated. The effect of improvements may also be predicted. A basis for decision-making in terms of the time, effort and cost of making the improvements, is thus provided. A flow model can, in addition, be used as a diagnostic tool in process failure, as condition changes will be indicated by flow pattern changes. The length of time necessary to reach steady state after a change in conditions, such as inlet

conditions, can be determined. Or, for example, if a pollutant enters a process, the flow patterns will show the quantitative distribution of the pollutant through the process.

Small-scale processes which will operate similarly to a full-size process can be constructed from a flow model. Trials, carried out when planning extensions to processes or modifications on processes, can be performed on a small-scale. In water treatment processes, typical changes investigated are : different blends of raw water ; different flocculants and coagulants ; the effect of pre-ozonation or chlorine dioxide addition ; and the need for and efficiency of granular or powdered activated carbon processes. Trials conducted on a full-size process are usually undertaken sequentially and the water quality must therefore be assumed constant. The advantages of having a small-scale process would be ease of testing, reduced cost where chemicals are needed, as well as being able to undertake side-by-side trials.

To improve reacting processes, a classical chemical engineering approach is to combine a flow model of the process with a kinetic model of the process. Two types of information are necessary to predict the performance of reacting processes : flow patterns and kinetics (Himmelblau and Bischoff, 1968). Flow patterns in reacting processes determine the heat and mass transfer, affecting the process kinetics.

1.1.3 Use by plant staff

Flow modelling of a process and analysis of a process from a flow model needs to be accessible to the staff managing and operating water and waste water treatment works. Staff should be able to use the results to improve the performance of the works. Staff training has been recognised as crucial by the Water Institute of South Africa and the Department of Water Affairs and Forestry (WRC, 1992). This training should include flow modelling of the works.

1.1.4 Residence time distribution method

A technique for determining the flow model of processes is the residence time distribution method. Danckwerts (1953) developed the residence time distribution concept to characterise the overall flow behaviour in a process. The effluent stream from a continuous flow process is a mixture of fluid elements that have resided in the process for different lengths of time ; the distribution of these residence times is an indicator of flow patterns within a process.

1.2 Objective

The objective of this study is to provide an accessible technique, based on the residence time distribution of a process, for modelling, assessing and improving flow in water and waste water treatment works, by the staff managing and operating the works. This study aimed to critically evaluate the technique developed.

1.3 Approach

The general approach of this study was to review existing modelling techniques that use residence time distribution methods, and develop an accessible technique for modelling and assessing water and waste water treatment processes. The technique developed was then evaluated using experimental data from treatment processes.

Chapter 2, *Residence time distribution techniques*, is a review of the literature and associated theory. Methods of obtaining experimental data are contrasted, with an emphasis on tracing water treatment and waste water treatment processes. Residence time methods for analysis of experimental data are discussed and a rationale for the decision to use and develop a particular technique of data analysis is developed. This technique is used to determine the flow model of a conceived process. The flow model can then be combined with a kinetic model.

In Chapter 3, *Using IMPULSE for flow modelling*, a computer program, IMPULSE, written specifically for this study is detailed. The relationship between IMPULSE and the flow modelling approach outlined in Chapter 2 is shown. The main program features and limitations are given.

Chapter 4, *Applications of IMPULSE*, details investigations into its applications in water and waste water treatment works. IMPULSE is applied to residence time data from an anaerobic digester, a biofilter and a flash mixer. For all experiments, the experimental method for residence time data collection is given. The results are presented and discussed. For the anaerobic digester experiment, reaction kinetics are combined with the flow model to predict digester performance.

Chapter 5, *Discussion*, is a discussion of the technique used in the experiments of Chapter 4. The significance and usefulness of IMPULSE is discussed.

Finally, in Chapter 6, *Conclusion and recommendations*, the significance of this study is summarised, and suggestions for further work are made.

CHAPTER

TWO

Residence time distribution techniques

2.1 Introduction

Danckwerts (1953) introduced the residence time distribution method to enable a quantitative description of the effect of flow patterns on kinetic processes in a reacting process.

Previously, it was usual to assume either perfect mixing or plug flow (Figure 2.1).

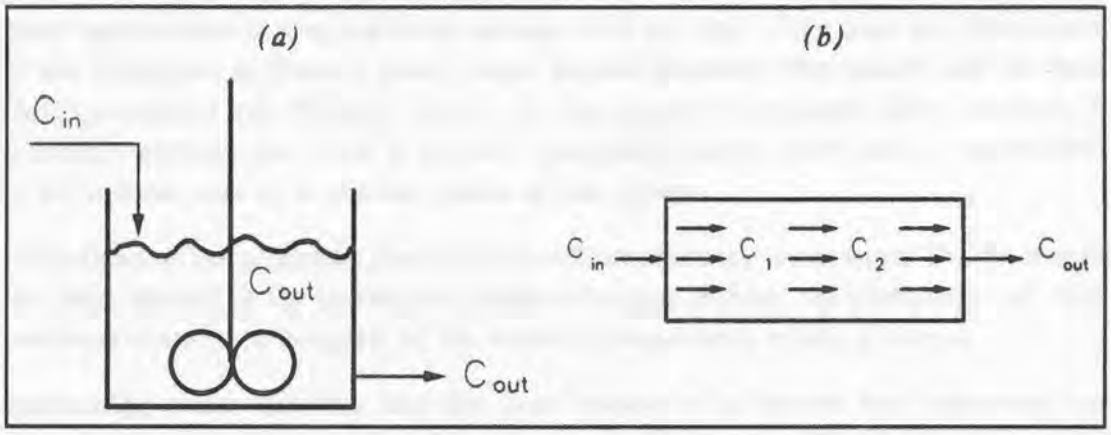


Figure 2.1 : *Description of ideal processes : (a) perfect mixing ; (b) plug flow*

Perfect mixing supposes the fluid in the process to be completely mixed, so that the properties of the fluid and effluent stream are uniform; plug flow supposes no mixing in the direction of flow, so that elements of fluid entering the process at the same moment move through it on parallel paths, and leave at the same moment. The flow patterns found in real processes usually lie between these two extremes (Smith, 1981), due to bypassing, channelling, dead space, dispersion and recycling (Figure 2.2).

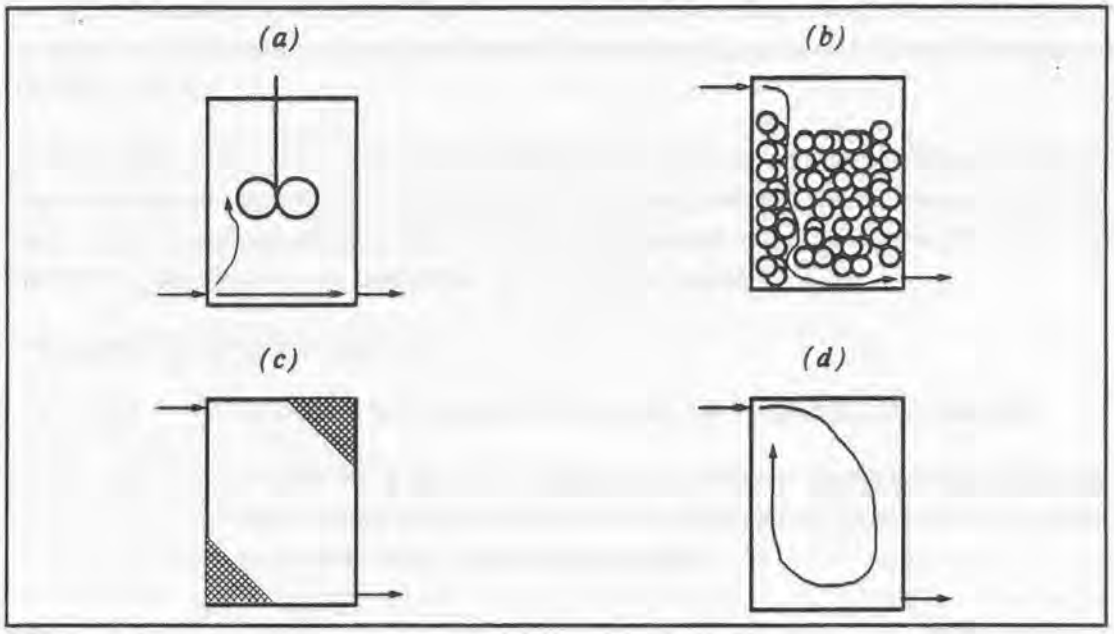


Figure 2.2 : *Deviations from ideal processes : (a) bypassing ; (b) channelling ; (c) dead space ; (d) recycling*

In bypassing some elements of fluid bypass the entire process, whereas in channelling some elements of fluid move through the process significantly faster than others do. Dead space refers to a region in the process with no flow. This does not often occur in real processes, as there is usually some contact between "dead space" and the bulk fluid (Levenspiel and Bischoff, 1963). As this contact is extremely slow, however, it is usually assumed that there is no flow. Recycling occurs when fluid is recirculated to the process inlet or to another region of the process.

In continuous flow processes, therefore, the effluent stream is a mixture of fluid elements that have resided in the process for different lengths of time; the distribution of these residence times is an indicator of the overall flow patterns within a process.

Introducing tracer particles into the inlet stream of a process and measuring the concentration-time relationship of the tracer particles in the effluent stream provides an indication of the distribution of residence times of the tracer particles. If the tracer particles have the same flow attributes as the fluid, their residence time distribution can be said to approximate the residence time distribution of the fluid (Naumann and Buffham, 1983). A flow model of the process can be determined using the tracer residence time distribution response, and the overall flow pattern of the process can be established from the flow model. In this study it was assumed that "flow model" referred to a model of the overall flow patterns determined from the residence time distribution,

and not to a model of the actual flow vectors in a process. In general, tracer tests cannot be used for determining the residence time distribution of processes with open boundaries (Gibilaro, 1978).

In this chapter, common experimental techniques used to determine the tracer residence time distribution response are contrasted, and a general experimental approach is outlined. Data analysis methods are discussed. A conceived process is modelled and the conceived kinetics of the process are combined with the flow model.

The objectives of this chapter are:

(i) to review the literature and theory on residence time methods.

(ii) to provide a basis for choosing a particular experimental technique when performing residence time distribution experiments on water and waste water treatment processes.

2.2 Experimental approach

The first step in the residence time analysis of a process is to obtain experimental residence time distribution responses. A tracer is introduced into the influent stream of the process and the time dependence of the tracer is measured in the effluent stream. An experimental residence time distribution response, $f(t)$, is determined from the measurement.

The selection of a tracer is discussed in this section and methods of tracer input and monitoring outlined.

2.2.1 Selection of a tracer

A tracer requires certain characteristics to make it suitable for the determination of the experimental tracer output response. Three classes of materials have characteristics which are applicable for tracing processes : radiotracers, dyes and electrolytes. At least one material in each class is suitable for tracing water treatment processes.

Tracer characteristics

A tracer is used to label substances or objects in order to distinguish them, to follow their movement, changes of concentration and distribution between phases. The tracer should allow sensitive detection and should not significantly change the properties of the fluid being traced (Foldiák, 1986).

For residence time tests on continuous flow processes, the major consideration is that the tracer flows with a residence time distribution identical to that of the fluid of interest. Thus it should have approximately the same density and viscosity as the fluid of interest (Himmelblau and Bischoff, 1968). Naumann and Buffham (1983) state that a perfect tracer for residence time determination has exactly the same flow properties as the substance or particles it represents, but is sufficiently different in some non-flow attribute that can be detected analytically. Robinson and Tester (1984) comment that the tracer must not chemically react or absorb on the medium through which it is flowing. It should not be toxic to the process (Agg et al., 1961).

Classes of tracers

Three classes of tracers are commonly used : radiotracers, dyes and electrolytes. No references were found that compared different classes of tracers, although the advantages and disadvantages of a class of tracers are discussed. For example, Foldiák (1986) discusses radiotracers, and Smart and Laidlaw (1977) discuss dyes. Many workers determining experimental residence time distribution responses do not indicate a reason for their choice of tracer.

Radiotracers are radioactive isotopes used to label the substance being studied (Foldiák, 1986). Advantages of radiotracers include : quantitative determination with high sensitivity in low concentrations (Bergman, 1958); detection through the wall of a vessel (White, 1974), the possibility of on-line monitoring (Morel du Boil, 1980); and, if isotopes of the fluid being traced are used as radiotracers, the properties of fluid and tracer are perfectly matched (Naumann and Buffham, 1983). Disadvantages of radiotracers include the danger of using radioactive materials, with special personal qualifications required for work with radioactive isotopes; and the need for specialised detection and analysis equipment, not normally found in a laboratory or on a plant.

Dyes are generally used as visible indicators of flow patterns for clear fluids and open processes. Wang et al. (1993) used a dye to colour trace solid particles. For quantitative measurement the concentration of a dye may be determined colorimetrically or spectrophotometrically. An advantage of using dyes is that visual observations can enhance an understanding of the flow patterns. However, techniques for measuring concentrations are not always specific or sensitive. A further disadvantage is that certain processes cannot be coloured, such as those in the food industry. Smart and Laidlaw (1977) evaluated fluorescent dyes for

water tracing, investigating sensitivity and minimum detectability, toxicity and effect of water chemistry. They recommend specific dyes depending on the process traced.

Electrolytes are recommended by Naumann and Buffham (1983) for tracing aqueous processes. Conductivity may be used for measuring tracer concentration in processes where the conductivity of the process is not high or variable. Concentrations of the ions may also be measured, using flame photometry or atomic absorption spectrophotometry for metallic ions, or potentiometric methods for anions. Advantages of electrolytes are that they can be detected in small amounts (often to mg/l), and they are usually relatively inexpensive. Many are non-toxic and easy to handle. A disadvantage of electrolyte tracers is that they may react with ions in the bulk fluid or be absorbed by surfaces.

Tracers selected for water treatment processes

Water and waste water treatment processes are aqueous flow processes in which dissolved or suspended solids are removed. In this application, tracers must not adsorb onto, or react with, the solids, and the tracer must have the same flow patterns as the solution. Further, the tracer should not be a pollutant or contaminant in the process.

Radiotracers, specifically water soluble salts of the solution isotopes, are recommended by Foldiák (1986) for tracing water and aqueous solutions. Many studies (Bergman, 1961; Nixon and Belcher, 1985; White, 1974) have used radiotracers for water treatment processes. These tracers include tritiated water, sodium-24 (as sodium), bromine-82 (as a bromide ion), and gold-98 (as a complex cation with ammonia).

Tritiated water has flow patterns identical to that of water. No specialised handling equipment is required for tritiated water as the radiation emitted cannot penetrate glass. Disadvantages are that it cannot be monitored on-line (White, 1974), it has a long half-life (12,3 y), so the amount used to trace must not contaminate the process, and it has a low (25 to 60 %) efficiency of detection (Kirk-Othmer, 1982). Sodium-24 has been used in water studies as a radiotracer. As the half-life is 15 h, no lasting contamination is possible. However, it requires specialised handling equipment as it is dangerous to handle (Smith, personal communication, 1991). Similarly, bromine-82 and gold-98 require specialised handling and detection equipment. Additionally, the use of any radiotracer requires permission from a controlling board.

Dyes are useful for visual interpretation of the flow patterns in open water treatment and waste water treatment processes. Fluorescein, a readily-available fluorescent dye, is recommended by Smart and Laidlaw (1977) for water studies. Fluorescein has been approved for external human use in the United States, and is detectable at 0,29 μg/l. The U.S. Geological Survey (in Smart and Laidlaw, 1977) recommend, however, where the water is to be used for human consumption, that the final concentration for all dyes used in tracer tests be below 10 μg/l. Where the water from any water or waste water treatment process being traced passes through the process into a reservoir or impoundment, the tracer will generally be diluted to below 10 μg/l. The concentration of the dye can be measured using a spectrophotometer.

The most common electrolytes used for tracing water processes are lithium chloride and sodium chloride (Agg et al., 1961; Naumann and Clark, 1991). Both tracers have been used with success in the sugar industry to trace aqueous flow processes (Rouillard and Smith, 1981). The lithium and the sodium were detected, respectively. Sodium fluoride has been used as a tracer in waste water treatment processes (Vissers and Williams, 1984), where the anion was detected. Recommended concentrations in drinking water for these determinands are 100 mg/l for sodium, 2,5 mg/l for lithium, 250 mg/l for chloride and 1 mg/l for fluoride (Pieterse, 1989).

Sodium chloride is inexpensive and non-hazardous. Sodium is generally present in higher concentrations in water treatment processes than lithium and is less easily detectable. The background level is often variable. Thus the concentrations of sodium chloride used are higher. Sodium chloride cannot, therefore, be used if the concentration in the effluent stream will exceed recommended limits, such as for drinking water. The concentration of sodium can be determined by atomic absorption spectrophotometry or by conductivity determinations using a conductivity probe. Tests should be done prior to the tracer test to determine the amount of adsorption onto the solids present in the process.

Lithium chloride is relatively inexpensive and lithium is detectable in μg/l concentrations by flame photometric methods (Agg et al., 1961). It is used where it is difficult to add large quantities of tracer to the process, and where the concentration of ions in the effluent stream must be minimised. Lithium is stable in solutions and is not lost by deposition (Agg et al., 1961).

2.2.2 *Tracer input and monitoring*

A tracer is introduced into the process and its traceable property measured in the effluent stream, giving an experimental tracer output response, $f(t)$. The introduction may be as a random signal, as a cyclic signal, a step or jump, as a pulse or as any arbitrary signal (Levenspiel and Bischoff, 1963). Kramers and Alberda (1953) apply sinusoidally varying concentrations to determine residence time distributions. The most common tracer signals, however, are pulse inputs, or changes in the form of step functions (Himmelblau and Bischoff, 1968). Under ideal experimental conditions, the normalised tracer response is identical to the residence time distribution. Physical addition and measurement of the tracer are discussed in this section, and the pulse test and step test are detailed.

Physical addition and measurement of the tracer

The experimental tracer output response may be influenced by the method of tracer addition and measurement, particularly when the fluid velocity is not uniform across the cross-section of the tracer injection point (Levenspiel and Turner, 1970; Levenspiel et al., 1970). Different methods of addition and measurement of the tracer will give different tracer responses. These responses can be related to the true residence time distribution, but are not identical to it.

Levenspiel and Turner (1970) give the method of addition and measurement for determination of the true experimental residence time distribution. Input tracer quantities must be proportional to the velocity of the fluid at each position in the cross-section : this may be approximated by a rapid turbulent jet of tracer (a pulse), or by a step change. Measurement must be by means of the "mixing cup reading", where samples are collected at different times and the average concentration of each of the samples is measured. Adding the tracer evenly across the injection point or measuring the tracer on-line, without disturbance of the flow, does not give the true residence time distribution response. Levenspiel et al. (1970) relate the different responses mathematically.

The pulse test

M units of tracer are instantaneously introduced into the stream of a process at $t = 0$ and the traceable property $f(t)$ is measured in the effluent stream. Figure 2.3 shows the form of a pulse input and a typical response.

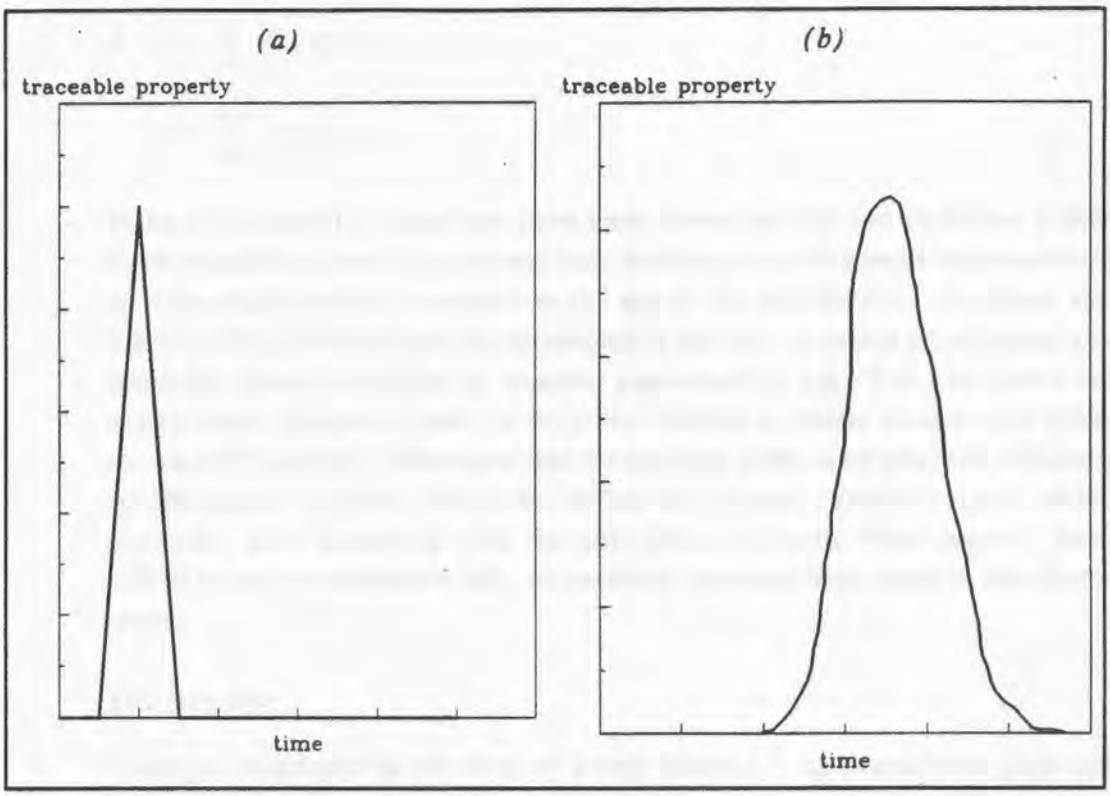


Figure 2.3 : *Traceable property-time representation of : (a) pulse input for a tracer test on a continuous flow process ; (b) a typical response*

Typically, the traceable property is concentration, or is related to concentration (for example, a spectrophotometer output), giving a concentration-time ($C(t)$) response. A material balance compares the actual amount of tracer added (M units) with the amount that leaves the process, found from the response :

$$M = A \cdot q$$

where :

A = area under the response

q = the volumetric flow rate of the effluent stream

The area under the response, A, is found from:

$$A = \int_0^\infty C(t)dt$$

$$\cong \sum_0^\infty C(t) \cdot \Delta t$$

Material balances for pulse tests have been shown by Curl and McMillan (1966) to have significant error due to analytical limitations, as very small concentrations of tracer might not be measured in the tail of the distribution. Robinson and Tester (1986) overcome this by extrapolating the tail, assuming an exponentially decaying, linearly decaying or constant concentration tail. The area under the extrapolated response is made to equal the fraction of tracer unrecovered (from the material balance). They show that the assumed shape often has little influence on subsequent analysis. However, where the process contains regions which have very slow contacting with the bulk fluid (not quite "dead space"), there will be a long concentration tail. An assumed tail shape may result in significant errors.

The step test

Tracer is introduced in the form of a step function : as a saturation (step-up) or elution (step-down) step. In a saturation step, m units/time of tracer are instantaneously introduced into the influent stream of a process at $t = 0$ and the traceable property $f(t)$ is measured in the effluent stream. In an elution step, the reverse occurs. Figure 2.4 shows the form of a saturation and elution step and typical responses.

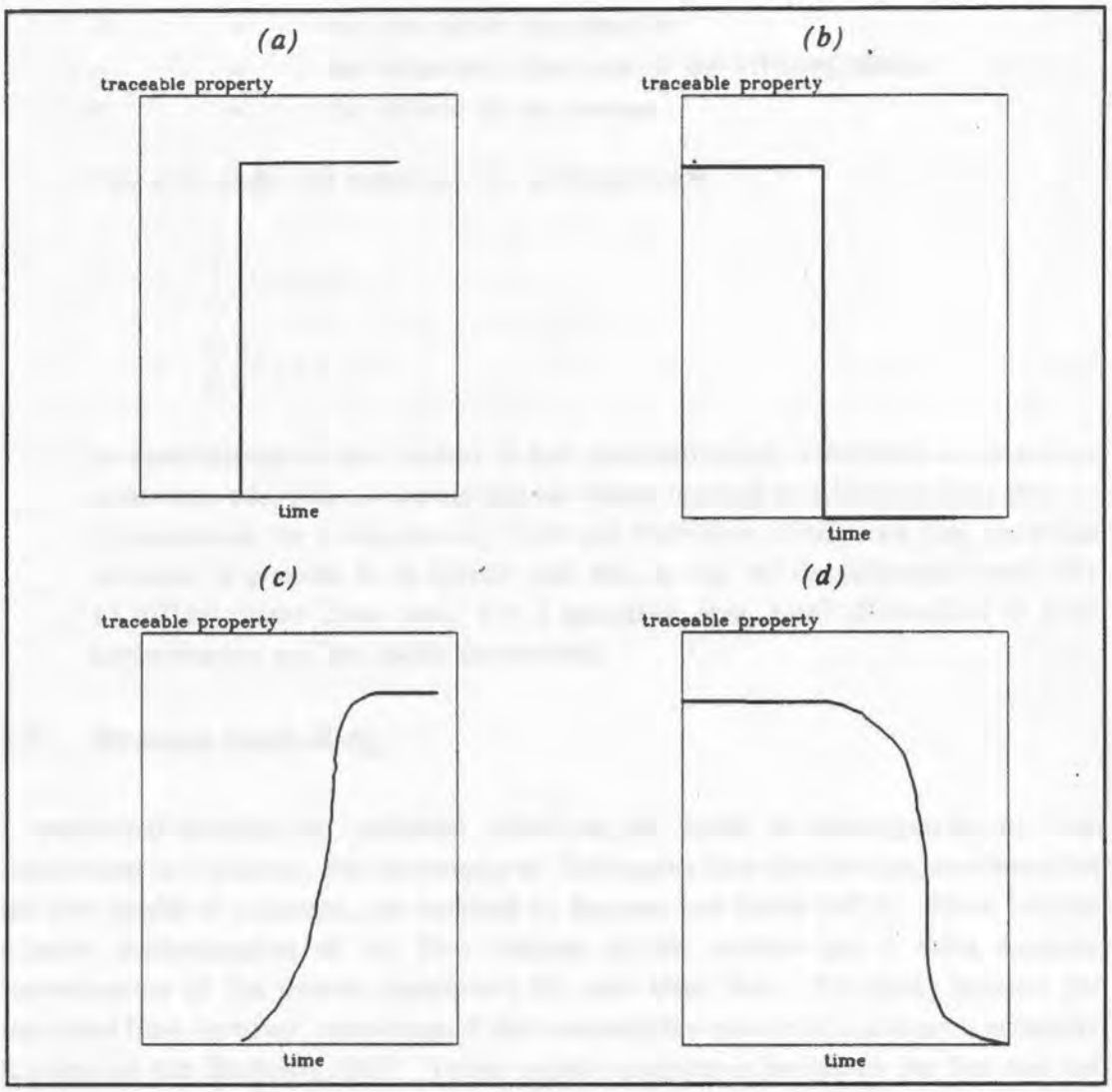


Figure 2.4 : *Traceable property-time representation of : (a) a saturation step input for a tracer test on a continuous flow process ; (b) an elution step input ; (c) a typical response to a saturation step input ; (d) a typical response to an elution step input*

A material balance compares the actual amount of tracer added (m units/time) to the amount that leaves the process, found from the response :

$$m = \frac{A \cdot q^2}{V}$$

where :

A = the area under the response
q = the volumetric flow rate of the effluent stream
V = the volume of the process

The area under the response, A, is found from :

$$A = \int_0^\infty C(t)dt$$

$$\approx \sum_0^\infty C(t) \cdot \Delta t$$

A disadvantage of this method is that the distribution is difficult to determine accurately where the concentration has almost reached its maximum for a step-up (or minimum for a step-down). Curl and McMillan (1966) state that analytical accuracy is greatest in an elution step test, as the tail concentration need only be differentiated from zero. For a saturation step, small differences in large concentration are less easily determined.

2.3 Process modelling

A tracer test provides an indicator which can be useful in investigating the flow distribution in a process. The advantages of finding the flow distribution, and therefore the flow model of a process, are outlined by Snyman and Smith (1975). These include a better understanding of the flow patterns in the process and a more accurate determination of the process parameters for non-ideal flow. To totally account for non-ideal flow, however, knowledge of the complete flow pattern of a process is necessary (Levenspiel and Bischoff, 1963). Tracer experimentation is limited by the fact that the measurement is of residence times and not the particular location of fluid in space (Robinson and Tester, 1986). The residence time distribution indicates the length of time spent in the process by any fluid element, but not the time when fluid elements of different ages mix in the process (Bailey and Ollis, 1986). Information from the residence time distribution is therefore not sufficient to completely define non-ideal flow.

Additionally, flow in real processes can be classified as segregated or non-segregated. Segregated flow means that the elements of fluid do not mix locally (Smith, 1981), called the macromixing in a process (Himmelblau and Bischoff, 1968). Non-segregated flow refers to the extent of local, or micromixing, between the fluid elements in a process.

The residence time distribution is not sufficient to determine the extent of segregated flow in a process, and there are many different mixing conditions that give the same residence time distribution (Smith, 1981).

The approach taken is to propose a flow model which reasonably approximates real flow and is realistic for the process under consideration (Levenspiel and Bischoff, 1963). Flow models simulate the overall behaviour of the process and are not necessarily representative of the actual flow in a process (Bryson, 1983). These models can be used to diagnose possible flow problems (Rabbitts et al., 1983) and to assess where improvements can be made. In reacting processes, the flow patterns affect the process kinetics (Himmelblau and Bischoff, 1968); the flow model can be combined with the applicable rate processes to predict conversion and reaction yields.

This section outlines the flow modelling approach. Initially, an overall view of the general modelling approach is given. In subsequent sections the areas outlined in the general modelling approach are examined in more detail. Various mathematical techniques are available for evaluating the chosen flow model for a process. The different techniques are compared briefly.

2.3.1 Modelling approach

The general modelling approach is shown in Figure 2.5.

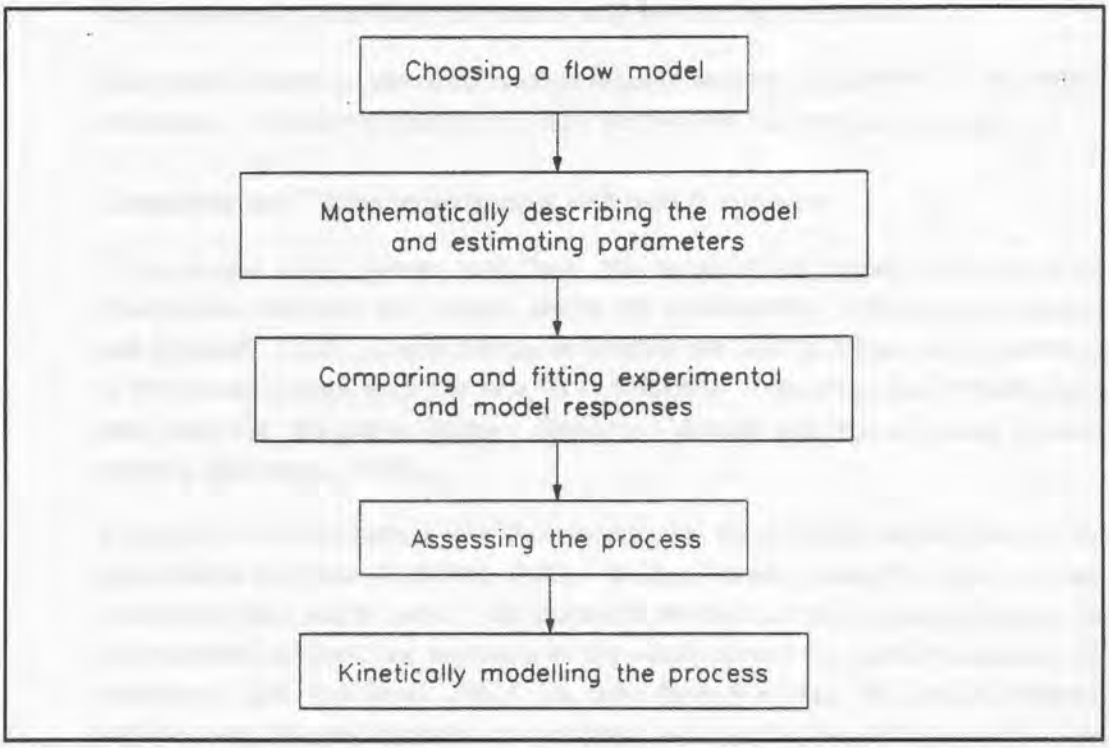


Figure 2.5 : *Pictorial representation of flow modelling approach*

Choosing a flow model

A flow model is chosen that reasonably approximates the real flow. This is done by qualitatively examining the experimental response and comparing it to the residence time distribution responses from known flow models, and by observing the physical process.

The residence time distribution responses for common flow models are documented (Levenspiel and Bischoff, 1963). Matching the shape of the experimental response to the responses for flow models is useful in choosing a flow model. Knowledge of the physical process can be used to choose a model that reasonably approximates real flow. If any visual test was performed (for example, a dye test on an open process), elements of the visible flow pattern can be used. The model must contain the necessary elements to be physically meaningful (Himmelblau and Bischoff, 1968).

Mathematically describing the model and estimating parameters

The chosen model is described mathematically and the parameters of the model estimated. A model response can then be derived for any given input.

Comparing and fitting experimental and model responses

If the model approximates real flow, the form of the model residence time distribution response will closely match the experimental response (Levenspiel and Bischoff, 1963). Curve fitting techniques are used to adjust the parameters of the model chosen until the best fit is obtained. Two principal methods have been used for this curve fitting : frequency domain analysis and time domain analysis (Jeffreson, 1970).

Frequency domain analysis uses Fourier series to characterise the residence time distribution response (Rabbitts, 1982). In time domain analysis, there are two procedures that can be used : the moments method, or time domain fitting. In the moments method, the moments of the experimental and model response are compared (Otto and Stout, 1961). In time domain fitting, the model response and the experimental response are compared with each other directly in the time domain (Naumann and Clark, 1991).

Assessing the process

Given that the model is a suitable representation of the process, the parameters of the model, found by fitting the experimental and model responses, are the parameters of the process. These parameters are examined to determine the extent of the deviation of the process from ideal flow.

Kinetically modelling the process

After determining the flow model of a process and the flow parameters, the kinetic rate equation can be combined with a mass balance performed over the flow model. This yields the effluent stream concentration of the reacting species with respect to the flow parameters of the flow model.

2.3.2 *Choosing a flow model*

The most common models chosen from a qualitative examination of the experimental response are outlined. The reasons for observing the physical process are detailed.

Examining the experimental response

The residence time distribution responses for documented flow models can be qualitatively compared to the experimental response. The most common models are the dispersion model, the tanks-in-series model, and the compartment model (see below). The dispersion model and the tanks-in-series model are simple two-parameter models, whereas the compartment model can have as many parameters as required. Criticisms of the simple models have led to some authors presenting models similar to the compartment model, but with a set number of parameters. For example, Wolf and Resnick (1963) present a number of flow models that can be represented by a single equation of two parameters, but which are more general than the dispersion or tanks-in-series models; Rogers and Gardner (1979) present a six parameter model which they have found to represent a wide range of ball mills. The compartment model is unrestricted in this study.

These models will be briefly outlined and their applicability indicated. Solutions of the equations of the models are not given here.

Common flow models

The dispersion model

The dispersion model represents the process as plug flow in which axial mixing, or dispersion, takes place (Smith, 1981). Mixing is caused by flow around particles and variations in velocity, as well as molecular and turbulent diffusion (Levenspiel and Bischoff, 1963). Molecular diffusion is generally considered less important (Kramers and Alberda, 1953), except in laminar flow for Reynolds numbers less than 1 (De Backer and Baron, 1994). It is used when the deviation from plug flow is due to axial dispersion and is not complicated by other deviations, such as bypassing (Tsamatsoulis and Papayannakos, 1994).

The model is often a good approximation of flow in packed beds, turbulent flow in tubes, and laminar or turbulent flow in long tubes or long channels. Crawshaw et al. (1993) noted that, although many authors have done so, the model is not representative of gas flow in moving beds. Use of the model is thus subject to confirmation that the process is not liable to have other flow non-idealities. The dispersion model is particularly useful for modelling the residence time distribution of processes with open boundaries (Gibilaro, 1978).

The dispersion model may be described by a diffusion equation with independent variables in dimensionless form (Naumann and Clark, 1991):

$$\frac{dC}{d\tau} + \frac{dC}{dx'} = \frac{1}{Pe} \cdot \frac{d^2C}{dx'^2}$$

where :

C	=	the tracer concentration
τ	=	dimensionless residence time, $\theta \cdot \bar{u}/L = \theta/\bar{t}$
θ	=	elapsed time
$\bar{u}$	=	average fluid velocity
L	=	length of process
x'	=	dimensionless axial coordinate, z/L
z	=	axial coordinate or axial displacement
Pe	=	axial Peclet number, $\bar{u} \cdot L/D$
D	=	axial dispersion coefficient

The axial dispersion coefficient, D, represents the deviation from plug flow, the "spreading process" (Levenspiel, 1979). The Peclet number, Pe, is the dimensionless group characterising the rate of "spreading", or the residence time distribution in a region of length L. For a small deviation from plug flow the dispersion is small and thus Pe is large. For a large deviation from plug flow the dispersion is large and Pe is small. Levenspiel (1979) considers a small deviation from plug flow to be $Pe > 100$.

Figure 2.6 shows responses for various degrees of mixing, for a pulse input, as predicted by the dispersion model.

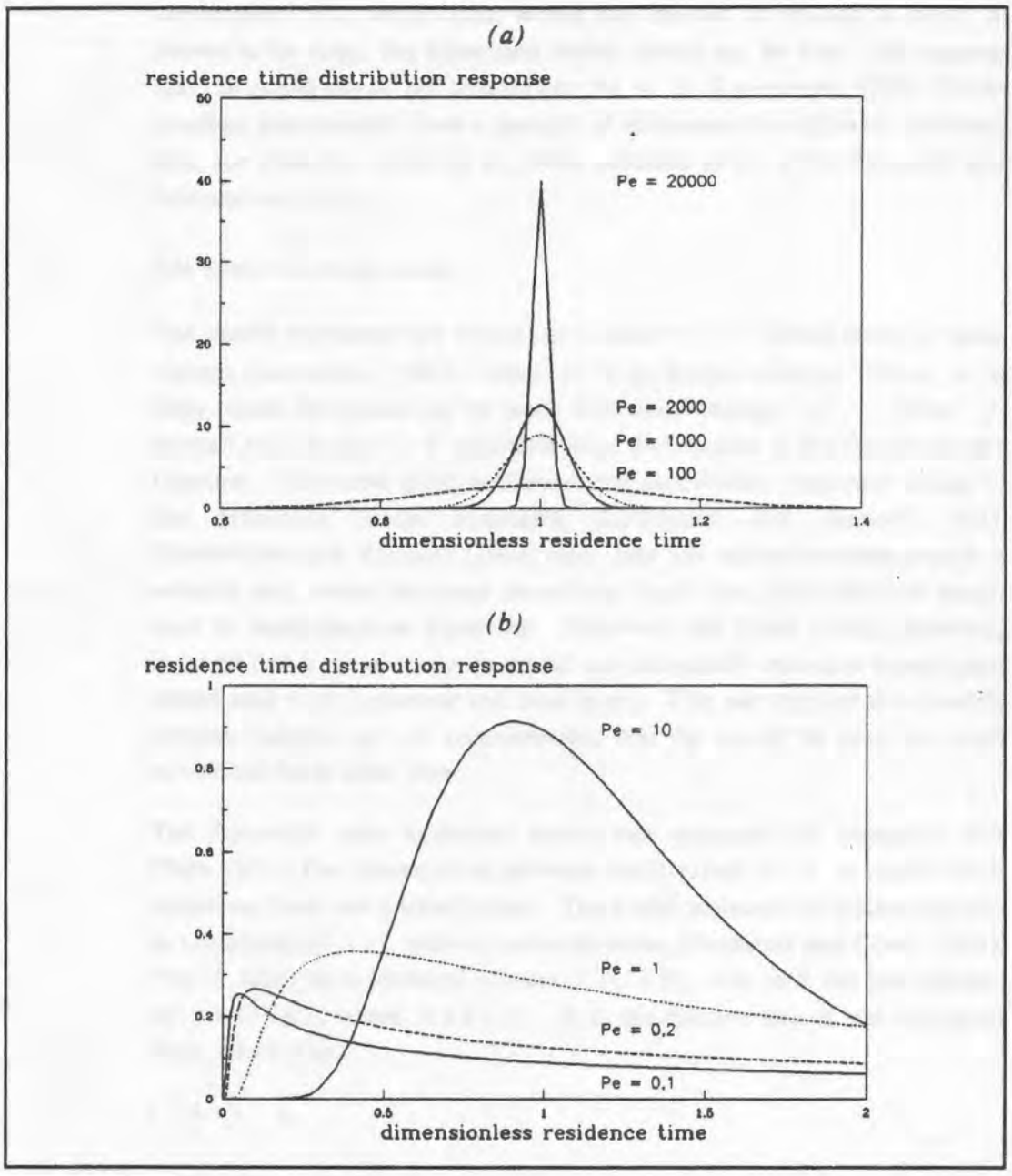


Figure 2.6 : *Responses for various degrees of mixing for a pulse input, as predicted by the dispersion model : (a) small deviation from plug flow ; (b) large deviation from plug flow (Note the change in horizontal scale)*

Levenspiel (1972) warns that, where the amount of mixing is large, or known to be large, the dispersion model should not be used. He suggests that the model should not be used for $Pe < 1$ (Levenspiel, 1979). Peclet numbers are available from a number of references for different processes (see, for example, Leitão et al., 1994, Addison et al., 1994, Benezech and Maingonnat, 1993).

The tanks-in-series model

The model represents the process as a series of N stirred tanks of equal volume (Levenspiel, 1962), where N is an integer number. When N is large, small deviations can be made with small changes to N. When N is small any change in N produces large differences in the residence time function. The model gives residence time distribution responses similar to the dispersion model responses (Levenspiel and Bischoff, 1963). Himmelblau and Bischoff (1968) state that the tanks-in-series model is suitable only where no large deviations from ideal flow patterns occur, such as dead space or bypassing. Grayman and Clark (1993), however, indicate that a tanks-in-series model can adequately represent a non-ideal mixed tank with bypassing and dead space. This was applied to a specific process, though, so it is recommended that the model be used for small deviations from ideal flow.

The fractional tank extension model was proposed by Naumann and Clark (1991) for interpolating between small values of N to model small variations from one perfect mixer. The model is described mathematically as consisting of $I+1$ stirred tanks-in-series (Naumann and Clark, 1991). The I tanks have identical volume $V/(I+\beta)$; one tank has the volume $(\beta \cdot V)/(I+\beta)$, where $0 \leq \beta \leq 1$; β is the relative size of the fractional tank. Note that :

$$I + \beta = N$$

where :

I = an integer just less than or equal to N

β = a fractional number of stirred tanks

Figure 2.7 shows responses for various degrees of mixing as predicted by the tanks-in-series model.

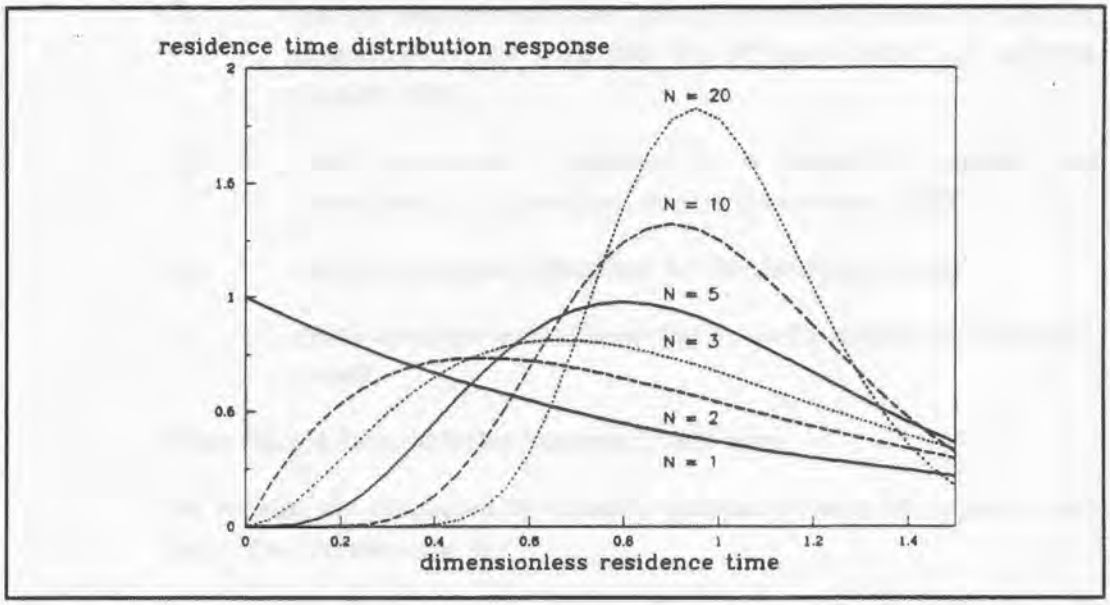


Figure 2.7 : *Responses for various degrees of mixing as predicted by the tanks-in-series model*

The compartment model

The compartment model represents the process as being composed of elementary flow regions with independent residence times (Sinclair and McNaughton, 1965). The flow regions are generally interconnected plug flow regions, perfect mixers and dead space (Himmelblau and Bischoff, 1968). The present study extended the concept of the compartment model to include a dispersion region, described by the dispersion model, and a tanks-in-series region, described by the fractional tank extension model. It is used where the dispersion model or tanks-in-series model alone cannot adequately represent the flow in the process (Levenspiel and Bischoff, 1963).

The model consists of :

(i) plug flow where there is no mixing in the direction of flow, so that elements of fluid entering the region at the same moment move through it on parallel paths, and leave at the same moment (Smith, 1981).

(ii) perfect mixers where the fluid is completely mixed, so that the properties of the fluid and the effluent stream are uniform (Smith, 1981).

(iii) dead space which is assumed to be completely stagnant, but contributes to the process volume (Levenspiel, 1972).

(iv) dispersion regions described by the dispersion model.

(v) tanks-in-series regions described by the fractional tank extension model.

These regions have volumes associated with them.

The regions are connected by streams, assumed to have no volume, only flow. The streams may be :

(i) connecting streams which lead directly from one region to another.

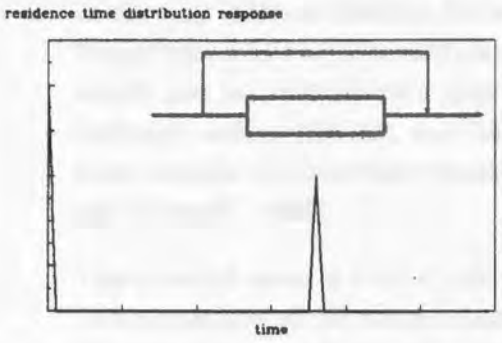
(ii) bypassing streams where some of the fluid bypasses a region or regions (Levenspiel and Bischoff, 1963).

(iii) recycle streams where some of the fluid in the effluent stream of a region is returned to mix with an influent stream (Levenspiel and Bischoff, 1963).

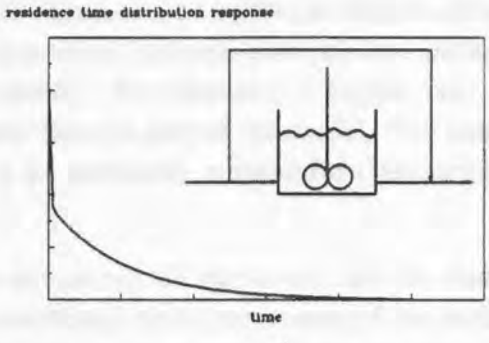
A compartment model is made up of these components as theoretical parts of the real process. Some common models and residence time distribution responses are given in Table 2.1.

Table 2.1 : *Some common models and residence time distribution responses ; a pulse input is assumed : (a) bypassed plug flow ; (b) bypassed mixed flow ; (c) plug flow regions in parallel ; (d) mixed flow regions in parallel ; (e) plug flow region in series with mixed flow region*

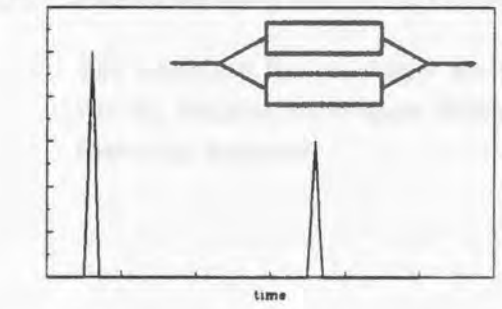
(a)



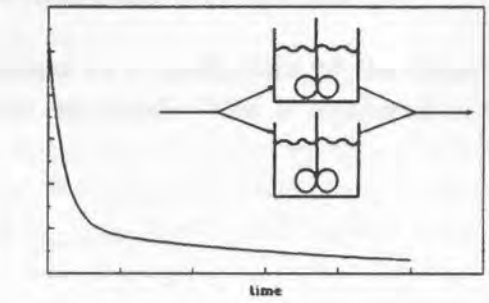
(b)



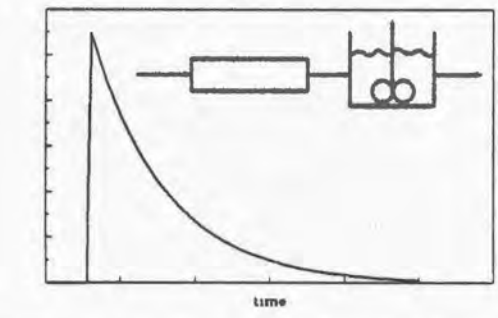
(c)



(d)



(e)



Although a complex compartment model may fit the data accurately, it need not necessarily represent the actual flow accurately.

Observing the physical process

An examination of the physical process is necessary when choosing a model. The shape of the process vessel, positions of inlet and outlet pipes, baffles, and so on, may indicate whether, for example, bypassing or mixing is likely to occur. Visual tests may be performed on open processes, indicating overall flow patterns which can be incorporated into the model. For example, a bypass may be indicated using a dye test, and the bypass must be part of the model. The model must contain the necessary elements to be physically meaningful (Himmelblau and Bischoff, 1968).

The physical process is also useful in estimating the parameters of the model. The parameters of the process must be correlated to the parameters of the model. For example, the total volume of the unit or units of the model should equal the total volume of the process.

2.3.3 *Mathematically describing the model and estimating parameters*

The equations for the model are formulated by a combination of the equations for the regions and a mass balance over the model. This is illustrated in the following example.

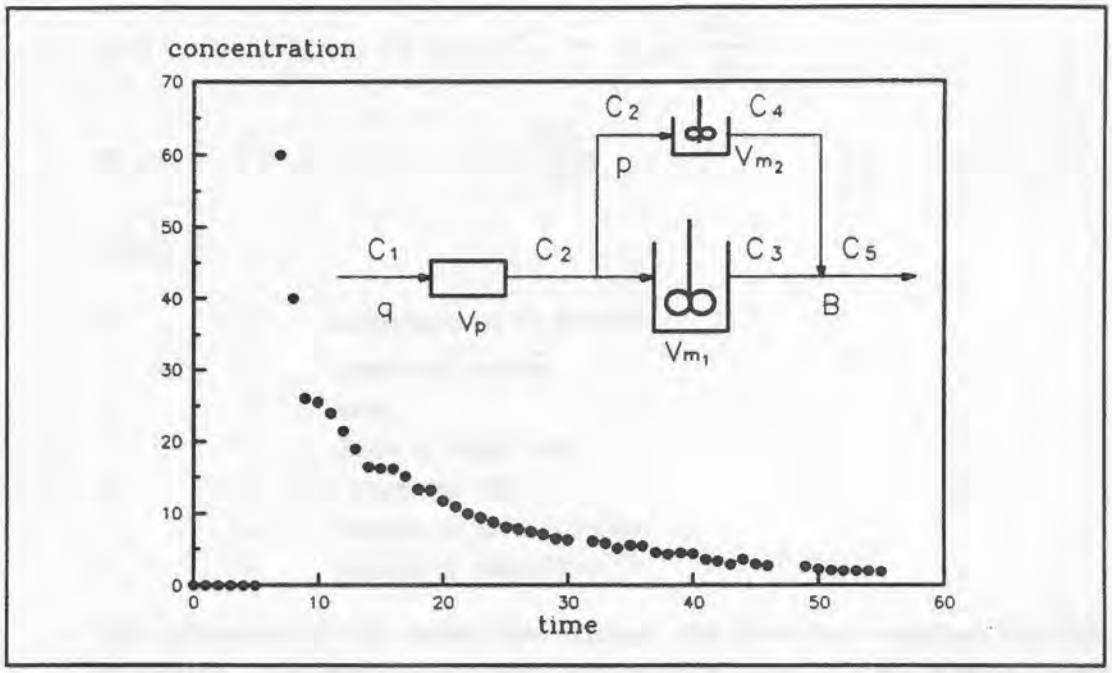


Figure 2.8 : *Concentration-time data and assumed model : delay indicates plug flow ; peak indicates bypass ; exponential response indicates active mixing, modelled by a perfect mixer*

Given data as in Figure 2.8, assuming a tracer impulse at $t = 0$, plug flow in series with a bypassed perfect mixer may be assumed. The delay between the time of tracer addition and the time of tracer measurement indicates plug flow in the real process. The initial peak indicates a bypass of fluid across an active mixing region in the real process. The peak, too, has a response associated with it; the bypass therefore includes some mixing.

The model equations are developed by a mass balance at point B, and the equations for plug flow and perfect mixers (Levenspiel, 1972).

At point B :

$$C_5 = p \cdot C_4 + (1 - p) \cdot C_3$$

Over the plug flow :

$$C_2(t) = C_1(t - \tau)$$

Over the perfect mixer :

$$q \cdot (1-p) \cdot C_2 - q \cdot (1-p) \cdot C_3 = V_{m1} \cdot \frac{dC_3}{dt}$$

$$q \cdot p \cdot C_2 - q \cdot p \cdot C_4 = V_{m2} \cdot \frac{dC_4}{dt}$$

where :

C_i	=	concentration of stream i
p	=	fractional bypass
t	=	time
τ	=	delay of plug flow
q	=	volumetric flow
V_{mi}	=	volume of perfect mixer i
V_p	=	volume of plug flow

The parameters of the model (for example, the flows and volumes) are then estimated. These parameters should be physically realistic. The model response is then derived using the mathematical description of the model. The model response is calculated using the experimental tracer input.

2.3.4 *Comparing and fitting experimental and model responses*

The parameters of the model are adjusted using curve fitting techniques until the best fit is obtained. The two principal methods for this curve fitting are outlined : frequency domain analysis and time domain analysis (the moments method or time domain fitting).

Frequency domain analysis

Frequency domain analysis uses the coefficients of the Fourier Series to characterise the residence time distribution response (Rabbitts, 1982). The Fourier coefficients are found for both the experimental and model responses, and the parameters of the model are adjusted until the best fit between the coefficients is obtained.

The normalised residence time distribution response can be represented by a Fourier series (Rabbitts et al., 1983) :

$$C(t) = \sum_{n=1}^{\infty} a_n \cdot \sin \frac{n \cdot \pi \cdot t}{T} + \sum_{n=0}^{\infty} b_n \cos \frac{n \cdot \pi \cdot t}{T}$$

where :

$$a_n = \frac{1}{T}\int_0^{2T} \sin\frac{n\cdot\pi\cdot t}{T}\cdot dt$$

$$b_0 = \frac{1}{2T}\int_0^{2T} C(t)\cdot dt$$

$$b_n = \frac{1}{T}\int_0^{2T} \cos\frac{n\cdot\pi\cdot t}{T}\cdot dt$$

$$n = 0,1,2,3...$$

where :

T = half the time duration of one experiment

The Fourier coefficients (a_n, b_n) of the experimental response are determined by numerical integration. The coefficients from the experimental response are compared to the coefficients derived from the model response. Rabbitts (1982) derives Fourier coefficients for a number of models.

There are a number of advantages to using frequency domain analysis. Rabbitts (1982) states that the process response to any input disturbance, as well as the correction for a non-ideal pulse input, are simple algebraic manipulations in the frequency domain. Also, experimental noise can be diminished by reducing the number of Fourier coefficients found for the experimental response. This effectively eliminates the higher frequencies, which usually correspond to noise (Duffy and Al-Hassan, 1988).

Disadvantages of frequency domain analysis were found in this study. One disadvantage is that the determination of Fourier coefficients for complex models is complicated, involving reduction of complex functions. As the data is transformed into the frequency domain, the results are difficult to interpret. Another disadvantage is that the residence time distribution response is assumed to be a periodic function. Only one cycle of this periodic function is of interest, however, when representing the response as a Fourier series. The boundaries (ends) of the response cannot be accurately represented as they do not continue to another cycle (as is mathematically assumed).

Time domain analysis

Two procedures are generally used in time domain analysis : the moments method, or time domain fitting. The methods are outlined.

The moments method

The moments are calculated from the experimental residence time distribution response and then compared to the moments derived from the chosen model. The model and its parameters are adjusted until the moments are similar.

The absolute moments, μ_n , are given by :

$$\mu_n = \int_0^\infty t^n \cdot f(t) \cdot dt$$

where :

n	=	the number of the moment, n = 0.1.2....
$f(t)$	=	the residence time distribution function

Otto and Stout (1961) demonstrate that moments may be quantitatively used to describe the process dynamics and a numerical description of process dynamics is possible without the presumption of a specific model.

The moments method is frequently used as it is simpler than the Fourier transform fitting method. Anderssen and White (1970) argue that if it is known that the model will give excellent agreement to the data, the moments method will give a good estimate of parameters. Bryson (1983) shows that the method of moments leads to simple expressions for complicated models. Gibilaro and Lees (1969) use moments to reduce complex transfer function models to simple models. Rabbitts (1982) derives moments for number of models.

The moments method has disadvantages (Rabbitts, 1982). Simandi et al. (1988) indicate that highly inaccurate estimates of parameters result from the large weight in the value of the moment at the end of the response, t^n . Also, due to limitations in the accuracy of chemical analyses, only the first two moments are usually adequately reproducible, and accurate third moments are not usually available. However, more than two moments are needed for model discrimination (Naumann and Clark, 1991), therefore,

unless a specific model is given for a process, the moments method is not suitable for determination of a model. Also, the moments method assumes that the model chosen is a good fit to the data, so no comparison between models on the basis of "goodness of fit" is possible (Hays et al., 1967).

The method of weighted moments has been proposed as an alternative to the method of moments to overcome the excessive influence of errors in the tail. Simandi et al. (1988) review this method, its application and the estimation of errors. They conclude that the method of weighted moments always yields better estimates of the model parameters than the method of ordinary moments. Naumann and Clark (1991) state that, even with weighted moments, the method is still heavily dependent on data taken at large time values.

Addison et al. (1994) discuss the use of inventory measurements to overcome the weighting problem. They suggest the use of step change experiments to determine the tracer inventory in the process. The moments are then given by an integral of the holdup (amount of tracer left in the process), with a t^{n-2} weighting, as opposed to a t^n weighting. Although this method is preferable to the ordinary moments method, proper discrimination between distributions requires high order moments, which may still be fairly inaccurate.

Time domain fitting

In time domain fitting, the model response and the experimental response are compared with each other directly in the time domain (Naumann and Clark, 1991). The parameters of the model are chosen to minimise the sum-squared error (SSE) between the experimental data and the model data :

$$SSE(P_1, P_2, \ldots) = \sum_i (f_{expt(t_i)} - f_{model(t_i)})^2$$

where :

$P_1, P_2, \ldots$ = parameters of the model

$f_{expt(t_i)}$ = experimental data point at time t_i

$f_{model(t_i)}$ = model data point calculated at time t_i

An advantage of this method is that discrimination between different models is possible by examination of the SSE : a lower SSE indicates that the model fits the data better. Also, for any particular model, a lower SSE indicates that the parameters estimated fit the data more closely.

A feature of this method is that discrete data points are necessary. Thus a continuous experimental response must be translated into discrete data time values for evaluation. The method is numerically time consuming when comparing different models or determining parameters. Simandi et al. (1988) state that the computer time requirements for time domain fitting are greater by an order of magnitude than for the method of weighted moments. With the currently available, and continually increasing computer power, this constraint is removed.

2.3.5 *Assessing the process*

The parameters of the model can be considered the parameters of the process. Thus, given that the chosen model is physically realistic, the process can be assessed using these parameters. The extent of the deviation of the process from non-ideal flow can be determined, and the significant features of the process noted. This provides a basis for decision-making in terms of the time, cost and effort of making process changes to correct deviations from non-ideal behaviour.

For example, the model for a stirred tank may show the tank to be a perfect mixer with dead space and a bypass. The implications of the tank not operating as a perfect mixer can be weighed against the time, cost and effort of modifying the process to reduce the bypass and dead space.

2.3.6 *Kinetically modelling the process*

The residence time distribution of a process, combined with the kinetics of the process, gives an estimate of the effluent stream concentration from a reacting process (Hanley and Mischke, 1978). This is always true for first order reactions, but may not be true for orders greater than one (Zwietering, 1959). The state of mixing in a process, or the time at which reactants mix, is important. For example, if the reactants mix early in a process, the reaction may be more complete than if they mix later, although the residence time distributions are identical. The residence time distribution completely defines the variation in the molecule residence times, the macromixing (Weinstein and Adler, 1967). It does not, however, define the amount of mixing on a molecular scale, the

micromixing. The micromixing is defined by Danckwerts (1958) as the degree of segregation in a process, and is an important parameter in chemical conversion prediction. Rippin (1967), however, states that, together with the degree of segregation and the residence time distribution, a more detailed model of the concentration history of the fluid elements is also required to completely predict chemical conversion.

The present study did not investigate the effect of the degree of segregation and the concentration history on reacting processes. The kinetics of the processes studied were adequately approximated as being of the first order, and the residence time distribution was therefore sufficient to predict conversion.

Kinetic data is often determined in a laboratory on near-ideal equipment. Using the flow model of the process, which incorporates the non-idealities of the process equipment, together with kinetic data determined in a laboratory, gives a better estimate of the kinetic performance of the process. After determination of the flow model of a process and the flow parameters, the kinetic rate equation, using data obtained on laboratory equipment, can be combined with a mass balance performed over the flow model. This yields the effluent stream concentration of the reacting species with respect to the flow parameters of the flow model. Even where the residence time distribution is not sufficient to predict the exact kinetics on scale-up from a laboratory, for second order and higher reactions, a comparison of the residence time distributions for the small- and large-scale different processes often gives a good indication of the changes to be expected on scale-up (Naor and Shinnar, 1963).

Further, the effect of process changes on the kinetics of the process can be estimated. For example, if the mixing in a process is improved, a new model may be postulated without repeating the tracer experiment, and the effect on the process kinetics shown. This, again, provides a basis for decision-making in terms of the time, cost and effort of making a process change.

An example can be used to illustrate the technique. A mass balance is performed over a flow model incorporating a simple first order kinetic equation. Figure 2.9 shows the assumed model and kinetic equations.

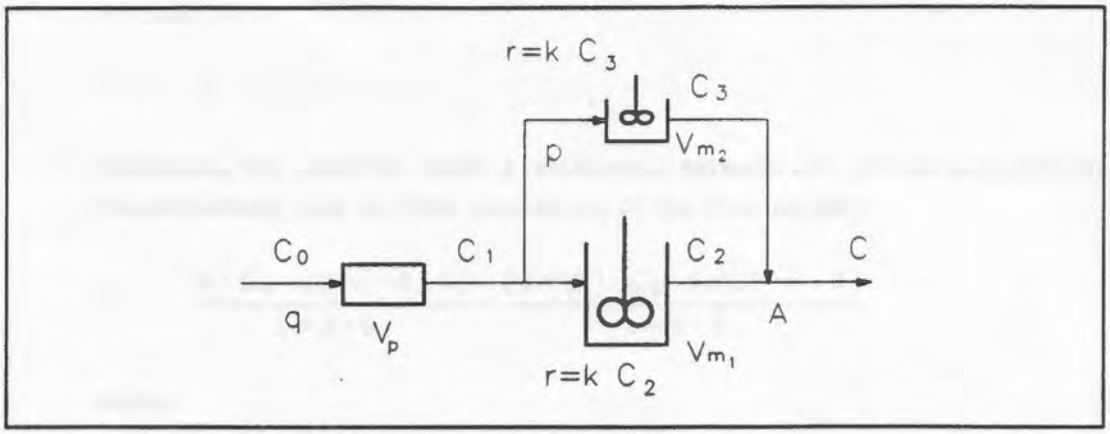


Figure 2.9 : *Assumed model showing kinetic equations and concentration labels for performing the mass balance*

Kinetic equation :

$$r = k \cdot C$$

Over the plug flow :

$$q \cdot C_0 - q \cdot (C_0 + dC) = r \cdot dV_p$$

$$\therefore \; -\frac{dC}{C} = k \cdot \frac{1}{q} \cdot dV_p$$

$$\therefore \; C_1 = C_0 \cdot e^{(-k \cdot \tau)}$$

Over the mixed flow :

$$q \cdot (1-p) \cdot C_1 - q \cdot (1-p) \cdot C_2 = r \cdot V_{ml}$$

$$\therefore \; C_1 - C_2 = k \cdot C_2 \cdot \theta_1$$

$$\therefore \; C_2 = \frac{C_1}{1 + k \cdot \theta_1}$$

and, similarly :

$$C_3 = \frac{C_1}{1 + k \cdot \theta_2}$$

At point A :

$$C = p \cdot C_3 + (1-p) \cdot C_2$$

Combining the equations yields a relationship between the influent and effluent concentrations, and the flow parameters of the flow model :

$$C = \frac{p \cdot C_0 \cdot \exp(-k \cdot \tau)}{1 + k \cdot \theta_2} + \frac{(1-p) \cdot C_0 \cdot \exp(-k \cdot \tau)}{1 + k \cdot \theta_1}$$

where :

r	=	reaction rate
k	=	reaction constant
C_i	=	concentration of stream i
θ_i	=	mean residence time of perfect mixer i
V_i	=	volume of i
τ	=	delay of plug flow V_p/q
p	=	fractional bypass
q	=	volumetric flow
t	=	time

2.4 Conclusion

Although the concept of the residence time distribution of a process was first conceived by Danckwerts in 1953, little progress has been made in bringing the techniques involved into ordinary engineering practice. The analysis has often been limited to qualitative observation of the experimental response and, where quantitative analysis has been performed, this has been tedious and difficult to interpret. One reason for this limitation was numerical complexity; with currently available computer power, this constraint is removed.

In this chapter, the literature and theory on residence time methods was reviewed. A general experimental approach for determining the experimental response of a water or waste water treatment process was outlined. In a review of the literature it was found that, although methods were given, no reasons for the choice of a particular tracer were given. In this chapter, the different tracers that have been used for experiments on water and waste water treatment processes were compared.

Some of the techniques available for flow modelling from residence time data were reviewed briefly, and their advantages and disadvantages outlined. This provides a basis for the choice of a flow modelling technique, detailed in **Chapter 3**.

CHAPTER

THREE

Using IMPULSE for flow modelling

3.1 Introduction

In **Chapter 2**, the general modelling approach for flow modelling a process from residence time data was discussed. This involved choosing a realistic flow model by examinination of the experimental response and then mathematically describing the model and estimating parameters. The experimental and model responses are then compared and fitted by adjustment of the model parameters using either frequency domain or time domain analysis. The process can then be assessed using the parameters of the flow model.

Although choosing a flow model, estimating parameters and assessing the process are qualitative steps and cannot be performed by a computer, mathematical description of the model and fitting of the experimental and model responses by adjustment of the model parameters are easily performed by a computer. Performing these numerical steps using a computer simplifies flow modelling and reduces the time required for numerical calculation.

A computer program, IMPULSE (Barnett et al., 1993), was developed in this study to perform the numerical steps required for flow modelling from residence time data. In this chapter, IMPULSE is introduced as a tool for flow modelling from residence time data.

The objectives of this chapter are:

(i) to show how IMPULSE fits into the general flow modelling approach.

(ii) to show the main program features and limitations.

3.2 Flow modelling using IMPULSE

A conclusion to the review of the literature and theory of residence time distribution techniques in **Chapter 2** was that little progress has been made in bringing the techniques

involved into ordinary engineering practice. As the methods of analysis are well documented, it appears that the major reason for this has been numerical complexity. Also, where mathematical transformations have been used to simplify the numerics, interpretation often becomes difficult.

The recent advances in personal computers and computer software have brought the solution of complex equations within reach, and have alleviated the tedium of repetitive or iterative calculations. Thus quantitative flow modelling from experimental residence time data is accessible using personal computer software.

Any program written specifically for flow modelling from experimental residence time data would need to be able to perform two functions. The first is to be able to describe mathematically any flow model chosen. The second would be to adjust estimated model parameters in order to fit the experimental and model responses. The first function is accomplished by simultaneous solution of equations associated with all parts of the flow model chosen. The second function involves comparing and fitting responses using a fitting technique. IMPULSE was written to perform these two functions, in order to bring the flow modelling of residence time data within reach of staff managing processes at water and waste water treatment works. IMPULSE can, however, also be used for the flow modelling of many other processes.

The fitting technique chosen to compare the experimental and model responses is the time domain fitting method. This method was chosen as the results are easy to interpret as they are available in the time domain. The major disadvantage of time domain fitting is numerical complexity, which was overcome by the use of IMPULSE.

IMPULSE, therefore, is a tool useful for performing some steps of the general modelling approach given in **Chapter 2**. Figure 3.1 repeats the approach given in Figure 2.5, but shows where IMPULSE is used.

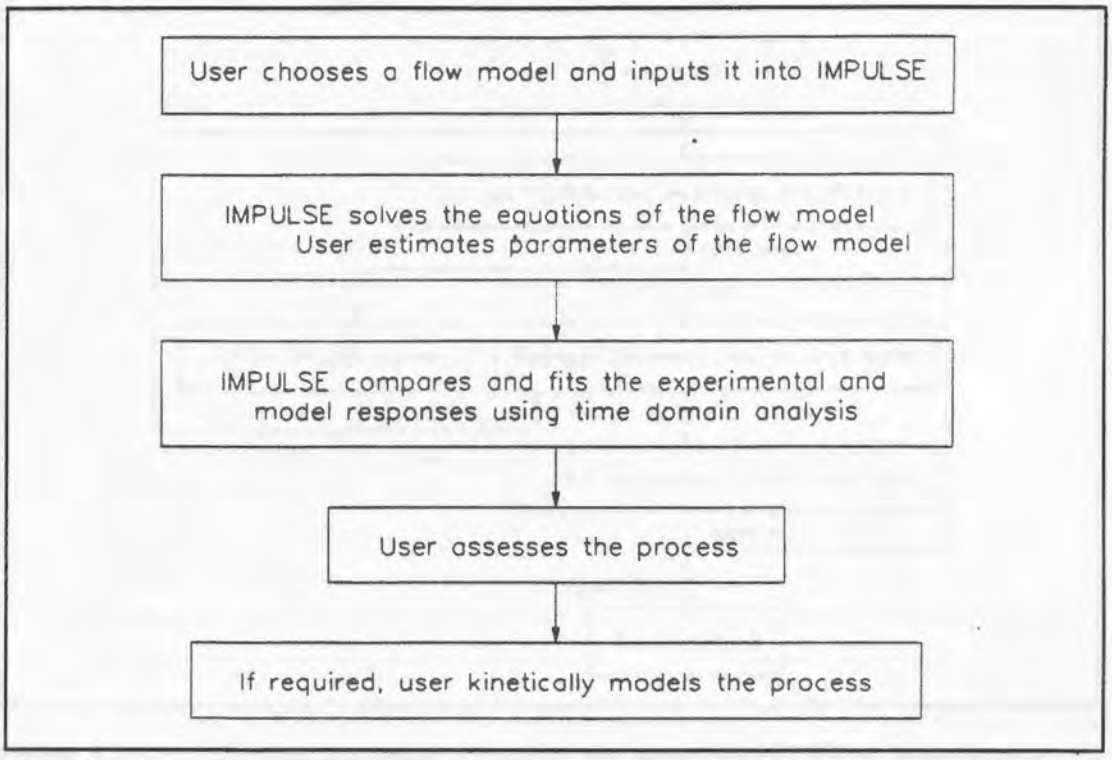


Figure 3.1 : ***Where IMPULSE fits into the flow modelling approach of Figure 2.5***

A flowsheet for the program is given in Figure 3.2. As IMPULSE is interactive, a flowsheet cannot show all the options available. This is, therefore, only one possible flowsheet.

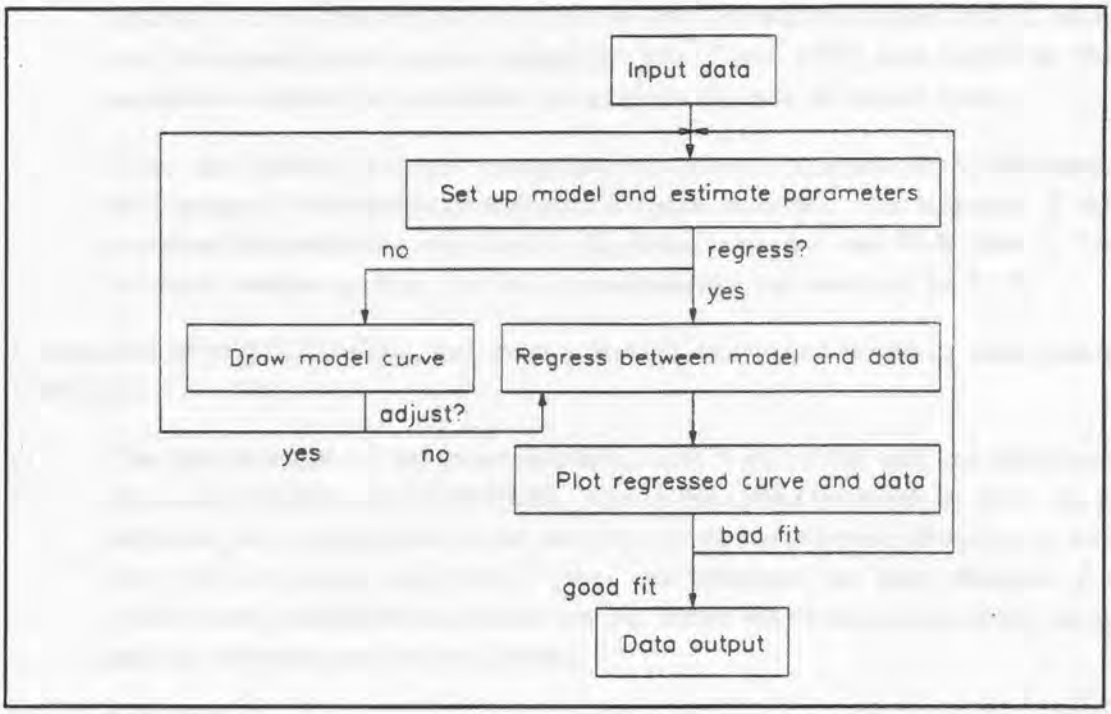


Figure 3.2 : *Typical suggested flowsheet for using IMPULSE to investigate a residence time problem for residence time modelling*

3.3 Main program features and limitations

The main program features are :

(a) The model constructed by the user may be modified at any time by simply adding or removing units and connections.

(b) Any set of concentration data generated by the model or entered by the user can be plotted on a single set of axes for comparative purposes. The plot is regenerated automatically as the user alters modelling parameters and re-runs the model, allowing for almost instantaneous feedback.

(c) Flow and concentration profiles can be loaded from an ASCII text file, which can be generated by a spreadsheet program or an ASCII text editor.

(d) The user provides estimates of the parameters of the model. Any of the parameters estimated may be chosen to be fitted to the experimental tracer response by regression or to be kept at the value estimated. Thus the effect of changing one or more, but not necessarily all, the parameters may be seen. The regression

procedure calculates the sum of square errors between the model output curve and the experimental curve (Naumann and Clark, 1991) and alters all the parameters chosen for regression to minimise the sum of square errors.

(e) If the user chooses the input concentration scale as a parameter to be regressed, the regressed value gives an estimate of tracer recovery. For example, if the regressed concentration scale is 0,9, the tracer recovery was 90 %, that is, for the mass balance to close, the input concentration was reduced by 10 %.

Limitations to IMPULSE exist, and certain precautions should be taken when using IMPULSE :

(a) The determination of the tracer response curve is not trivial and may influence the result obtained from IMPULSE. Thus a user must be aware of how this is obtained, any experimental error that may be associated with obtaining it, and how this influences the curve. Also, the program has been designed for conservative tracers, that is, tracers that are conserved in the process under study and are not consumed in the process.

(b) IMPULSE should only be used to model continuous or near-continuous flow processes. The technique and the program assume a continuous flow through the process. Additionally, the program models the liquid residence time of the process, and not the solids residence time. Tracing of the solids in a process is possible if they can be marked with, for example, a radioactive tracer. The residence time distribution of the solids could then be determined the same way as for liquid residence time given that the same information is known about the solids (for example, the flow of solids).

(c) IMPULSE works with concentration-time responses. Thus, if data is available in another form (for example, radioactivity-time data), this should be converted to concentration. Although the modelling will be possible without this step, the results will be meaningless as the parameters and data will not be in the same units.

(d) A user should have a physical knowledge of the process to be modelled and should be able to guess realistic flow models. Any parameters obtained from the flow model must have physical significance; thus a complex model may fit the tracer curve but may not be realistic. For open processes, a dye test may indicate the most realistic flow model. Further, tracer curves are not unique : they can be modelled accurately by more than one model. Sound engineering judgement is therefore necessary to choose the most realistic model.

(e) IMPULSE works by dividing time into "segments" and then applying the equations describing the process to each segment in turn. A model is sensitive to the number of segments chosen : in general, the larger the number of segments the more accurate the result.

3.4 Use of IMPULSE

IMPULSE works with concentration-time data directly in the time domain. Thus no transformation of experimental residence time distribution data (generally determined as concentration-time data) is usually necessary. The program allows for any input tracer signal and varying flow rates. Bischoff (1964), in his solution of the axial dispersion equation for time variable flow, states that the velocity varies in many applications. Generally, constant velocity solutions are used as approximations. It is desirable, however, to have exact solutions where possible. IMPULSE takes flowrate variation (and therefore velocity) into account.

The following data is entered into the program :

(i) the building blocks of the model (for example : plug flow, perfect mixer, dispersion unit, tanks-in-series unit)

(ii) the parameters associated with the building blocks (for example : volume, split fraction, Peclet number)

(iii) whether the parameters must be held constant or can be varied by IMPULSE

(iv) tracer input flowrate and concentration data

(v) the experimental tracer response data (called the REFERENCE) against which the model response is fitted

The output from the program after modelling is displayed on the screen and can be saved to a file. The data saved are :

(i) model parameters

(ii) tracer input concentration and flowrate data

(iii) reference concentration data

(iv) model concentration data

IMPULSE has seven building blocks which can be used as connected units to yield a model of the process. Some blocks have parameters associated with them. Every unit has a unique name identification and connection requirements. There is no restriction on the number of units. Dead space is not one of the building blocks, as it not determined explicitly. It is determined by difference between the known process volume and the volume of the model units.

Table 3.1 gives a description of the building blocks and their requirements.

Table 3.1 : *IMPULSE building blocks and their requirements*

Name	Description	Requirements	
Mixed flow reactor (MFR)	a perfect mixer	Inputs Outputs Parameters	1 1 volume
Plug flow reactor (PFR)	a plug flow	Inputs Outputs Parameters	1 1 volume
Axial dispersion (PFRDISP)	a region to which the dispersion model can be fitted	Inputs Outputs Parameters	1 1 volume; Peclet number
Tanks-in-series (MFRSER)	a region to which the fractional tank extension model can be fitted	Inputs Outputs Parameters	1 1 volume; number of tanks
Input	an input to the process : the tracer input	Inputs Outputs Parameters	none 1 flowrate; concentration
Output	the response curve of the model to the input, with either estimated or regressed parameters	Inputs Outputs Parameters	1 none none
Mixer/splitter (MixSplit)	a unit which joins or splits streams	Inputs Outputs Parameters	at least 1 at least 1 flow split

The user manual for IMPULSE is provided in **Appendix A.**

3.5 Conclusion

In this chapter, IMPULSE, a computer program for residence time modelling, is introduced. IMPULSE allows quantitative flow modelling of the process from experimental data, provided the user has some knowledge of the process, and of typical model residence time responses. There are limitations to IMPULSE, of which the user should be aware. One of the critical limitations is the need for good experimental data, without which a flow model is not representative of the real process.

CHAPTER

FOUR

Applications of IMPULSE

4.1 Introduction

In **Chapter 3**, a computer program for residence time modelling, IMPULSE, was introduced. From tracer test data, the flow model of a system can be quantitatively determined. The process can then be assessed using the flow model. In this chapter, the flow models of some water and waste water treatment processes are determined using experimental data. The experimental method for each process is outlined. Each experiment is discussed, and recommendations for future work on the processes given.

The objectives of this chapter are:

(i) to illustrate the use of residence time distribution and IMPULSE for the flow modelling of some water and waste water treatment processes.

(ii) to illustrate some of the pitfalls in residence time distribution analysis, and the importance of understanding the significance of the results.

(iii) to show the potential of the modelling approach for indicating possible changes for performance improvement.

(iv) to illustrate the technique of combining the flow model of a process with the known kinetic model to determine the effect of improvements on reaction yield.

4.2 Experiments on an anaerobic digester

Experiments were performed on an anaerobic digester at Durban Corporation's Northern Waste Water Treatment Works.

4.2.1 *Introduction to anaerobic digestion and anaerobic digesters*

Anaerobic digestion is typically the first or second process treating the sludge from the primary clarifiers in waste water treatment works. Waste water, composed of water and solid waste, is separated in the primary clarifiers into clarified water and sludge. The clarified water typically goes for aerobic biological treatment, and the sludge goes to the anaerobic digesters, often after passing through a concentration process. Anaerobic digestion aims to stabilise the sludge by decomposing the organic matter to methane and carbon dioxide.

Anaerobic digestion of the organic matter in the sludge takes place in the digesters by anaerobic bacteria. The kinetics of anaerobic digestion are complex, involving *... the consequences of intertwined populations with dynamic biochemical behaviour* ... (Harper and Suidan, 1991). Gujer and Zehnder (1983) identify six different conversion processes in the anaerobic digestion of raw domestic sludge. They conclude, however, that the overall particle decay or digestion may be described by first order kinetics. Eastman and Ferguson (1981) also note that a first order kinetic equation represents the cumulative effect of the processes occurring in the digester. The first order kinetic model given by Gujer and Zehnder (1983) is :

$$r = k_p \cdot S$$

where r is the specific rate of particle solubilisation, k_p is the first order rate decay constant for the net decay of biodegradable particulate organic material in the anaerobic digestion of domestic sludge, and S is the biodegradable substrate concentration.

Values of k_p determined by several authors are given in Gujer and Zehnder (1983). The biodegradable substrate concentration (S) is measured as the chemical oxygen demand (COD) of the sludge. Anaerobic digestion reduces the COD to a required level.

Anaerobic process efficiency, E , is defined by Parkin and Owen (1986) as :

$$E = \frac{S_0 - S}{S_0} \cdot 100\%$$

where S_0 is the influent COD.

The efficiency of anaerobic digestion is significantly affected by the mixing in the anaerobic digester (Verhoff et al., 1974). Mixing is required to ensure contact between the bacteria and the substrate and to ensure a uniform environment exists in the digester. (Monteith and Stephenson (1981) indicate that inadequate mixing and poor utilization of volume may jeopardize the stability of product sludge. The design of digesters usually specifies that the contents be ... *completely mixed* ... (Baumann and Huibregtse, 1982). Mosey (1974) states that ... *the importance of proper mixing of digester contents cannot be over-emphasised* ....

Anaerobic digesters are often, however, reported to have poor mixing, with the US EPA (1987) reporting an average active mixing volume of 55 %. This has implications for the efficiency of the operation and formation of a desired product, and will lead to the overdesign of digesters to overcome this problem, with concurrent increases in capital cost.

4.2.2 *Residence time distribution studies of anaerobic digesters*

It is necessary to determine the active mixing volume in a digester and to improve on the mixing if required. Residence time distribution is one technique that can be used to find the extent of mixing in anaerobic digesters. From the residence time distribution it is possible to establish the extent of mixing, by-passing and recycling in a process. The residence time distribution curve can also be used to predict a flow model for a process, including flow parameters, and may indicate where improvements can be made. Further, the microbial kinetics can be incorporated into the flow model to predict the overall performance of the digester and the implications of improved mixing.

The concept of residence time distribution has previously been used to identify mixing problems in anaerobic digesters : Tenney and Budzin (1972) determined the active mixing volume of a digester as 50 %; the aqueous and solids phases in a digester were traced and evidence of short-circuiting was found (Rundle and Whyley, 1981); Heertjes and Van der Meer (1978) distinguished three parts in an upflow anaerobic digester from tracer experiments.

Tracers

Tracers used in previous residence time studies of anaerobic digesters include fluoride (Monteith and Stephenson, 1981; Tenney and Budzin, 1972), tritium and gold-98 for aqueous and solids phases (Rundle and Whyley, 1981) and lithium (Grobicki and Stuckey, 1992; Heertjes and Van der Meer, 1978).

This study used two tracers for tracing anaerobic digesters : lithium (as lithium chloride) and sodium (as sodium chloride). The tracers chosen require no specialised detection equipment and are relatively inexpensive. Grobicki and Stuckey (1992) report that lithium does not absorb onto sludge particles. The tracers chosen were not toxic to the digestion process. A study by De Baere et al. (1984) on tannery waste water showed that initial inhibition of digestion occurred at sodium chloride concentrations of 30 g/l; the current study used concentrations less than 1 g/l. Lithium concentrations exceeding 20 mg/l lithium in the final solution may be toxic to anaerobic digestion processes (Anderson et al., 1991); the current study used concentrations of less than 0,1 mg/l.

Tracer addition

Two methods of tracer addition to anaerobic digesters are outlined by Tenney and Budzin (1972) : uniform distribution of the tracer by stopping sludge withdrawal during mixing, and tracer addition to the feed stream during normal operation.

In the first method, normal sludge withdrawal is restarted when the tracer concentration in the process is uniform. The wash-out of the tracer is monitored in the effluent stream. This method does not indicate a deviation from perfect mixing, besides the presence of dead space. A large number of sample points is necessary to determine when the tracer concentration is uniform, before restarting sludge withdrawal.

In the second method, the tracer concentration in the effluent stream is monitored continuously from the time of tracer addition to the influent stream. All deviations from perfect mixing may be determined.

4.2.3 Experiments at Northern Waste Water Treatment Works

Introduction

Durban Corporation's Northern Waste Water Treatment Works (Northern WWTW) uses two primary anaerobic digesters (Digesters 1 and 2) to treat sludge from their primary and secondary clarifiers. The staff operating the digesters have noticed that the performance of the digesters decreases gradually until, after a number of years of operation, they can no longer process the sludge produced. The digesters are then shut down and opened, and accumulated grit and fibre is manually dug out. The reason for the grit and fibre accumulation may be

imperfect mixing in the digesters. Flow modelling of the digesters will indicate any deviations from perfect mixing and if any changes can be made to improve the mixing.

The aims of these experiments were :

(i) to determine a flow model for Digester 1.

(ii) to determine the deviation from perfect mixing in Digester 1.

(iii) to analyse the performance of Digester 1 using both the flow model and a combination of the flow model and kinetic model.

Experimental results from previous studies were used together with data collected for this study.

The plant

Northern Waste Water Treatment Works

Durban Corporation's Northern WWTW is situated approximately 15 km north of Durban and treats wastewater from both industry and the residents of Durban. Treated effluent is discharged to the Umgeni River.

Raw waste water enters Northern WWTW and is screened before entering the primary clarifiers. The overflow water is treated in an activated sludge plant and then enters secondary clarifiers for further separation. The overflow from the secondary clarifiers goes through a series of ponds before being chlorinated and discharged to river.

The sludge from the primary clarifiers goes to thickeners. The sludge from the secondary clarifiers goes to the dissolved air flotation plant. The treated sludge from both of these processes forms one stream that is fed to one of two primary anaerobic digesters. Digested sludge from the digesters goes to smaller secondary digesters before being dewatered and spread on land.

The primary anaerobic digesters

Figure 4.1 is a diagram of the primary anaerobic digesters.

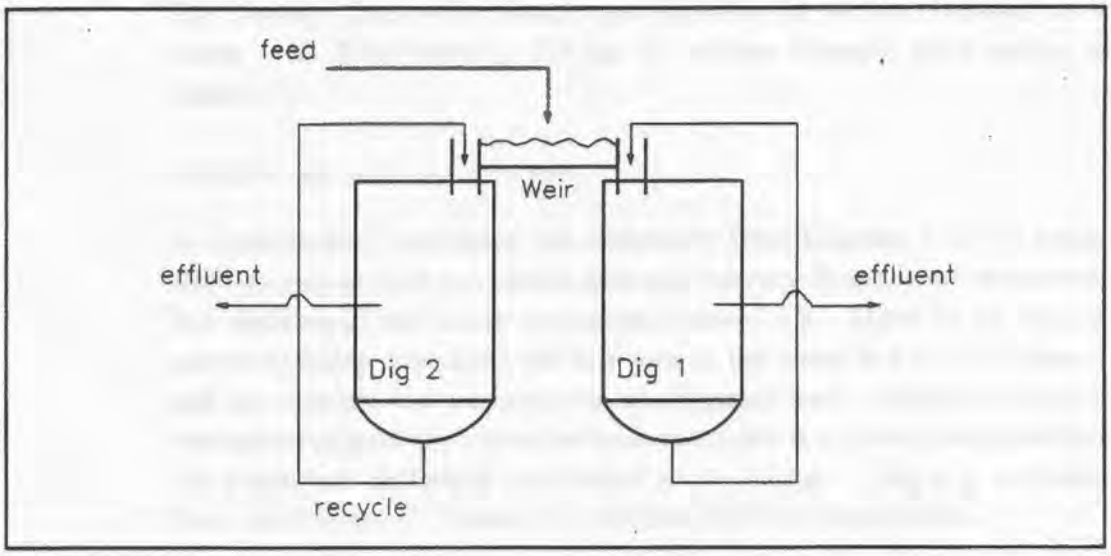


Figure 4.1 : *Diagram of the anaerobic digesters at Northern WWTW : not to scale*

The feed to the digesters is split to each digester after the flow is measured. Each digester has an external pumped recycle to assist mixing of the digester contents. The working volume of the digesters was 2 500 m^3 in 1985 and 2 300 m^3 in 1992.

Method

Two experiments were performed for the present study : Experiment 2 traced Digester 1 in March 1992 and Experiment 3 traced Digester 1 in October 1992. A previous study by the Durban Corporation traced Digester 1 in June 1985 (Experiment 1, Vissers, 1985). All details of the experimental method and results obtained for Experiment 1 are from Vissers (1985).

Tracers used

In the present study, sodium (as sodium chloride) was used as a tracer. The background level of sodium ranged between 30 and 80 mg/l. In Experiment 2, 1 200 kg of sodium chloride were added to Digester 1. The amount of sodium chloride to be added was calculated to give a sodium concentration of approximately 200 mg/l above background, assuming the digester is perfectly mixed. In Experiment 3, 800 kg were added to Digester 1.

The Durban Corporation study used fluoride (as sodium fluoride) as a tracer. In Experiment 1, 150 kg of sodium fluoride were added to Digester 1.

Addition and sampling of tracer

In Experiment 2, no sludge was withdrawn from Digester 1 during tracer addition and no feed was added, although the recycle continued to operate. The addition of the tracer took approximately 6 h. Three 50 kg bags of sodium chloride were dissolved at a time in tap water in a 1 m^3 container, and the solution was pumped into the digester feed. Sludge withdrawal was started once all the tracer had been added and it was not known whether the tracer was uniformly distributed in the sludge. This is a deviation from the method of Tenney and Budzin (1972) outlined above.

The recycle was sampled during tracer addition and hourly for 24 h thereafter. Samples from the bottom draw-off were taken hourly for 48 h after the start of sludge withdrawal, then twice daily for a week, and then daily for 20 d. Feed samples were taken daily. The bottom draw-off of Digester 2 was sampled daily to provide a background reading. The combined draw-off of both digesters was sampled daily to provide an indication of the relative flows to the digesters. The total flow to both digesters was noted.

In Experiment 3, sludge withdrawal was not stopped during tracer addition. The tracer was added in the same way as for Experiment 2, and was added over 3 h.

Samples of the combined feed, the bottom draw-off of Digester 1 and the combined draw-off of the digesters were taken. Samples were taken hourly during tracer addition and for two hours thereafter, and then daily.

In Experiment 1, sodium fluoride was dissolved in water and added to the feed to Digester 1 over 5 h. Sludge withdrawal was stopped during tracer addition and restarted 1 h after tracer addition had finished. Samples of the draw-off (it is not clear whether the top or bottom draw-off was used) were taken hourly for 24 h after addition, then 8 hourly for 3 d, and then daily for 50 d.

Tracer analysis

In Experiments 2 and 3, the samples were allowed to stand for a week or more so that the sludge settled to the bottom of the sample bottles. Using a syringe filter with 0,3 μm filter paper, approximately 10 ml supernatent was drawn from the sample. This was accurately diluted where appropriate, and analysed on an atomic absorption spectrophotometer operating in absorption mode. **Appendix B** gives the equipment details.

Results

Visual observations

No visual observations could be made as the digesters are closed processes.

Experimental response

The effluent tracer concentration data for Experiments 1 to 3 are presented in Figure 4.2. The raw data for Experiments 2 and 3 are in **Appendix D**.

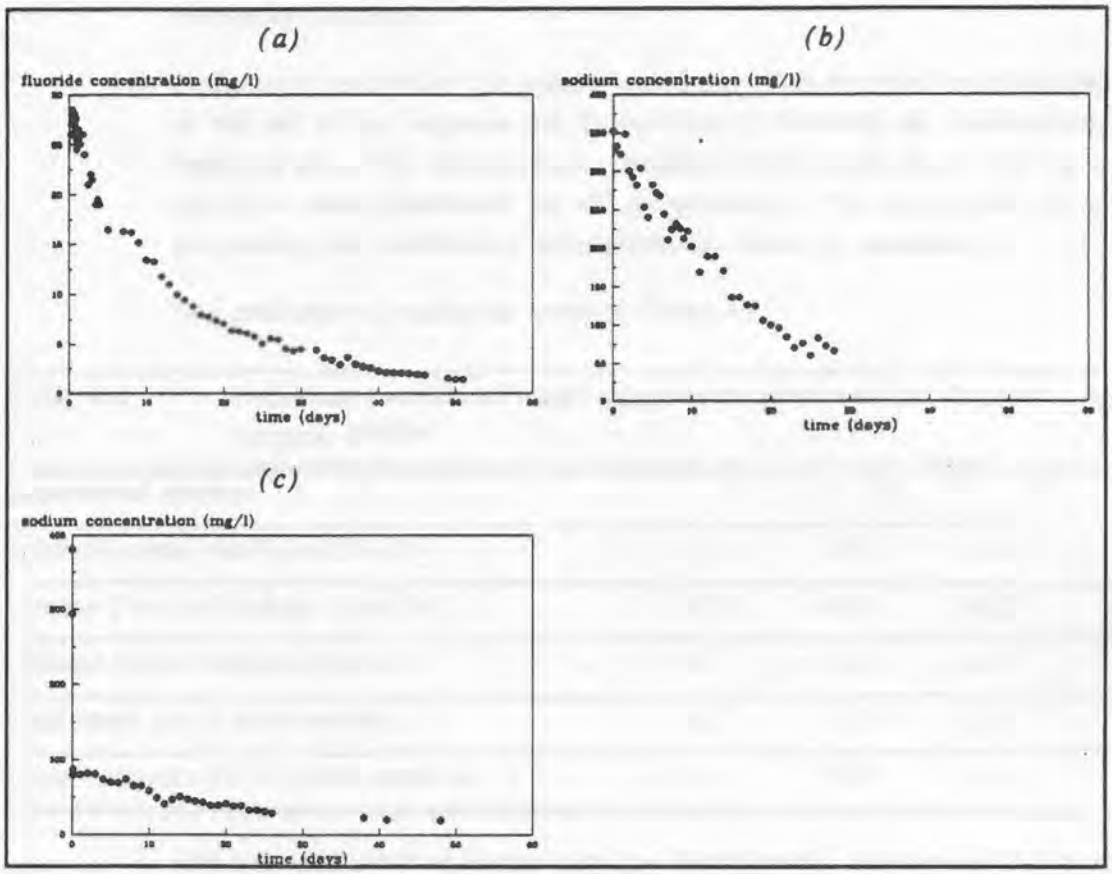


Figure 4.2 : *Results of tracer tests on Digester 1 at Northern WWTW ; concentration-time data, outlet tracer concentration : (a) Experiment 1 (1985) ; (b) Experiment 2 (March 1992) ; (c) Experiment 3 (October 1992)*

Experiment 1 shows an exponential response, typical of a mixed flow process. No deviations from this behaviour, such as a bypass, can be seen. This may be due to the experimental method, where sludge withdrawal was stopped during tracer addition. Experiment 2 also shows an exponential response, although sampling was stopped too early. Again, no sludge was withdrawn during tracer addition, and thus no other deviations can be seen. In Experiment 3, sludge withdrawal was continued during tracer addition, and a bypass (spike of tracer leaving early) can be seen. The remainder of the response shows exponential behaviour.

Preliminary analysis

Preliminary analysis of the results was done. This involved extrapolation of the tail of the response for Experiment 2, assuming an exponentially decaying tail. The realised mean residence time, dead space, and tracer recovery were determined for all experiments. The steps involved in performing the preliminary calculations are given in **Appendix C.**

The preliminary results are given in Table 4.1.

Table 4.1 : *Preliminary results of tracer experiments performed on Digester 1 at Northern WWTW*

Experiment number	**1**	**2**	**3**
potential mean residence time (d)	17,5	38,1	36,1
average flow to Digester 1 (m^3/d)	142,6	60,4	63,7
realised mean residence time (d)	14,7	15,3	35,1
dead space (% of total volume)	16,1	59,7	2,9
tracer recovery (% of tracer mass in)	81,4	70,9	50,1

The potential mean residence time for Experiment 1 is about half of that for Experiments 2 and 3. This is due to the difference in flow to Digester 1, where the flow in 1985 (Experiment 1) was more than twice that in 1992 (Experiments 2 and 3). This appears to ensure a lower dead space when Experiment 1 is compared only with Experiment 2 (16 % compared to 60 %). This hypothesis is reasonable too, as a higher flow may "force" sludge into volume not used at a lower flow. However, the results of Experiment 3 do not bear this out, as the dead space is only 3 %, and the flow is low. The tracer recovery for Experiment 3 is low (50 %) and the results should probably be discarded on this basis. The appearance of a bypass (from the experimental response) may be significant qualitatively, but may not be quantitatively meaningful due to the poor tracer recovery.

Flow modelling

The shape of the tracer response was examined qualitatively. This, combined with a knowledge of the physical process, assisted in the choice of a flow model or flow models for each digester that would reasonably represent the process. IMPULSE was then used to determine parameters of the flow model chosen.

Examining the experimental response

The responses indicate that the digesters operate as perfect mixers. This appears reasonable as they are designed to operate as such. The existence and amount of dead space cannot be determined by qualitatively examining the curve. This can only be determined as the difference between the sum of the volume or volumes for the flow model regions and the known volume of the digester. Experiment 3 indicates that there may be some bypassing of Digester 1.

Using IMPULSE to model the process

IMPULSE was used to model the processes. This was done by regression on the tracer response curve using the parameters of the defined models. The parameters were estimated from a knowledge of the process and were adjusted manually at first without regression on the tracer response. This shortens the computing time of the program as the model response (using the model parameters) can be adjusted to fit the tracer response more closely. The time spent regressing on the tracer response is therefore shorter. The regressed parameters and an objective (the sum of square errors) are the results of the regression.

For all three experiments, a perfect mixer with dead space was chosen as a realistic flow model for flow modelling. A number of other models were tested, however, for the different experiments. For Experiments 1 and 2, a tanks-in-series model was tested, and for Experiment 1, two perfect mixers in parallel were tested. For Experiment 3, a bypassed perfect mixer was tested.

The models chosen are shown in Figure 4.3.

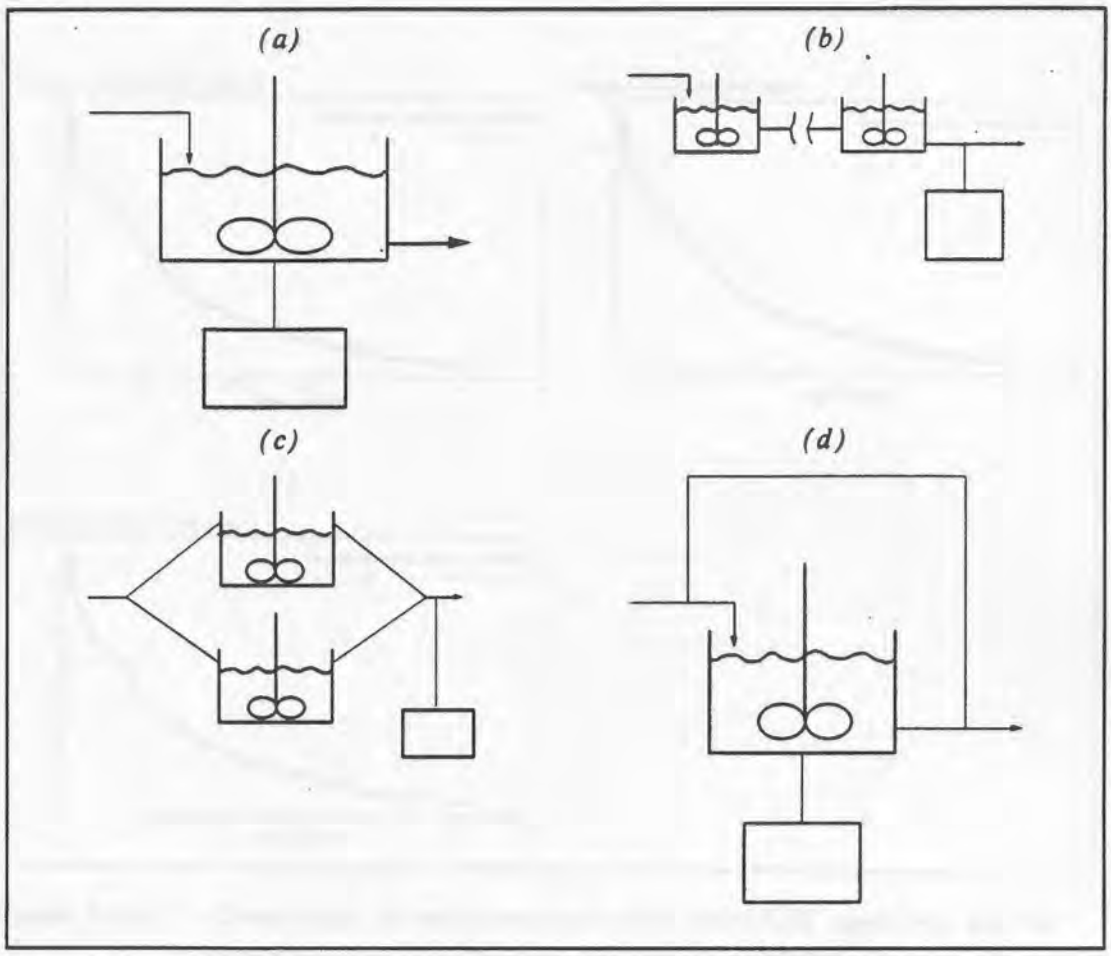


Figure 4.3 : *Models chosen for IMPULSE modelling of Digester 1 at Northern WWTW : (a) a perfect mixer with dead space (Experiments 1, 2 and 3) ; (b) a tanks-in-series model with dead space (Experiments 1 and 2) ; (c) two perfect mixers in parallel, with dead space (Experiment 1) ; (d) a perfect mixer region with bypass and dead space (Experiment 3 only)*

The tracer response is compared to the model response for each case in Figure 4.4(a), Figure 4.4(b) and Figure 4.4(c).

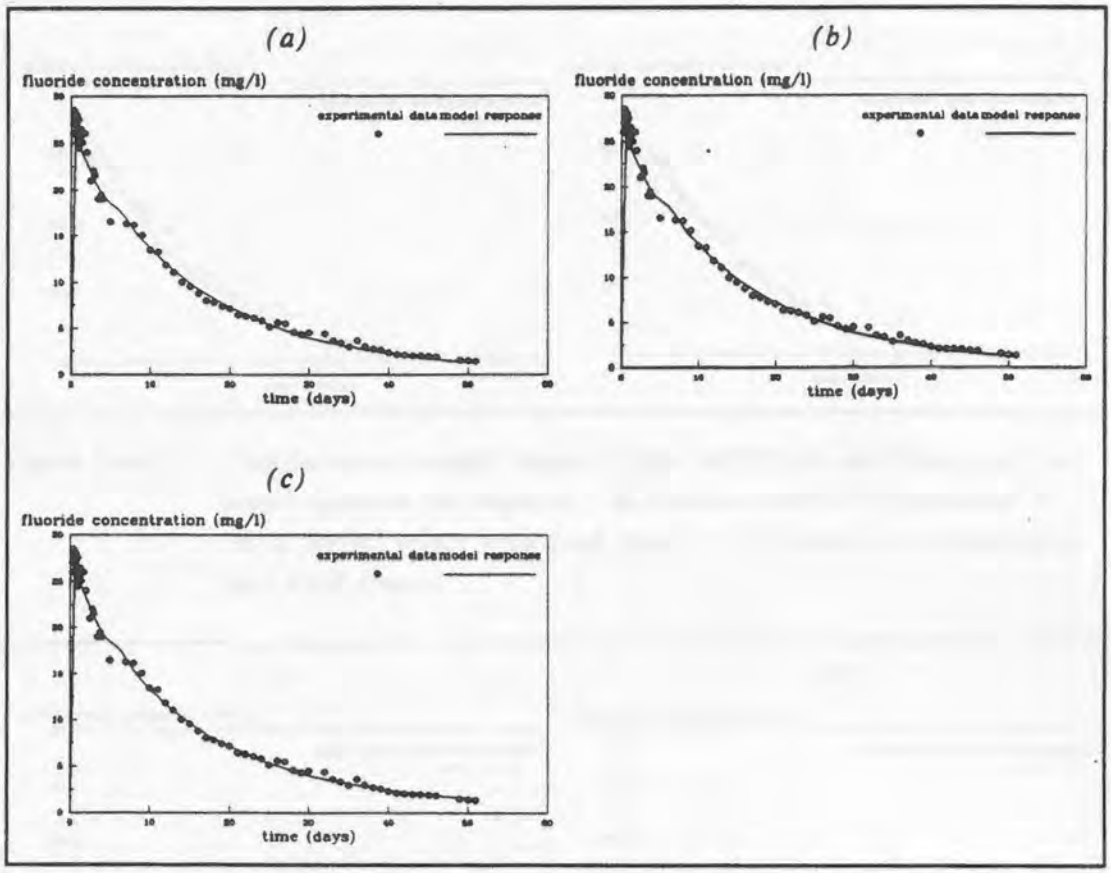


Figure 4.4(a) : *Comparison of model response after IMPULSE modelling and the tracer response for Digester 1 at Northern WWTW (Experiment 1) : (a) a perfect mixer with dead space ; (b) a tanks-in-series model with dead space ; (c) two perfect mixers in parallel, with dead space*

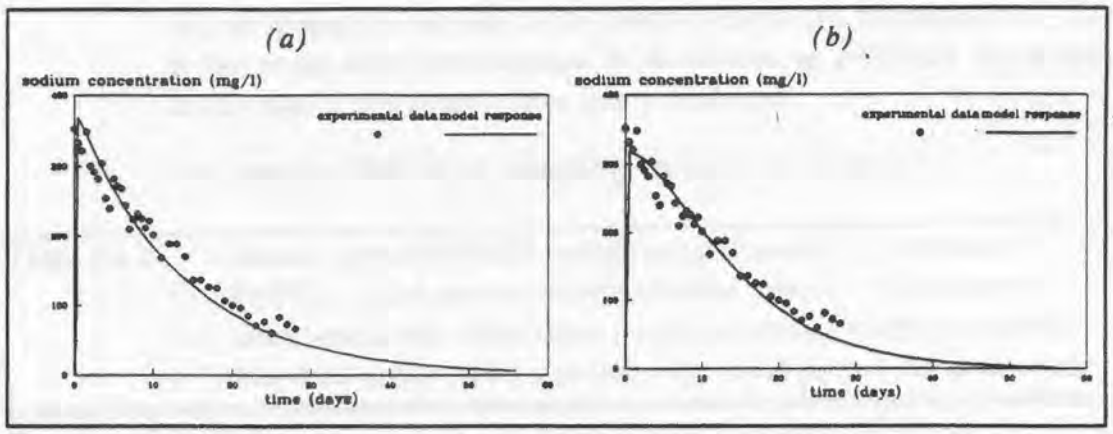


Figure 4.4(b) : *Comparison of model response after IMPULSE modelling and the tracer response for Digester 1 at Northern WWTW (Experiment 2) : (a) a perfect mixer with dead space ; (b) a tanks-in-series model with dead space*

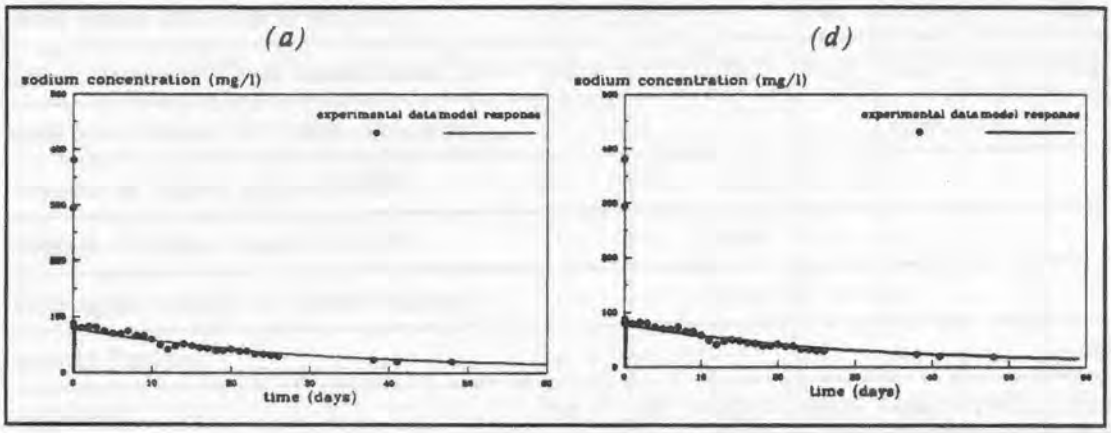


Figure 4.4(c) : *Comparison of model response after IMPULSE modelling and the tracer response for Digester 1 at Northern WWTW (Experiment 3) : (a) a perfect mixer with dead space ; (d) a perfect mixer with bypass and dead space*

From visual observation of the response comparisons, in all cases the simplest model, that of a perfect mixer with dead space, (a), appears to fit the data well. For Experiment 2, however, the tanks-in-series model, (b), appears to fit the data better. The parallel perfect mixers, (c), appears to fit the data of Experiment 1 the best. In the bypassed perfectly mixed flow region,

(d), no bypass can be seen in the model response for Experiment 3. This is due to the short time duration of the bypass, as IMPULSE has a limit on the size of the discrete time intervals chosen.

The results of IMPULSE modelling are given in Table 4.2.

Table 4.2 : *Results from IMPULSE modelling of Digester 1 at Northern WWTW : (a) a perfect mixer with dead space ; (b) a tanks-in-series model with dead space ; (c) two perfect mixers in parallel. with dead space ; (d) a perfect mixer with bypass and dead space*

Experiment number	**1**			**2**		**3**	
Model number	**a**	**b**	**c**	**a**	**b**	**a**	**d**
potential mean residence time (d)	17,5			38,1		36,1	
realised mean residence time (d)	16,1	16,1	18,7	13,6	11,8	33,4	33,4
dead space (% of total volume)	8,2	8,2	-	64,3	69,0	7,5	7,5
tracer recovery (% of tracer mass in)	90,4	90,3	92,8	64,5	62,3	50,2	45,7
number of tanks for tanks-in-series	-	1	-	-	1,49	-	-
volume of mixed region 1 (m^3)	-	-	1812	-	-	-	-
volume of mixed region 2 (m^3)	-	-	850	-	-	-	-
flow split fraction to mixed region 1	-	-	0,5	-	-	-	-
bypass fraction	-	-	-	-	-	-	0,003
objective	18	18	82	5615	4641	1142	1206

Comparison of the perfect mixer results, (a), with the preliminary results given in Table 4.1 indicates the difference between using actual flows to model the data, and average flows. In determining the preliminary results, a perfect mixer is assumed, but an average flow is used to determine the active mixing volume, the mean residence time and dead space. When modelling with IMPULSE, discrete time-flow data was used to determine the active mixing volume. The average flow is then used to determine the realised mean residence time from the active mixing volume. For Experiment 1, the dead space calculated using an average flow was 16,1 %, and using time-flow data, was 8,2 %. For Experiments 2 and 3, the dead space determined using time-flow data was larger than that determined

using average flows (64,3 % compared to 59,7 %; 7,5 % compared to 2,9 %). There is thus a significant difference between results obtained using average flows and those obtained using actual flows. In a process that has varying flows, therefore, it is important that the actual flows are used for modelling the process. This is possible using IMPULSE.

The tracer recovery for Experiment 1 is good, but the recovery determined by using IMPULSE is not good for Experiments 2 and 3. In Experiment 2, this is not due to the lack of later samples, as IMPULSE can be used to extrapolate data and tracer recovery.

The bypass fraction for the bypassed perfect mixer, (d), for the data of Experiment 3, is very small (0,003), and is not significant enough to show in the model response.

The objectives are useful for the models of Experiments 2 and 3, where the lower objective indicates a better model fit. For Experiment 1, the objectives are the same for two of the models. This is because they are essentially the same model, as the tanks-in-series model regressed to a single perfect mixer. The objective for the parallel perfect mixers is much larger, even though visually the fit appears the same or better. The active mixing volume is, however, larger than the actual volume, and the model is therefore not realistic.

Kinetic modelling

As the perfect mixer model appears reasonable for modelling the experimental data, it was used for kinetic modelling of the data. Kinetic data for Experiment 1 was not available.

For the perfect mixer model, a mass balance yields

$$\frac{S}{S_0} = \frac{1}{1 + k_p \cdot \bar{t}}$$

where :

S	=	effluent COD
S_0	=	influent COD
k_p	=	reaction constant
$\bar{t}$	=	mean residence time of active mixing zone

The first order reaction constant, k_p, predicted by Imhoff and Fair in 1956 (as given in Gujer and Zehnder, 1983) is 0,125 at the operating temperature of the digester (25 °C).

In order to check the accuracy of the kinetic model, the mean residence time of the system was predicted using influent and effluent COD concentrations from plant records. This was compared to the mean residence time predicted from the flow model. The results are in Table 4.3.

Table 4.3 : *Comparison of the predicted mean residence time using the kinetic model and known data from plant records, and the mean residence time determined from the flow model*

Experiment number	**2**	**3**
influent COD (mg/l)	74	100
effluent COD (mg/l)	24	26
predicted $\bar{t}$ (d) using kinetic model	16,7	22,8
$\bar{t}$ using perfect mixer flow model (d)	13,6	33,4

The value of the realised mean residence time predicted for Experiment 2 is 19 % different to that determined using the IMPULSE flow model. For Experiment 3, the value is 32 % different. These differences are significant, and may be due to poor flow modelling results. The poor tracer recovery in the flow modelling indicates that the results may not be quantitatively significant. The differences may also be attributable to the reaction constant chosen, as a number of authors have determined different reaction constants (Gujer and Zehnder, 1983). As the flow modelling residence times are smaller and larger, respectively, than the kinetic model residence times, however, another reaction constant would not satisfy both sets of data.

Another possible reason for the differences is that the plant COD data is very variable. The COD values chosen are monthly averages for the month in which the experiment was started. The yearly averages and the daily values are often significantly different to these averages.

Using the kinetic model and the potential mean residence time, the potential effluent COD was predicted. This gives the best possible COD at the process conditions, should the mixing be improved. The process efficiency and potential process efficiency can also be determined. The results are in Table 4.4.

Table 4.4 : *Comparison of the actual effluent COD and actual process efficiency with the potential effluent COD and potential process efficiency*

Experiment number	2	3
actual effluent COD (mg/l)	24	26
potential effluent COD (mg/l)	13	18
actual process efficiency (%)	68	74
potential process efficiency (%)	82	82

The process efficiency has the potential to rise by 14 % for the Experiment 2 data, and 8 % for the Experiment 3 data.

Discussion

The poor tracer recoveries for Experiments 2 and 3 indicate that the data is not quantitatively reliable. The reasons for this poor tracer recovery may be experimental error, or chemical analysis error. For Experiment 3, the tracer may have bypassed the digester quicker than the samples were taken, and a large quantity of tracer may therefore have left the digester unnoticed. In Experiment 2, the poor recovery may have been due to the short period of sampling - possibly the assumption of an exponential tail is incorrect, and the tracer leaves the digester more slowly. The experiments should be repeated and samples taken until the tracer concentration decreases to the background level.

Notwithstanding the above, the shapes of the tracer responses were reasonable for a mixed flow process. For Experiments 1 and 2, where sludge withdrawal was stopped during tracer addition, no bypass was evident. When sludge withdrawal was continued during tracer addition (Experiment 3), a bypass is evident in the first hours of tracer addition. The method of tracer addition is thus very important in order that all deviations should be determined. Flow should not be stopped during tracer addition in a continuous flow process, otherwise some deviations may be missed.

Although a number of different models were tested, the most reasonable model appears to be the perfect mixer model. This is realistic as digesters are designed to act as large perfect mixers. There is some difference between using an average flow value and using time-flow data to determined the active mixing volume. In the case of a process, such as anaerobic digestion, where the mean residence time is generally large, and the flow may change significantly with time, it is more accurate to use time-flow data. IMPULSE allows time-flow data input.

Assuming the data for Experiment 3 is the least reliable, given the poor tracer recovery, a comparison between Experiments 1 and 2 appears to indicate that the higher the flow, the lower the dead space. Experiment 3 is useful, however, as it indicates that bypassing of the digester may be a problem, and should be investigated.

The kinetic modelling requires good flow modelling data in order to yield significant results. The flow modelling data was not reliable enough to indicate absolutely the possible process efficiency improvements. Some indication is given by the data presented, however. Should good flow modelling data be available, the kinetic modelling should be repeated, and more reliable efficiencies determined.

Conclusion

A residence time experiment should be repeated on Digester 1, with particular attention paid to tracer addition and sampling. Tracer should be added during normal operation, and samples should be taken to check for any bypassing of the digester. Sampling should be continued until the concentration of the tracer has reached the background concentration. Control samples should be taken from Digester 2 to determine the background concentration. An accurate flow into Digester 1 must be known and recorded.

IMPULSE is useful for the flow modelling of residence time data, and yields an indication of data problems.

4.3 Experiment on a biofilter

The distribution and residence time of waste water in the processes of a waste water treatment plant influences the efficiency of the treatment processes. In a biofilter, the waste water is filtered past organisms that digest organic matter. The waste water must

be distributed evenly over the process and must be in plug flow to ensure even loading of the organisms. To ensure the organisms have time to process the organic matter, the biofilter must have a residence time greater than a predetermined value.

Determination of the residence time distribution of a biofilter will show whether the waste water is evenly distributed and in plug flow, as well as giving the average residence time of the waste water in the biofilter. Modelling the biofilter from the residence time distribution will show the possibility of altering the biofilter to improve its performance.

The aims of this experiment were :

(i) to determine a flow model for a biofilter.

(ii) to determine the deviation from plug flow and the mean residence time in a biofilter.

4.3.1 The plant

Umbilo Waste Water Treatment Works

Umgeni Water's Umbilo Waste Water Treatment Works (Umbilo WWTW) is situated approximately 20 km from Durban and treats wastewater from both industry and the residents of Pinetown. Umbilo WWTW discharges treated effluent to the Umbilo River. Although designed for a capacity of 10 Ml/day, at the time of the experiments they were running at 11 Ml/day.

Figure 4.5 is a diagram of the works.

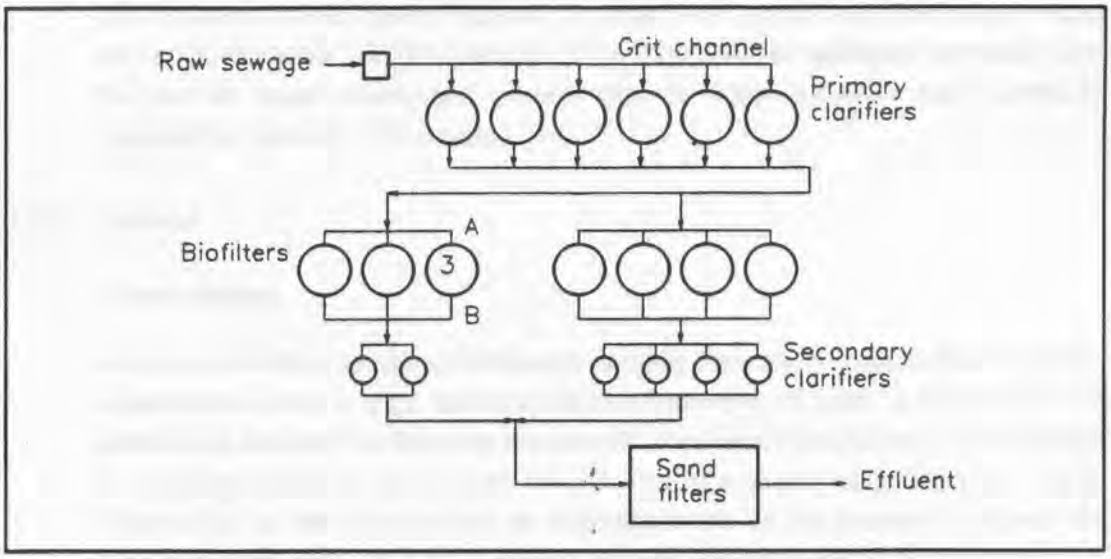


Figure 4.5 : *Diagram of Umbilo Waste Water Treatment Works, excluding sludge treatment*

The raw influent passes through a primary screen to remove large solids. Remaining heavy solids are removed in a grit channel. The water splits and enters one of six primary clarifiers. Water flows out of the clarifies over a weir at the circumference. The sludge settles to the bottom of the clarifier and is drawn off.

The flow is then split, one part goes to three biofilters, the other part goes to four biofilters. After the biofilters, the water, still split into two distinct parts, enters the secondary clarifiers. From the three biofilters the water enters one of two clarifiers, and from the four biofilters, the water enters one of four clarifiers.

The effluent from the clarifiers joins and passes through one of fourteen sand filters. Before entering the sand filters the surface of the water is sprayed with a fine spray of water. This causes foaming on the top of the water, forming scum which acts as a flotation medium. The water leaving the sand filters is chlorinated and discharged to the Umbilo River.

The biofilters

The biofilters are circular tanks of 36,35 m^3 packed with stones acting as points of attachment for organisms that digest organic matter. The water trickles from a rotating manifold over the stones and is drawn off at the bottom of the tank.

The process should ideally operate in plug flow, so all entering waste water moves through the biofilter evenly. Plug flow ensures adequate residence time for all the waste water, and ensures that no water bypasses the process by channelling through the stones.

4.3.2 *Method*

Tracer chosen

As the waste water contains continually varying amounts of organic and inorganic components, with a high background concentration of salts, a salt tracer was considered unsuitable. Radioactive tracers were considered unsafe for discharge to the river, even in trace quantities. A dye was chosen as a tracer for visual observation of the distribution, as although much of the process is closed, the distribution of the water through the rotating manifold could be observed.

Fluorescein was chosen as a readily available, easily analysed, non-toxic fluorescent dye. As the water is heavily coloured by textile effluents, a fluorescent dye would be more easily observed. The concentration of a fluorescent dye may be determined using a spectrophotometer.

Addition and sampling of tracer

Solid fluorescein dye (100,04 g) was dissolved in waste water (5 l) in a beaker. The solution was poured rapidly into the water influent to Biofilter 3 (point A on Figure 4.5), and the beaker was washed out with waste water into the flowing liquid. The time of injection was noted. Discrete samples were taken at the outlet of the biofilter for analysis.

The sampler consisted of a plastic beaker attached to a pole to dip into the flowing liquid at the exit of the biofilter (point B on Figure 4.5). The liquid samples (approximately 50 ml each) were poured from the beaker into clean sample bottles and sealed. Samples were taken every 30 seconds until the dye was observed in the effluent. Samples were then taken every 15 seconds. The sample interval was then gradually decreased as the colour became less intense.

Tracer analysis

The samples were filtered using a vacuum filter system through 0,5 μm filter paper and analysed at 490 nm on a spectrophotometer. **Appendix B** gives the equipment details.

The concentration-absorption relationship for fluorescein dye in waste water was established by the addition of known masses of fluorescein dye to measured amounts of waste water. The absorption of the measured amounts was then determined to give a relationship between absorption and concentration of fluorescein.

4.3.3 Results

Visual observations

The dye appeared in the waste water leaving the manifold of Biofilter 3 almost immediately after addition of the tracer to the inlet. The colour of the dye was fairly intense, and the dye appeared to be leaving the manifold evenly. No channelling out of the manifold was observed, and the colour decreased rapidly until no dye could be observed.

The dye could be observed in the waste water effluent from Biofilter 3 approximately six minutes after tracer addition. The colour quickly increased in intensity and then gradually decreased in intensity until the dye was no longer visible.

Experimental response

The effluent tracer concentration data for Biofilter 3 are presented in Figure 4.6. The raw data are in **Appendix D.**

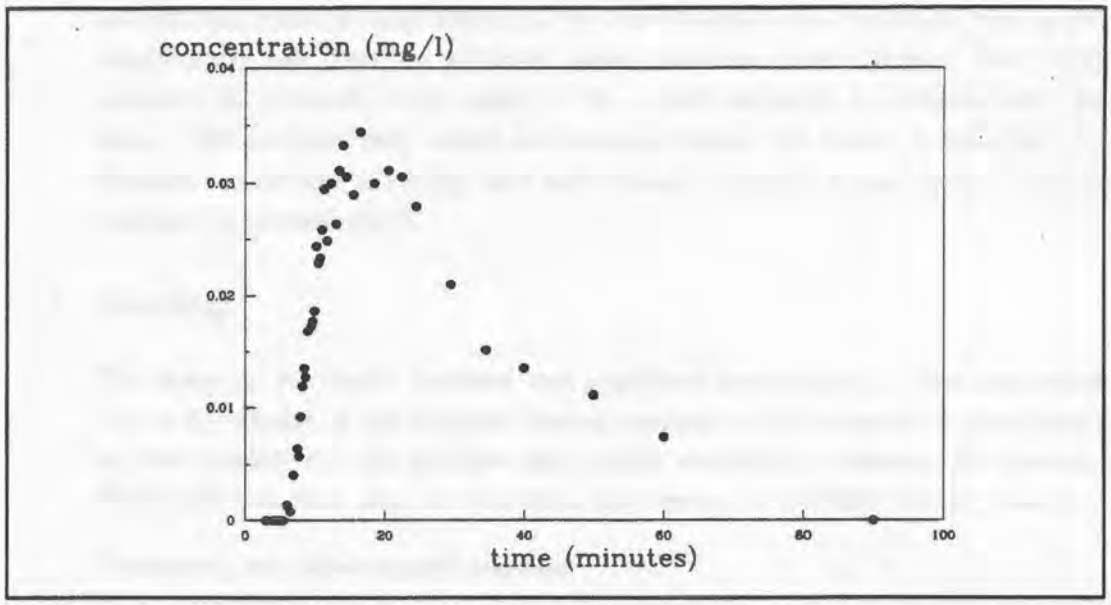


Figure 4.6 : *Results of a tracer test on Biofilter 3 at Umbilo WWTW : concentration-time data, outlet tracer concentration of fluorescein dye*

The response indicates that there was significant deviation from the expected plug flow behaviour. There was some tracer spreading, and the exponential tail of the response indicates some mixed flow behaviour.

Preliminary analysis

Preliminary analysis of the results was done prior to modelling. This involved determination of the realised mean residence time, dead space and tracer recovery. The steps involved in performing the preliminary calculations are given in **Appendix C.**

The preliminary results are in Table 4.5.

Table 4.5 : *Preliminary results of a tracer test on Biofilter 3 at Umbilo WWTW*

potential mean residence time (min)	33,4
realised mean residence time (min)	29,4
dead space (% of total volume)	12
tracer recovery (% of tracer mass in)	1

As the dead space is quite small (12 %), the realised mean residence time is not significantly less than the potential mean residence time (14 %). The tracer recovery is, however, very small, (1 %), which indicates a problem with the data. The problem may either be process-related (the tracer is adsorbed) or method-related (the sampling may have missed the bulk of the tracer). This is discused in greater detail.

4.3.4 Modelling

The shape of the tracer response was examined qualitatively. This, combined with a knowledge of the physical process, assisted in the choice of a flow model or flow models for the biofilter that would reasonably represent the process. IMPULSE was then used to determine parameters of the flow model chosen.

Examining the experimental response

The experimental response indicates that there was deviation from ideal plug flow. The response shows that the tracer was slightly delayed in leaving the process, and that it spread while in the process. The spreading was not even about a mean, however, and the tail of the response appears to be exponential. There does not appear to be any substantial channelling in the process.

Spreading of the tracer in the channel leading to the biofilter may have occurred, which would increase the dispersion of the plug flow. Given the visual observation that the all the dye appeared to leave the manifold simultaneously, however, the spreading of the tracer probably occurred in the biofilter, and not in the channel.

A model that reasonably represents the process would include some plug flow behaviour, to take the slight delay into account. The spreading of the tracer indicates that the plug flow has some axial dispersion, and can be represented by the dispersion model. The exponential tail indicates that some mixed flow behaviour is present.

Several models that could reasonably represent the process were proposed, including : a perfect mixer; tanks-in-series; a plug flow region in series with a perfect mixer; a dispersion region; a dispersion region in series with a perfect mixer.

Using IMPULSE to model the process

IMPULSE was used to model the process. The model responses and the parameters of the models proposed were found by regression against the experimental response. By using the objective, where a lower objective indicates a closer fit, as well as visual observation of the fit of the curves, the two best models were finally chosen : a dispersion region, and a dispersion region in series with a perfect mixer.

The final chosen models and the parameters of the models given by IMPULSE are in Figure 4.7.

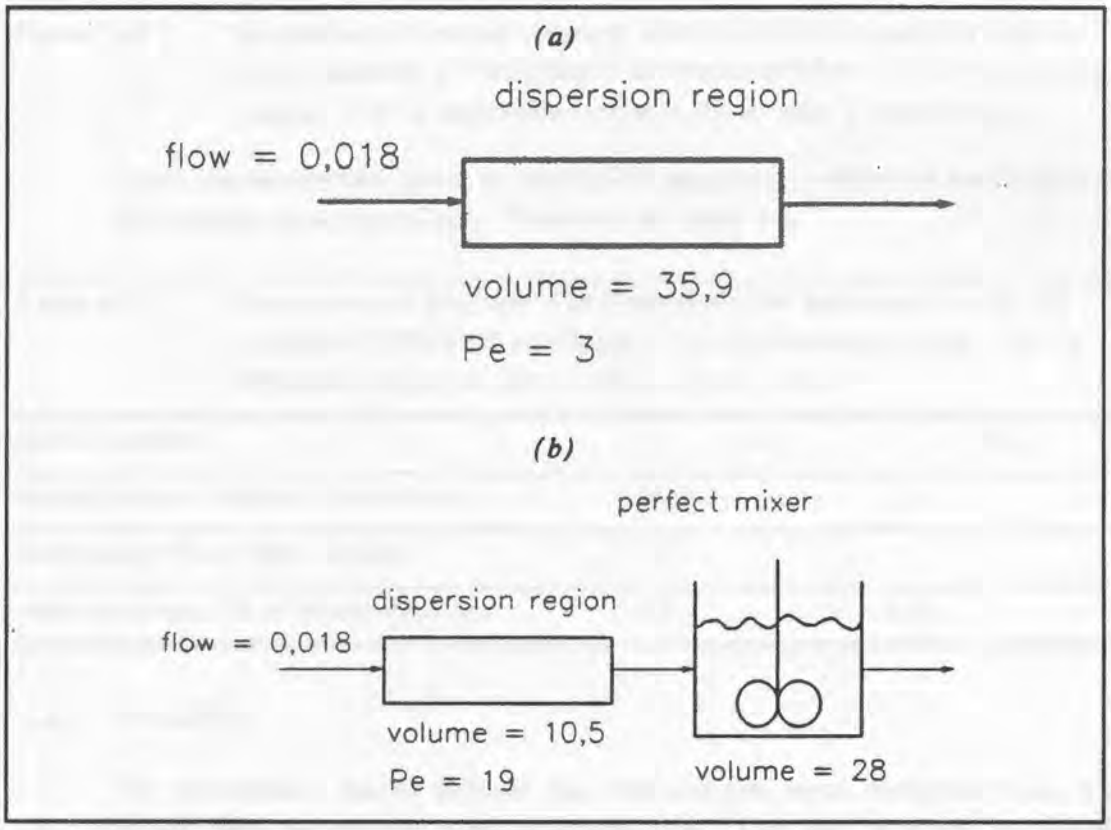


Figure 4.7 : *Models chosen and model results for IMPULSE modelling of Biofilter 3 at Umbilo WWTW : (a) a dispersion region ; (b) a dispersion region in series with a perfect mixer*

The tracer response is compared to the model response for each case in Figure 4.8.

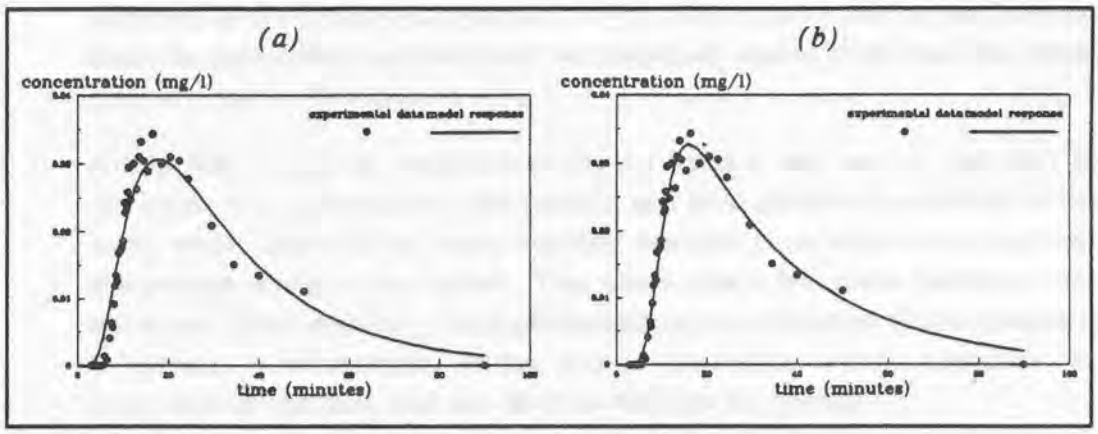


Figure 4.8 : *Comparison of model response after IMPULSE modelling and the tracer response for Biofilter 3 at Umbilo WWTW : (a) a dispersion region ; (b) a dispersion region in series with a perfect mixer*

Using the parameters given by IMPULSE modelling, additional parameters of the process were determined. These are in Table 4.6.

Table 4.6 : *Parameters of Biofilter 3 at Umbilo WWTW determined using the results of IMPULSE modelling : (a) a dispersion region ; (b) a dispersion region in series with a perfect mixer*

Model number	(a)	(b)
realised mean residence time (min)	32,9	35,5
dead space (% of total volume)	1,5	-
tracer recovery (% of tracer mass in)	1,2	1,2

4.3.5 Discussion

The preliminary results indicate that the potential mean residence time was greater than the realised mean residence time. This was, however, calculated from the total volume of the biofilter and the flow of liquid through the biofilter. Most of the volume of the biofilter is, however, packed with stones. Assuming a voidage of 0,3 for the packing, the potential mean residence time is 10 minutes. One realistic explanation for a realised mean residence time that is greater than the potential mean residence time is that the tracer is not inert and has been

absorbed in the process (Levenspiel, 1979). This is borne out by the fact that both the preliminary analysis and the modelling results show that the tracer recovery was in the region of 1 %.

A hypothesis using the explanation that the tracer is not inert is that most of the tracer was absorbed onto the packing and onto particles or bacteria in the waste water. Some of the tracer was then desorbed from its absorbent and left the process where it was traced. This would give a late mean residence time and a poor tracer recovery. The experimental response obtained, if this hypothesis is correct, is meaningless, as the rate of desorption would determine the experimental response, and not the flow through the process.

If the tracer recovery was poor, but the realised mean residence time was less than or equal to the potential mean residence time, the experimental response is only meaningful if the tracer is not adsorbed in the process. A poor tracer recovery, with realised mean residence time less than potential mean residence time may indicate that some of the tracer bypasses the process, but the rest of the tracer is adsorbed.

Another explanation for a realised mean residence time that is greater than the potential mean residence time is that the volume or flow of the process was measured incorrectly. The total volume of the process is known accurately. Even using a voidage of 0,7 for the packing (which is highly unlikely by observation of the packing) gives a potential mean residence time of 23 minutes, which is still smaller than the realised mean residence time. The flow through the process is not measured explicitly, and may be a source of error. However, the flow would have to be in error by about 67 % to increase the potential mean residence time to the point at which it is greater than the realised mean residence time.

4.3.6 Conclusion and recommendations

Due to the inaccuracy of the results, no true model for the process can be proposed, and the parameters of the process cannot be determined. So although the experimental response appears reasonable in shape, and the models found appear likely for the process, no conclusions can be drawn as to the efficiency of the process.

It is recommended that the experiment be repeated using a tracer that is known to be inert to the process. The tracer recovery should be reasonable in the experiment, and the mean residence time should not be greater than the potential mean residence time. The voidage of the packing in the biofilter should be determined from either theory or experiment to get a more accurate estimate of the potential mean residence time.

4.4 Experiments on a flash mixer

The Process Evaluation Facility at Umgeni Water's Wiggins Water Treatment Works (Wiggins WTW) has a small-scale water treatment works, the Water Treatment Evaluation Unit, that incorporates most of the processes occurring in a full-size water treatment plant. Raw water from the head of the full-size works is piped to the small-scale works so different treatment chemicals can be tested without disruption of the full-size works. A direct comparison of treatment performance between the small-scale and full-size works can be made, as the raw water is used simultaneously.

This is only true, however, if the small-scale processes operate similarly to the full-size ones. Comparison of the flow models of small-scale and full-size processes indicates whether the flow in the processes is similar. In this study, the flow model of a small-scale flash mixer of the Water Treatment Evaluation Unit at Wiggins WTW was determined. The flow model of the full-size process was not determined.

The aims of this experiment were :

(i) to determine a flow model for the small-scale flash mixer on the Water Treatment Evaluation Unit.

(ii) to determine whether there is any bypassing of the small-scale flash mixer.

4.4.1 The plant

Water Treatment Evaluation Unit

Raw water from the head of Wiggins WTW is pumped to a 1 m^3 pre-treatment reactor, to which water treatment chemicals are added. The water then flows into the small-scale flash mixer, approximately 3 m below the reactor. The water leaves this vessel and enters a pulse column to which a vacuum is applied to draw water into a pulsating sludge blanket clarifier. The overflow from the clarifier goes through a sand filter and exits the process.

Small-scale flash mixer

The flash mixer is required to mix treatment chemicals and influent water immediately and intensely. One of the parameters characterising the mixing in a flash mixer is the mean residence time, τ. The determined mean residence time should be equal to the specified mean residence time (dependent on the volume of, and flow through, the flash mixer). This indicates that there is no dead space in the flash mixer.

Figure 4.9 is a diagrammatic representation of the small-scale flash mixer.

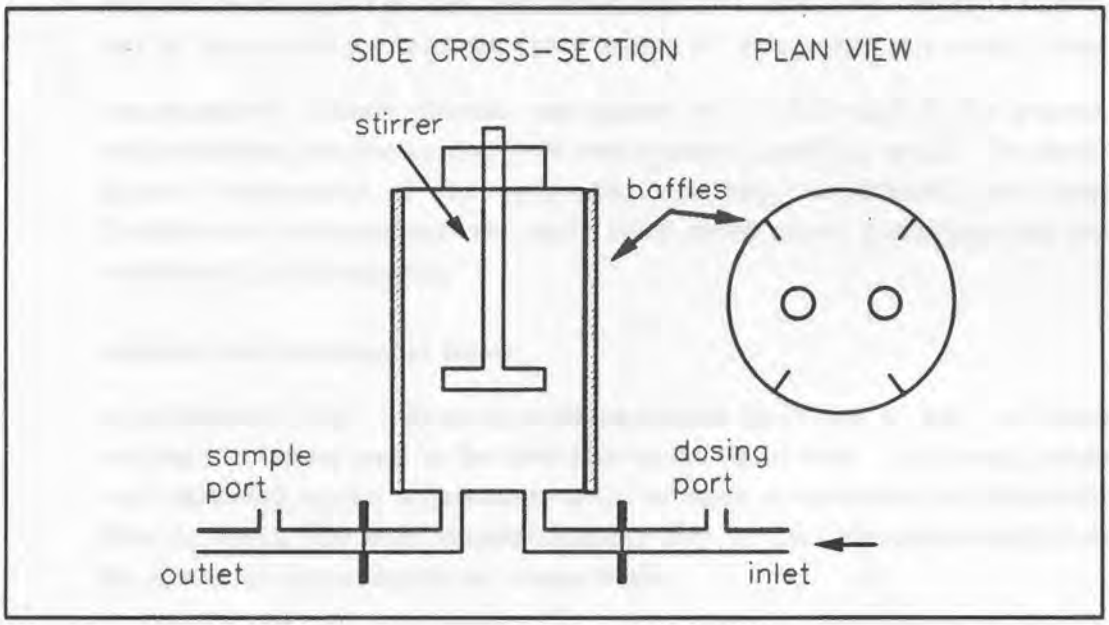


Figure 4.9 : *Diagrammatic representation of the small-scale flash mixer : not to scale*

The volume of the flash mixer is 167 l and the mixer is filled with water under the head from the pre-treatment reactor. The volumetric flow of water through the flash mixer can be adjusted. The inlet and outlet points are in close proximity. The Tracer is pumped by a dosing pump from a 1 m^3 tank to a dosing port on the inlet pipe to the flash mixer.

4.4.2 *Method*

Tracer chosen

As the effluent water from the Water Treatment Evaluation Unit re-enters Wiggins WTW for treatment, the choice of tracer was restricted to a material which will not adversely affect the treatment process. A second consideration was that it should be able to be monitored on-line as the flash mixing process is very rapid. Although some radioactive tracers can be monitored on-line, radioactive tracers were considered unsafe for discharge to Wiggins WTW. Dyes, too, can be monitored on-line, but the analysis is not considered highly accurate, and as the process is closed the visual benefit of using a dye as a tracer is lost.

An electrolyte, sodium chloride, was chosen as it is non-toxic to the process, and continuous on-line conductivity measurements could be made. The background conductivity of raw water does not vary considerably over time. Conductivity measurements are easily made using simple equipment and are considered highly accurate.

Addition and sampling of tracer

A solution of 40 g/l sodium chloride was made up in one of the 1 m^3 tanks leading to a dosing port on the inlet pipe to the flash mixer. The dosing pump was calibrated so that adjustments could be made to maintain the volumetric flow to dosing flow ratio at approximately 100 : 1. This was determined to be the optimum concentration for measurement.

Two step tests were undertaken on the flash mixer : during operation the dosing pump was switched on to provide an input step-up, and off to provide an input step-down.

Tracer analysis

A measurement port was constructed on the outlet pipe to house a conductivity probe. This probe was linked to a computer that logged time and conductivity data at user-determined intervals.

Calibration curves of conductivity and salt concentration were established, and the conductivity measurements were converted into concentration-time measurements. The background conductivity was measured before the dosing pump was switched on.

4.4.3 *Results*

Visual observations

No visual observations were made.

Experimental response

The effluent tracer concentration data for the flash mixer are in Figure 4.10. The raw data are in Appendix D.

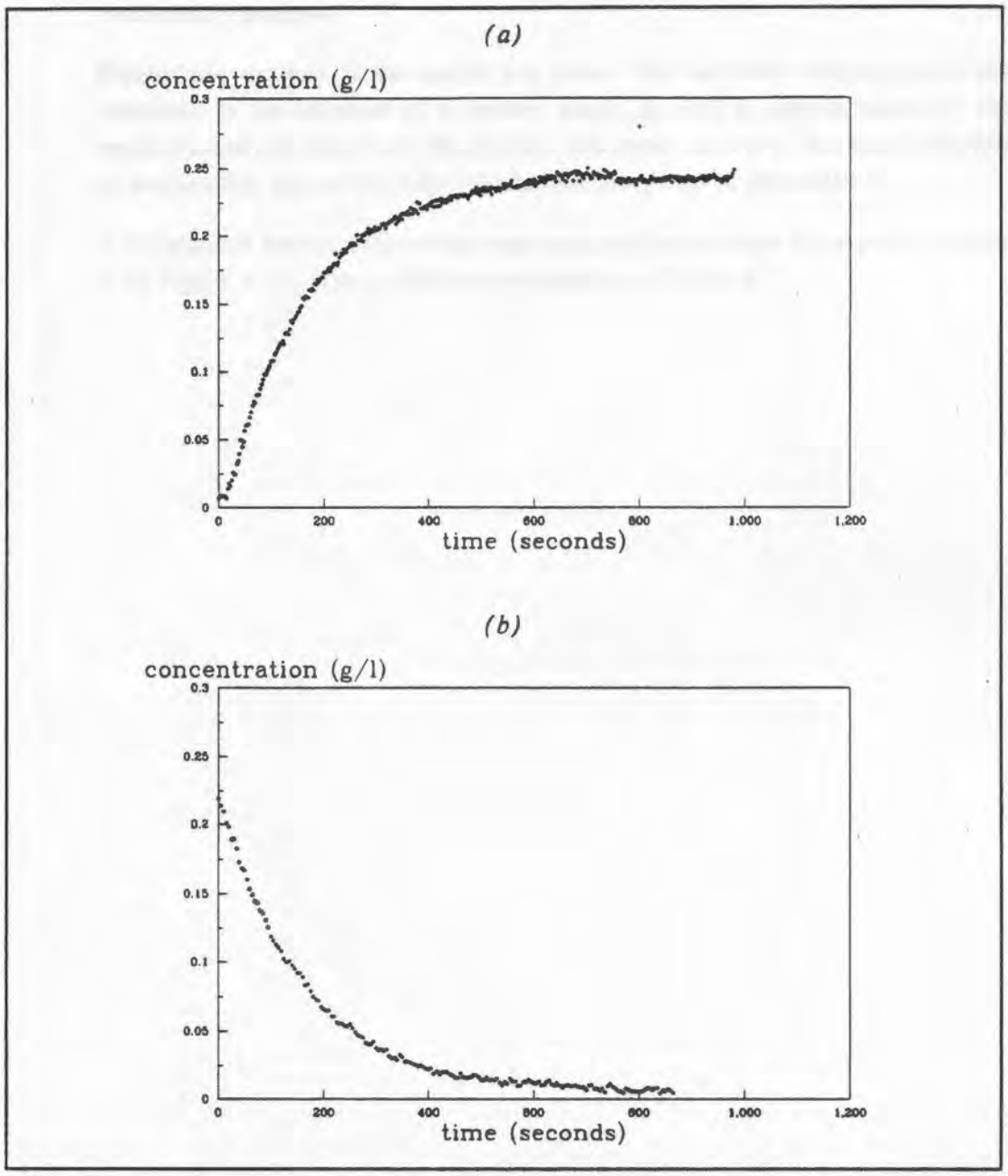


Figure 4.10 : *Results of a tracer test on the flash mixer of the Water Treatment Evaluation Unit at Wiggins WTW ; concentration-time data, outlet tracer concentration of sodium chloride : (a) a step-up test ; (b) a step-down test*

The responses look reasonable for step-up and step-down experiments on a mixed flow process. No deviations from ideal behaviour are obvious.

Preliminary analysis

Preliminary analysis of the results was done. This involved comparison of the responses to the response of a perfect mixer, as well as determination of the realised mean residence time, dead space, and tracer recovery. The steps involved in performing the preliminary calculations are given in **Appendix C.**

A comparison between the tracer responses and the response for a perfect mixer is in Figure 4.11. The preliminary results are in Table 4.7.

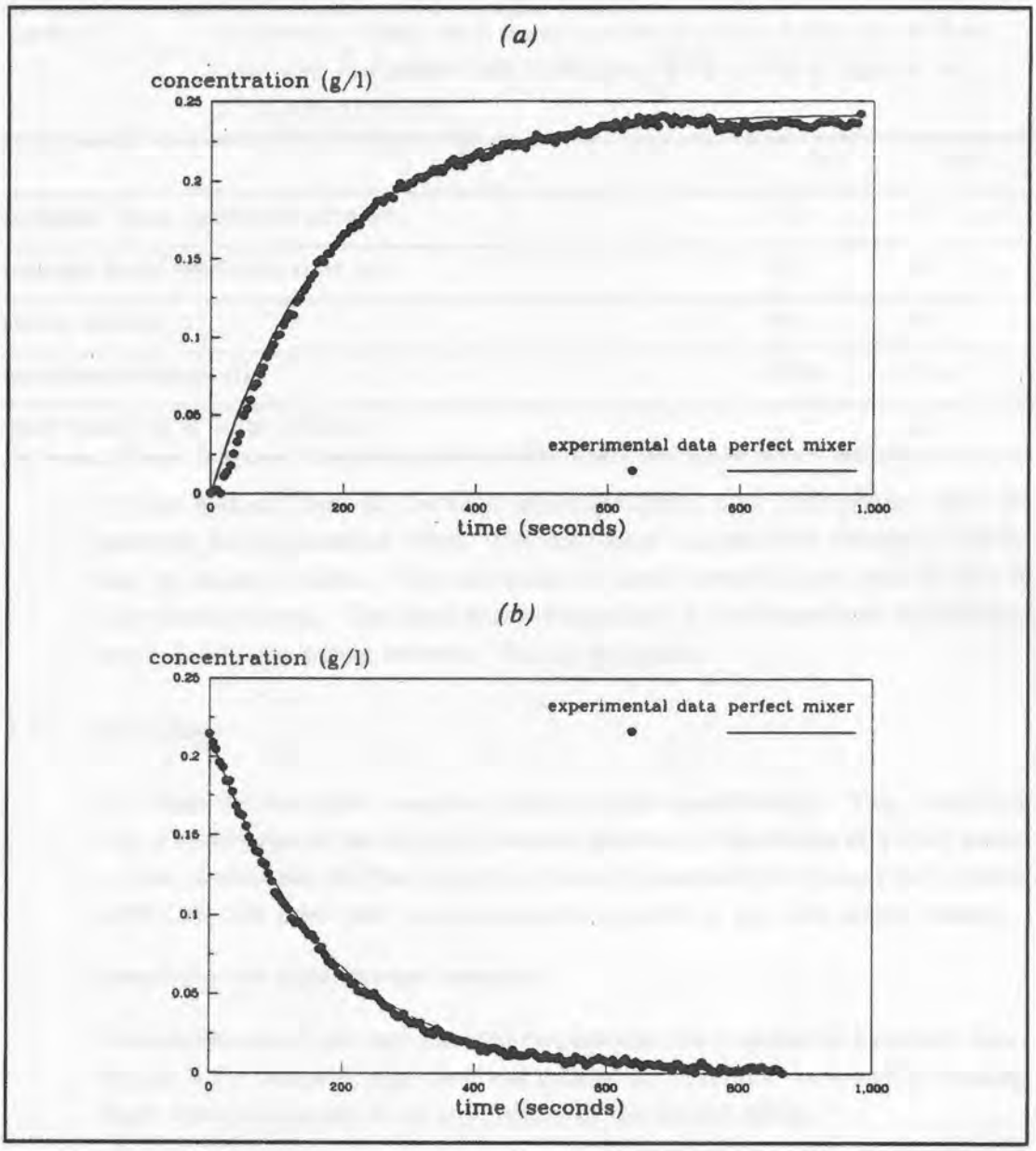


Figure 4.11 : *Comparison between the tracer responses from a tracer test on the flash mixer of the Water Treatment Evaluation Unit at Wiggins WTW and the response for a perfect mixer ; concentration-time data, outlet tracer concentration of sodium chloride : (a) a step-up test ; (b) a step-down test*

There is very little deviation between the tracer response and the response for a perfect mixer.

Table 4.7 : *Preliminary results of a tracer test on the flash mixer of the Water Treatment Evaluation Unit at Wiggins WTW : (a) a step-up test ; (b) a step-down test*

	(a)	(b)
potential mean residence time (s)	172	172
realised mean residence time (s)	184	163
actual volume (l)	167	167
calculated volume (l)	179,0	158,2
dead space (% of total volume)	-	5,2

For the step-up test, the realised mean residence time was greater than the potential mean residence time. The calculated volume was therefore greater than the actual volume. The difference is small, however, and may be due to experimental error. The dead space determined in the step-down experiment was 5,2 % of the actual volume. This is negligible.

4.4.4 *Modelling*

The shape of the tracer response was examined qualitatively. This, combined with a knowledge of the physical process, assisted in the choice of a flow model or flow models for the flash mixer that would reasonably represent the process. IMPULSE was then used to determine parameters of the flow model chosen.

Examining the experimental response

The comparison of the experimental responses to the response of a perfect mixer (Figure 4.11) indicates that there was little or no deviation from perfect mixing. There does not appear to be any bypass of the mixed region.

A model of a perfect mixer would represent the process adequately. A number of other models were tested, however, including a dispersed plug flow, tanks-in-series and a bypassed mixed flow region. The bypassed mixed flow region was not

Using IMPULSE to model the process

IMPULSE was used to model the process. As IMPULSE models data that begins at zero, the program cannot be used to model a step-down experiment. The

step-down response was thus converted into a step-up response by subtracting all concentration values from the maximum (initial) concentration. The model responses and the parameters of the model proposed were found by regression against the experimental response.

As the flash mixer is designed to be a perfect mixer, one model chosen was a perfect mixer. The second model chosen was two perfect mixers in parallel, which may represent a bypassed mixed region, provided one of the mixed regions is very small. For the step-up experiment, there was some delay in the data, indicating that there may have been a small plug flow region before the mixed flow region. This is realistic as the inlet or outlet pipes are in plug flow. The third model chosen, for modelling of the step-up data, was a plug flow in series with a mixed flow. The models chosen are shown in Figure 4.12.

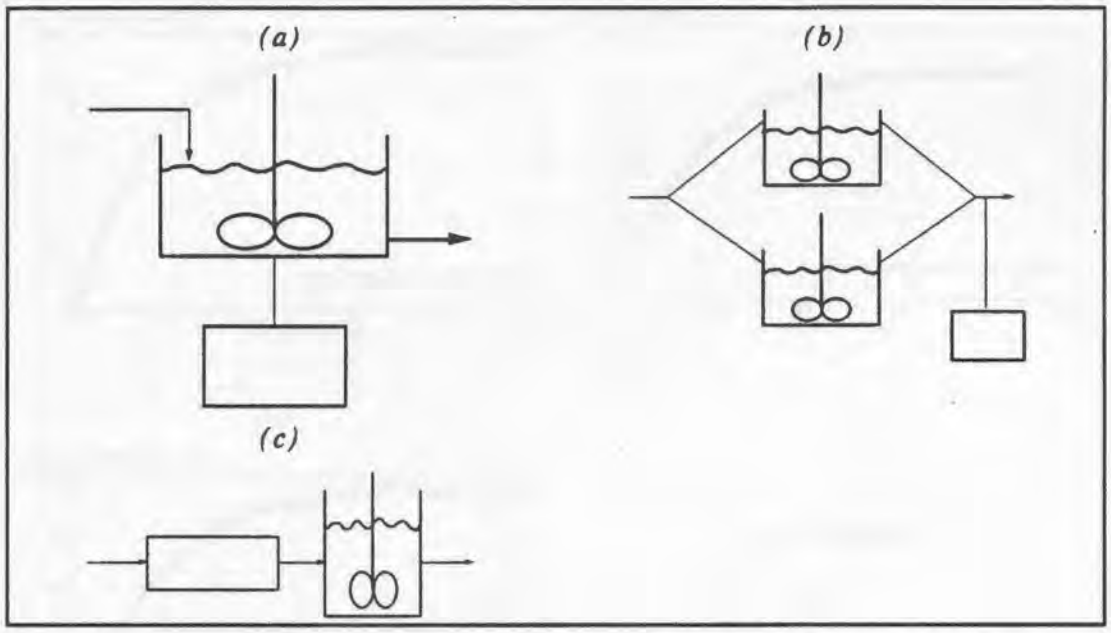


Figure 4.12 : *Models chosen for IMPULSE modelling of small-scale flash mixer at Wiggins WTW : (a) a perfect mixer with dead space ; (b) two perfect mixers in parallel, with dead space ; (c) a plug flow region in series with a perfect mixer*

The tracer response is compared to the model response for each case in Figure 4.13.

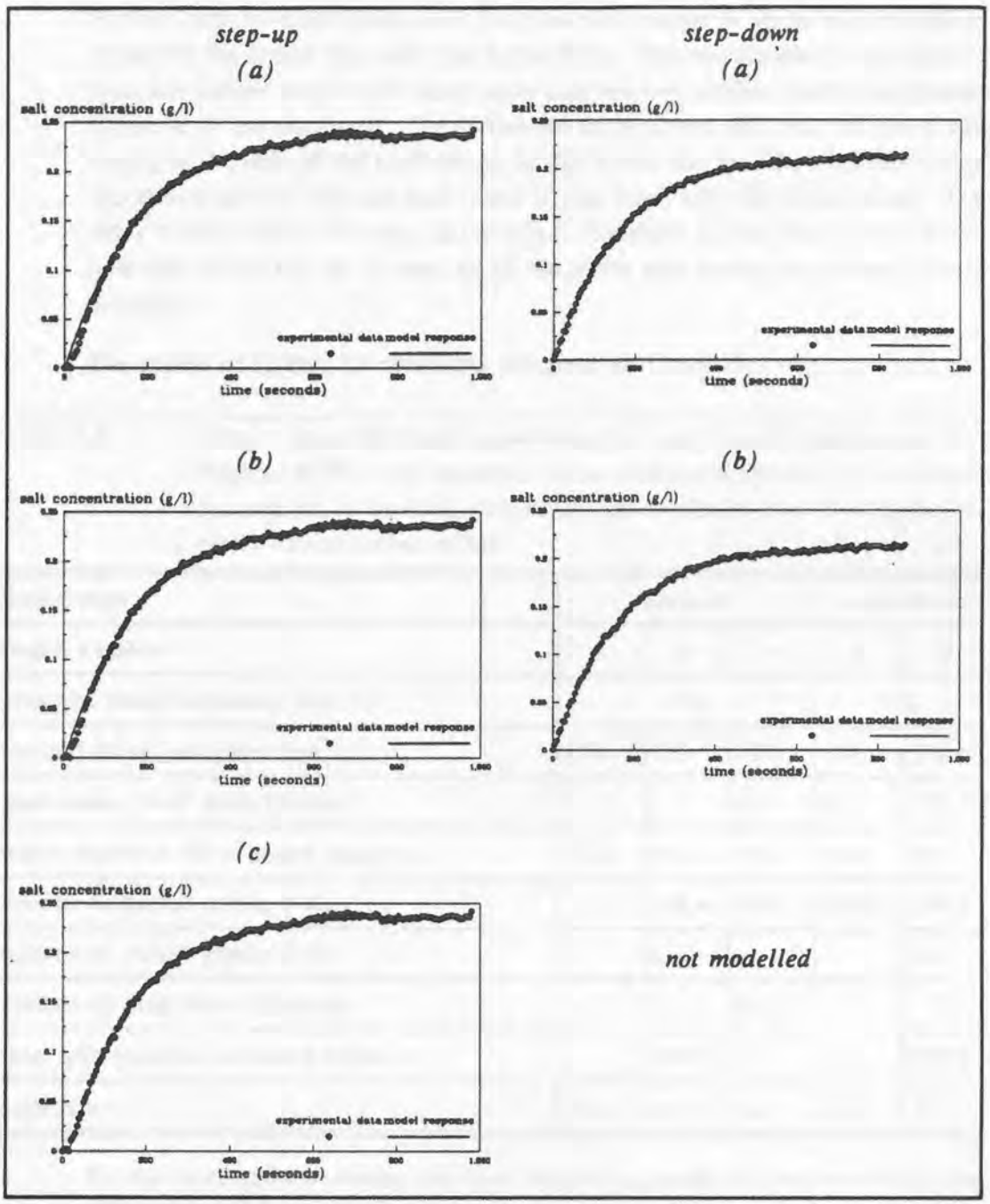


Figure 4.13 : *Comparison of model response after IMPULSE modelling and the tracer response for a small-scale flash mixer at Wiggins WTW : (a) a perfect mixer with dead space ; (b) two perfect mixers in parallel, with dead space ; (c) a plug flow region in series with a perfect mixer (Note that the step-down data has been transformed)*

For the step-up experiment, only the plug flow region in series with a perfect mixer fits the initial data well, due to the delay. For the step-down experiment, both the perfect mixer with dead space and the two perfect mixers in parallel appear to fit the data well. The difference in the initial data may be due to the timing of the start of the experiment, or due to the fact that the step-down data was converted into step-up data, when it may have "lost" the initial delay. The delay is very small, however, and is due to the delay in the pipe, either on the inlet side where the salt is does, or on the outlet side where the conductivity is measured.

The results of IMPULSE modelling are given in Table 4.8.

Table 4.8 : *Results from IMPULSE modelling of a small-scale flash mixer at Wiggins WTW : (a) a perfect mixer with dead space ; (b) two perfect mixers in parallel, with dead space ; (c) a plug flow region in series with a perfect mixer*

Experiment	step-up			step-down	
Model number	a	b	c	a	b
potential mean residence time (s)	172			172	
realised mean residence time (s)	176	173	157	161	159
dead space (% of total volume)	-	-	6,0	6,1	7,2
tracer recovery (% of tracer mass in)	99,2	99,1	98,3	99,6	99,6
volume of mixed region 1 (l)	171,3	166,4	153	156,8	149,3
volume of mixed region 2 (l)	-	2,2	-	-	5,6
volume of plug flow region (l)	-	-	11,7	-	-
flow split fraction to mixed region 1	-	0,987	-	-	0,977
objective	183	148	45	23	21

For the step-up experiment, the flow modelling results are not reasonable for either the perfect mixer model, (a), or the two perfect mixers in parallel, (b), as the active mixing volume is larger than the actual volume. When a delay is introduced, (c), however, there is 6 % dead space, and the objective is much smaller, indicating a better fit of the data. The dead space value is reasonable

when a comparison to the results from the step-down experiment is made, as the dead volumes determined are 6 and 7 % for the two models chosen. The tracer recovery for both experiments is good, and the results are reliable.

There appears to be very little bypass of the flash mixer : for the step-down experiment, the objective is smaller when a parallel mixed flow region is introduced, but the difference in dead space and mean residence time is negligible.

4.4.5 Discussion

Although preliminary analysis of residence time data is useful, it cannot model any deviations from ideal behaviour. In the case of the step-up experiment, the only model which is realistic is one where a plug flow region is in series with a perfect mixer. After introduction of a plug flow region into the step-up model, the results from both the step-up and step-down experiments are comparable, with the dead space being 6 to 7 % and the mean residence time between 157 and 161 s. This is reasonable from a knowledge of the process, and the good tracer recovery indicates that the results are reliable.

4.4.6 Conclusion and recommendations

The small-scale flash mixer can be modelled as a perfect mixer with about 6 % dead space. No bypassing is evident, although care must be taken when sampling to ensure there is no delay in the piping around the flash mixer.

IMPULSE was useful in allowing determination of a number of different models from a large number of data points.

4.5 Conclusion

Although IMPULSE is a useful tool for analysis of residence time data, it is critical that a good experimental method is followed in the determination of experimental data. IMPULSE does, however, yield a tracer recovery result, which can show if results are reliable or not. Many residence time experiments which look reasonable from a qualitative examination of the tracer curve may not, in fact, be representative of the process. A knowledge of the process is critical in choosing realistic models for IMPULSE modelling.

CHAPTER

FIVE

Discussion

5.1 Experimental method

The residence time distribution technique, including experimental method and data analysis, developed from a review of the literature in **Chapter 2**, was applied to experimental data in **Chapter 4**. In discussions of the results and conclusions to the experiments, the experimental method was shown to be critical in order to draw the correct conclusions from any data analysis. In some cases the experimental data appeared correct from a qualitative examination, but was shown to be unreliable upon quantitative examination. The main indicator of unreliable data was an unexplained poor tracer recovery.

Previously, it was found that authors concentrated only on one tracer or method, with little comparison to other tracers or methods available. Where there was comparison or discussion of methods available, it was often included in mathematical journals, and was not accessible and readily understandable to the staff managing water and waste water treatment works. It was therefore difficult for the staff to perform residence time experiments with a full knowledge of the methods available. The advantages of a particular method and the pitfalls to look out for were not readily accessible. Data must therefore have been assumed correct, and analysed as fully as the available technique allowed, with little thought to the quality of the data gathered.

Chapter 2 draws together all available tracers and methods that were found in the literature, with some discussion as to their merits. A personal preference, and reasons therefore, is given for both a tracer and experimental method. Particular emphasis was placed on choosing tracers for water and waste water treatment works.

5.2 Data analysis

As discussed in **Chapter 2**, data analysis has previously been simplified for accessibility. Although techniques were available for fuller data analysis, numerical complexity and,

sometimes, sheer difficulty, has ensured these techniques are not available to the plant staff. With increasing computer power, the constraint of numerical complexity was overcome, but the constraint of understandability still existed. What was necessary was a technique which would be accessible to staff managing water and waste water treatment plants for analysing residence time experimental data.

The data analysis technique needed to include the ability to flow model the process under consideration, to enable possible flow improvements to be postulated. Also, the effect of making flow improvements on the process should be readily seen, including, where possible, the effect on a reacting process.

Where small-scale models of water and waste water treatment processes are available, the technique would allow a comparison of the flow models of the small-scale process to the full-size process. Trials carried out on the small-scale could therefore be directly translated into effect on the full-size.

5.3 Significance of IMPULSE

As shown in the analysis of the experiments of **Chapter 4**, IMPULSE is a tool for analysis of experimental residence time data. It allows quantitative comparison of chosen flow models for a set of data (the objective) and provides parameters of the chosen flow models. Included in the output data from IMPULSE is a tracer recovery which is useful for providing an indication of result reliability.

IMPULSE therefore provides a readily accessible, easily understood tool for analysis of residence time data for staff managing water and waste water treatment processes. IMPULSE allows flow modelling of the data and, from the flow model, staff can assess the performance of the process under consideration and postulate flow improvements. For reacting processes, the flow model can be combined with a kinetic model to quantitatively determine the effect of process improvements.

As discussed in **Chapter 1**, improvements to existing water and waste water treatment processes may increase the throughput of a works. Thus more water can be treated without the capital expenditure involved in building more works. This is significant in reducing the cost of water treatment and providing more water. Also, the quality of the potable water and of the waste water produced may be significantly improved, or worse quality water may be treated without a loss in output quality. This is particularly significant in a country such as South Africa, where the water quality is dropping, but water needs are rising.

CHAPTER

SIX

Conclusion and recommendations

The summary of tracers and experimental methods in **Chapter 2**, and the development of IMPULSE provides an accessible technique for collection and analysis of residence time data. Staff managing water and waste water treatment works can model and assess the performance of water treatment processes. The effect of possible process improvements can be postulated. Understanding and use of the technique will involve some training, but is now readily accessible to staff without specialised knowledge.

Recommendations for future work are :

(a) A guide should be produced drawing out the main points raised in this study. The guide should be made available for staff managing water and waste water treatment works. It should include guidelines to tracer choice and experimental method. IMPULSE should be included as an integral part of this guide, as the tool for data analysis.

(b) Training should be given to potential users of this technique, to enable good understanding of the pitfalls involved.

(c) IMPULSE should continue to be updated, as the program is still in a testing phase. Examples of possible improvements are : allow actual step-down data to be an IMPULSE input; make the outputs more meaningful; make the objective dimensionless, so that comparison between systems is possible. A central *suggestions centre*, possibly on the Internet, should be made available for all users to leave queries, suggestions for improvements and problems.

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APPENDIX

A

IMPULSE manual

The original manual for IMPULSE was written by J L Barnett. It has since been modified by L A D Baddock and C J Brouckaert, and the updated version is included here.

IMPULSE :

a computer program for residence time modelling

manual revision 1.1

for use with IMPULSE version 1.023

Developed during a Water Research Commission Project.
by :

J.L. Barnett
L.A.D. Baddock
C.J. Brouckaert
C.A. Buckley

Pollution Research Group, University of Natal
Private Bag X10, Dalbridge
4014 South Africa
e-mail : Buckley@che.und.ac.za
fax : (031) 260-1118

Updates to the manual and program together with help files are available on Internet through ftp (file transfer protocol). The host computer is *aqua.ccwr.ac.za* and the directory is */ftp/pub/impulse/.*

This manual is for use with **IMPULSE : a computer program for residence time modelling** (beta version).

An introduction to the concept of residence time distribution and residence time modelling is given. **IMPULSE** structure and limitations are examined. A user manual then follows.

CHAPTER 1 Introduction

1.1 Introduction to the residence time distribution concept

To optimise continuous flow processes it is necessary to understand and assess the physical process. Possible improvements for more efficient operation and process intensification must be postulated and the effect of improvements must be predicted, providing the basis for decision-making in terms of the time, effort and cost of making the improvements.

In systems where a flow model does not have significant meaning alone, a knowledge of the flow patterns in the system can be used as a diagnostic tool analyse the cause of process failure, as condition changes will be indicated by change in flow patterns. Further, the flow patterns will indicate the length of time required to reach steady state after a change in conditions in the system.

After determining the flow model of a system and the flow parameters, the overall kinetic rate equation of the reaction occurring in the system can be combined with a mass balance performed over the flow model. This yield the outlet concentration with respect to the flow parameters of the flow model. Thus the effect on the outlet concentration of a change in the flow parameters can be quantified.

To understand and assess a system it is necessary to model the system. For the modelling of a system a knowledge of the flow patterns in the system is important (Rabbitts, 1982). Danckwerts (1953) introduced residence time distribution methods to enable a quantitative description of the flow patterns in a system. Previously, it was usual to assume either *perfect mixing* or *plug flow* (Figure 1.1).

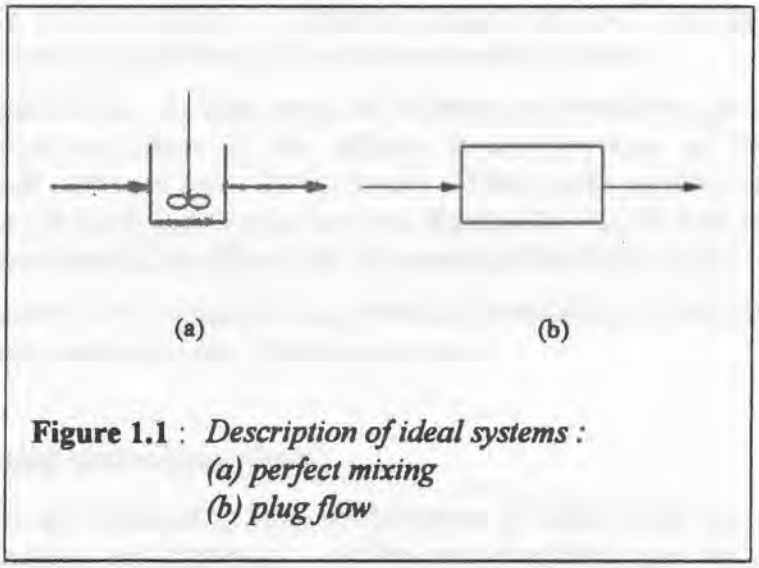


Figure 1.1 : *Description of ideal systems :*
(a) perfect mixing
(b) plug flow

Ideal mixing implies the fluid in the system is completely mixed, so that the properties of the fluid in the system and in the effluent stream are the same ; **plug flow** implies no mixing in the direction of flow, so that elements of fluid entering the system at a particular time flow through the vessel together and leave at the same time in the future. The flow patterns found in real processes usually lie between these two extremes (Smith, 1981), due to *bypassing*, *channelling*, *dead space* and *recycling* (Figure 1.2).

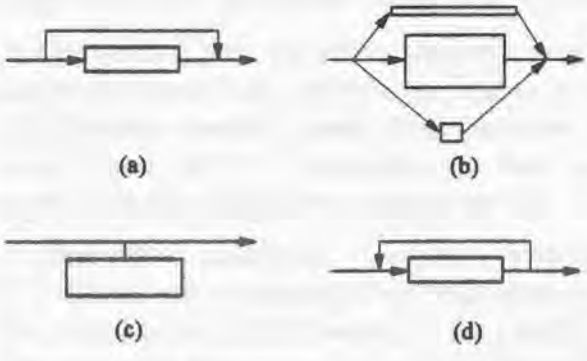


Figure 1.2 : *Deviations from ideal systems : (a) bypassing ; (b) channelling ; (c) dead space ; (d) recycling*

In *bypassing* and *channelling*, some elements of fluid move through the system significantly faster than others do. *Dead space* refers to a region in the system with extremely poor contacting with the bulk fluid ; fluid in the dead space will generally remain in the system significantly longer than the bulk fluid. *Recycling* occurs when fluid is recirculated to the system inlet or to another region of the system.

Thus, the effluent stream of a continuous flow system is a mixture of fluid elements that have resided in the system for different lengths of time ; the distribution of these residence times is an indicator of flow patterns within a system.

Introducing tracer into the inlet stream of a system and measuring the concentration-time relationship of the tracer in the effluent stream provides an observation of the distribution of residence times for the tracer. If the tracer particles have the same flow attributes as the fluid, their residence time distribution can be said to approximate the residence time distribution of the fluid (Naumann and Buffham, 1983).

The flow pattern of the system is determined by establishing a flow model of the system from the tracer residence time distribution curve.

1.2 Flow model determination

Flow models are constructed from combinations of ideal mixed and plug flow **blocks**, joined by recycles and bypasses. A flow model of this type, and its parameters, is guessed from the tracer residence time distribution curve. The model residence time distribution curve is determined from known equations associated with the ideal blocks.

This curve is compared to the tracer curve and the parameters of the model adjusted until the closest fit is obtained.

In the past, this procedure was not easily accomplished due to mathematical complexity associated with finding the closest fit between the tracer curve and the model curve. Therefore, finding the best flow model and parameters of the model was a time consuming and inaccurate procedure, particularly if different models were attempted.

1.3 Computer programs for determining flow models

A procedure to model systems from the tracer residence time distribution curve using a Turbo Pascal computer program was reported by Barnett et al. (1992). This program found the closest fit between a model guessed from the tracer residence time distribution curve and the tracer curve itself to determine the flow parameters of the system. However, the program was not interactive nor user-friendly.

A user-friendly, interactive computer program, **IMPULSE**, was written by Baddock (1992). It allows easy modelling of systems using curves obtained from tracer response tests. The user assumes a flow model for the system ; the program determines the theoretical response curve for the model, and optimises a chosen set of parameters of the model to fit the experimental curve.

The program is currently in its beta, or testing, phase. It has been designed for conservative tracers, that is, tracers that are not consumed in the system. It is suitable for a wide range of applications of continuous flow processes.

These include :

- continuous flow anaerobic digesters
- clarifiers
- mixing systems
- reaction vessels
- pipelines

CHAPTER 2 Program structure

2.1 Introduction

The program was written in Turbo C++ and is executable on all IBM and IBM compatible personal computers. with Hercules, EGA or VGA graphics cards.

IMPULSE was developed with a menu system, consisting of a main menu and submenus, which allow the user to select a desired program option from a list of possible options displayed on the screen. A number of user-friendly features have been included in the program, for example :

- on certain options the program guards against meaningless data input by evaluating data entered into the program as the keys are pressed
- the user can choose whether to display the model curve with guessed parameters before curve fitting, to reduce the time spent by the program fitting the curve
- automatic updates of the screen curves are done as data is entered into the program

Input to the program is via the ADD and EDIT options on the main menu. Also on the main menu is a FILE option, allowing file handling ; a PLOT option, to add or remove data sets from the plot displayed on the screen ; a CONSTANTS option, setting the mathematical constants for the curve fitting ; and a RUN option, which starts calculations and curve fitting. The program exits to DOS by pressing the *Escape* key.

A complete description of the menu system and the running of the program is presented in Chapter 4.

2.2 Data input

Data is entered into the program via the ADD and EDIT options on the main menu (see Chapter 4). The following data may be entered into the program :

- the building blocks of the model (mixed flow, plug flow, mixer/splitter, input, output)
- the parameters associated with the building blocks (volume, split fraction)
- whether the parameters must be held constant or can be varied by **IMPULSE**
- an tracer input curve as a flowrate and concentration history
- a tracer response curve (called the REFERENCE curve) against which the model curve can be fitted

* C++ is a registered trademark of Borland International Inc.
** IBM is a registered trademark of International Business Machines Corporation

2.3 IMPULSE flow diagram

As **IMPULSE** is interactive, a flowsheet cannot show all the options and the paths between the options. A flowsheet showing possible user interaction with the program is given in Figure 2.1.

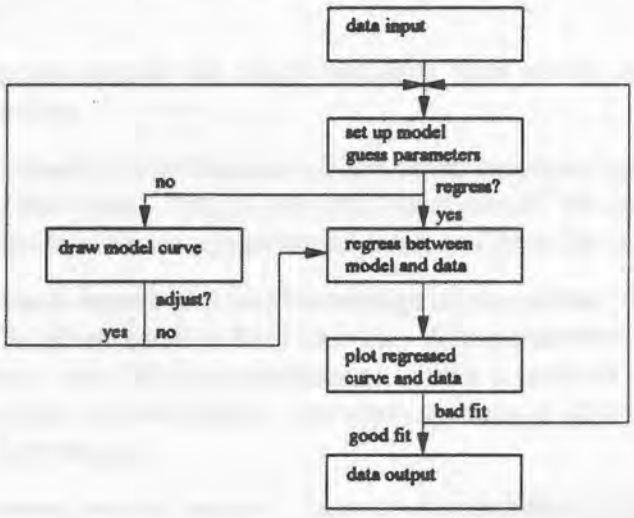


Figure 2.1 : *Typical suggested flowsheet for using IMPULSE to investigate a residence time problem for residence time modelling*

2.4 Output from the program

The output from the program after modelling is displayed on the screen and can be saved to a file, the filename of which is entered by the user. The following is saved in the file :

- modelling units and associated parameter
- unit connections
- any curve that is currently in the set that is to be plotted (Section 4.2.7).

CHAPTER 3 Program limitations

Certain limitations exist for the use of **IMPULSE**. These are listed below :

- **IMPULSE** should only be used to model continuous or near-continuous flow systems.
- The program models the liquid residence time of the system, and not the solid residence time.
- The experimental determination of the tracer response curve is not trivial and may influence the result. Thus a user must be aware of the techniques for tracer tests, and be able to estimate experimental error, and how this influences the curve.
- A user should have a physical knowledge of the system to be modelled and should be able to guess feasible flow models. Any parameters obtained from the flow model must have physical significance ; thus a complex model may fit the tracer curve but may not be feasible. For open systems, a dye test may indicate the most feasible flow model.
- Tracer curves are not unique : they can be modelled accurately by more than one model. Sound engineering judgement is therefore necessary to choose the most feasible model.
- **IMPULSE** works by dividing up time into **'segments'**, and then applying the equations describing the system to each segment in turn. Any model constructed is thus sensitive to the number of segments. The larger the number of segments, where $n_{segments} = \frac{StopTime - StartTime}{deltaT}$, the more accurate the results, but the more time required to reach a result (Section 4.2.8).

4.1 Installing the program

4.1.1 System requirements

IMPULSE is executable on all IBM PC, XT, AT or true IBM compatibles. It requires DOS 3.00 or higher and at least 512K of RAM to run. **IMPULSE** includes routines that allows the program to make use of an 8087, 80287 or 80387 numeric co-processor if available. It can only be used on a system with Hercules, EGA or VGA compatible graphic adapters.

It is recommended that **IMPULSE** be run on a 386 or, preferably, a 486 computer with a numeric co-processor and a colour monitor for optimum performance.

4.1.2 Files on the distribution disk

The distribution disk contains the following files :

- IMPULSE.EXE : the executable program file
- EX?.REF : the reference time-concentration data for the examples described in Section 4.3
- EX?.FLO : The time-flowrate data for the examples described in section 4.3
- EX?.CON : the time-concentration data for the examples described in Section 4.3

4.1.3 Installing and running IMPULSE

The most convenient method for running **IMPULSE** is on a hard disk system. The procedure outlined below can be used to set up **IMPULSE** on a hard disk :

Assuming that the hard disk is designated as drive C, make a subdirectory to work in, and change to that subdirectory by typing the following commands (pressing *Enter* at the end of each line) :

- C:
- CD\
- MD IMPULSE
- CD IMPULSE

Place the distribution disk in the disk drive (presumably drive A)

Copy the files on the distribution disk by typing the following command and pressing *Enter* :

- COPY A:*.* C:

To run the program from anywhere on the hard disk, type the following commands (pressing *Enter* at the end of each line) :

- C:
- CD \IMPULSE
- IMPULSE

4.2 Using the program

4.2.1 Starting Program Execution

Once the program has been run the title page will gradually be displayed, as shown in Figure 4.1. Press any key to advance execution as indicated on the screen.

Figure 4.1 : *Title page of the IMPULSE program*

Information about the program will then be displayed, as shown in Figure 4.2. Press any key to advance execution as indicated on the screen.

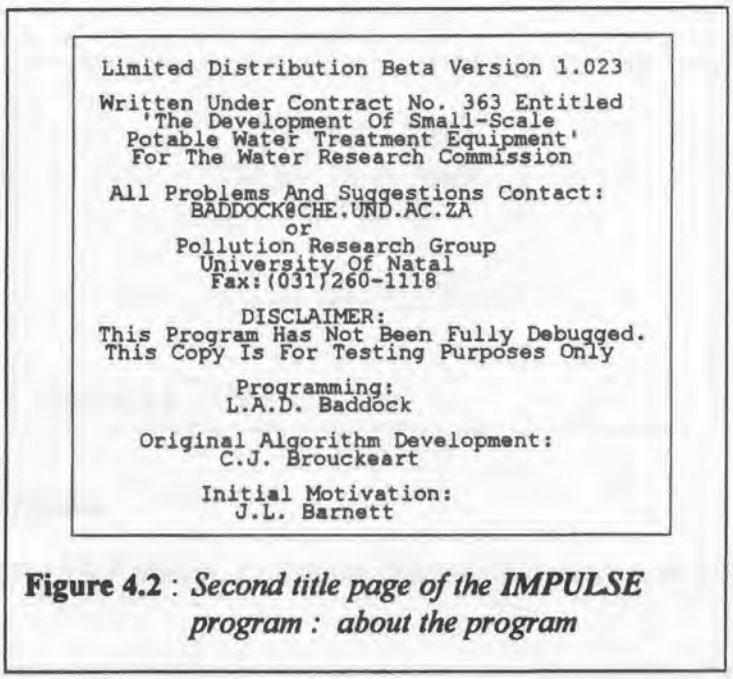


Figure 4.2 : *Second title page of the IMPULSE program : about the program*

4.2.2 The main menu

After continuation from the title page, the main menu of the program appears (Figure 4.1)

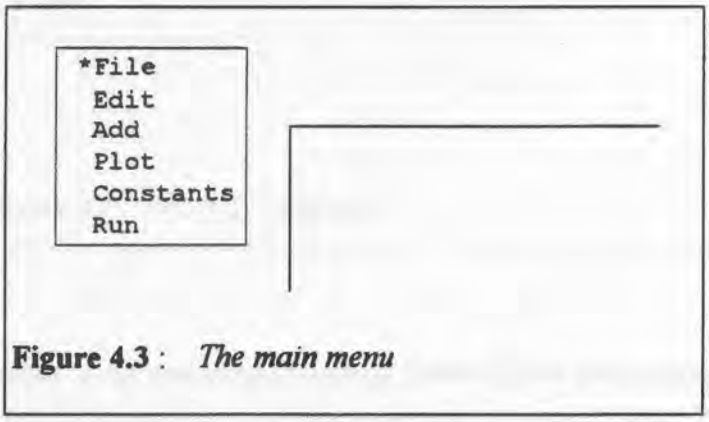


Figure 4.3 : *The main menu*

When the menu first appears, the cursor (shown as an asterisk) is positioned next to the FILE option. A menu option (or submenu option) can be selected by using the *Up* and *Down* arrow keys on the keyboard to move the cursor through the list of options, and pressing *Enter* when the cursor is positioned next to the desired option.

Pressing *Escape* when the cursor is in any of the submenus return the cursor to the main menu and erases the submenu from the screen.

4.2.3 To leave IMPULSE

When the cursor is in the main menu, pressing *Escape* prompts a confirmation query (Figure 4.4). Pressing *'y'* or *'Y'* exits to DOS.

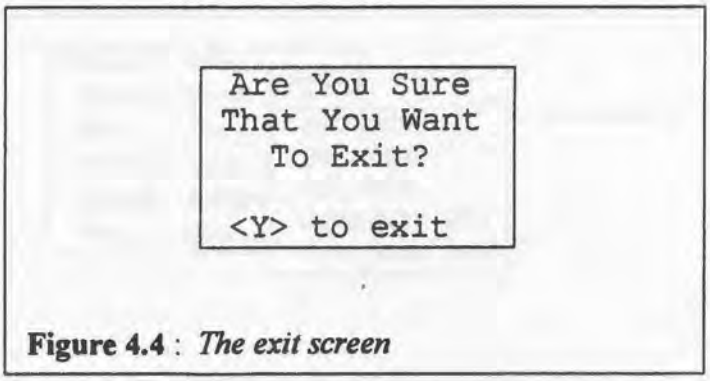


Figure 4.4 : *The exit screen*

4.2.4 The FILE option

By selecting the FILE option, a submenu appears on the screen as shown in Figure 4.5.

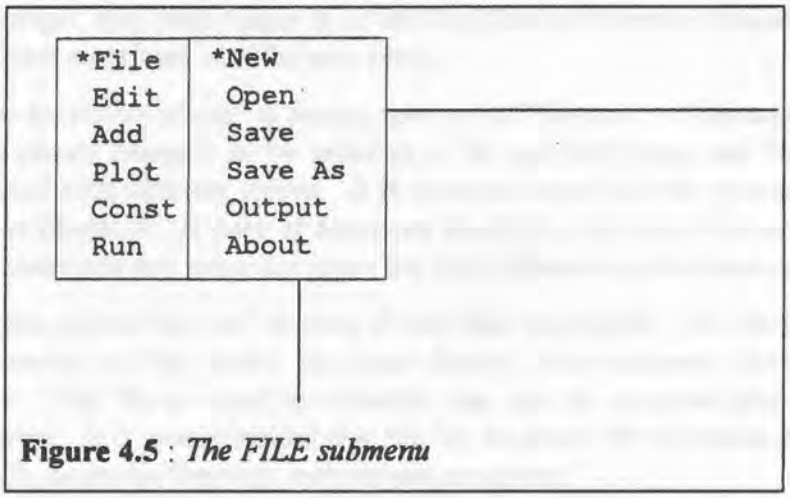


Figure 4.5 : *The FILE submenu*

Moving the cursor to an option and pressing *Enter* selects that option.

- **New** clears the screen and starts a blank file.
- **Open** opens a file specified. The user is prompted for a filename, as shown in Figure 4.6. A filename can either be entered using the keyboard, and the asterisk deleted using the *Delete* or *Backspace key*, or a list of possible files can be called by pressing *Enter*. Positioning the cursor next to one of the filenames and pressing *Enter* loads the file. The default extension is *rtd* : if the filename does not have this extension, the default can be deleted using the *Delete* or *Backspace* key, and replaced with an asterisk, or the actual extension can be entered from the keyboard.

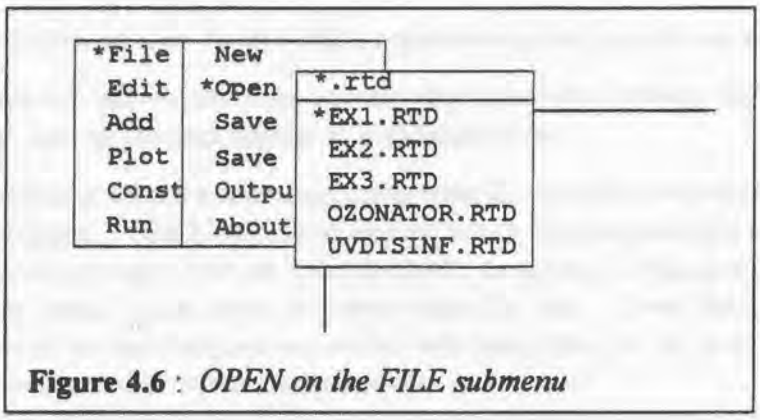


Figure 4.6 : *OPEN on the FILE submenu*

- **Save** allows the user to save a new file under a name of their choice, or saves an old file under its name. It is recommended that the extension *.rtd* be added to any filename.
  If changes have been made to an existing file, and **Save** is chosen, the old settings will be overwritten with the new ones.
- **Save As** allows a user to save a new or old file under a filename of their choice. This allows changes to be made to a file and both new and old versions to be retained with different names. It is recommended that the extension *.rtd* be added to any filename. A note of filenames should be kept by the user, as the program will overwrite any other file given the same filename and extension.
- **Output** allows the user to save all the data associated with the file, including the parameters of the model, the input history, the reference curve and the model curve. The file is saved in a format that can be imported into any spreadsheet program. It is recommended that the file be given the extension *.prn*, as this is the default extension for most spreadsheet programs.
- **About** gives information about the program, as shown in Figure 4.2.

4.2.5 The EDIT option

By selecting the EDIT option, a submenu appears on the screen as shown in Figure 4.7.

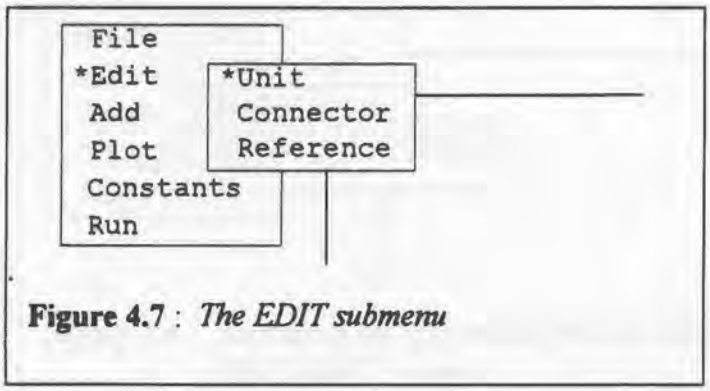


Figure 4.7 : *The EDIT submenu*

Moving the cursor to an option and pressing *Enter* selects that option.

- **Unit** allows the user to add edit the parameters for any unit on an existing model.
- **Connector** allows the user to edit any connector linking objects in an existing model, and to connect objects in a different order.
- **Reference** is where a reference curve (that is, the tracer response curve) is linked to the program. This is the curve against which the program fits the model curve for the model chosen. It is an editable curve, as shown in Figure 4.8. A scaling factor can be added to the curve to compensate for units. Data can be entered from the keyboard as time and concentration, with each data set on a separate line and time and concentration separated by a space.

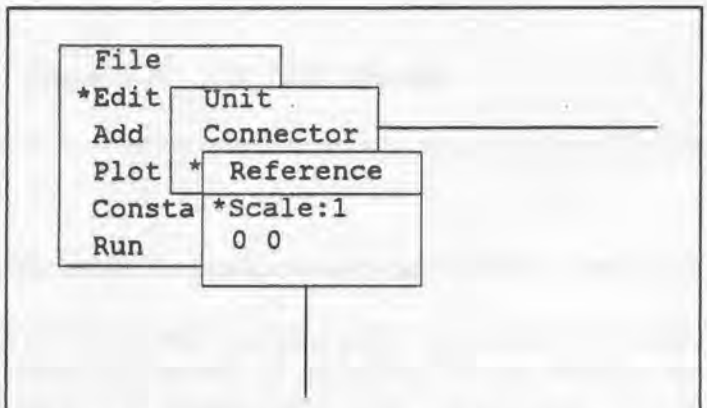


Figure 4.8 : *REFERENCE on the EDIT submenu*

Data can also be imported from a file made in a spreadsheet program. The file should contain only time and concentration, with each data pair on a separate line. The elements in each data set should be separated by spaces. To start importing processes, *F1* is pressed. The filename is then entered in the space provided (Figure 4.9).

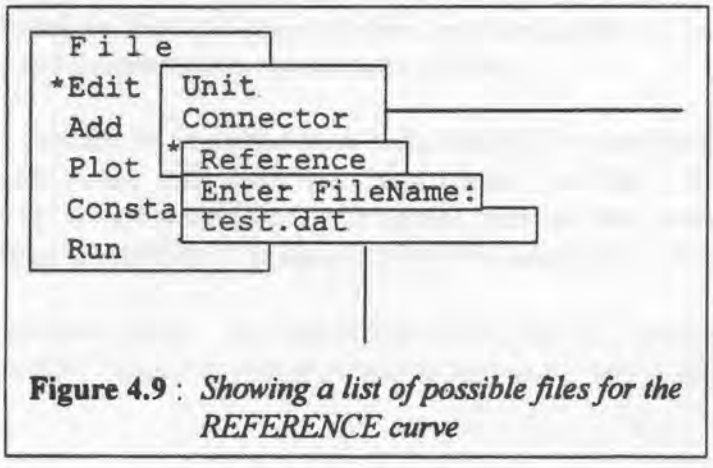


Figure 4.9 : *Showing a list of possible files for the REFERENCE curve*

4.2.6 The ADD option

By selecting the ADD option, a submenu appears on the screen as shown in Figure 4.10.

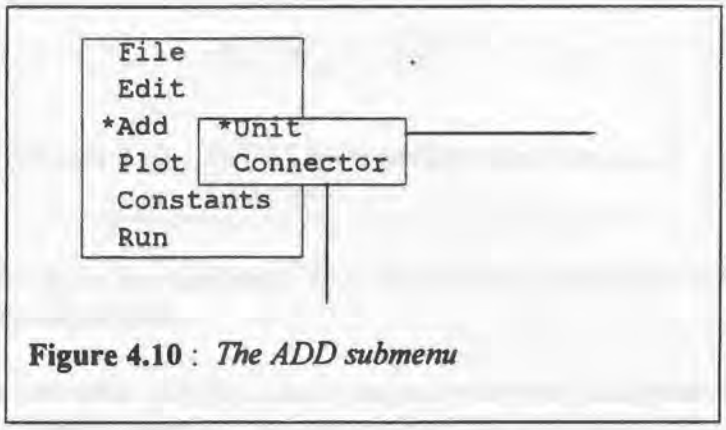


Figure 4.10 : *The ADD submenu*

Moving the cursor to an option and pressing *Enter* selects that option.

- **Unit** allows the user to add a unit to the model. The user is asked to name the unit, guess parameters for the unit and decide whether the parameters must be held constant or whether they can be varied during curve fitting. It is required that the user give a different name to each unit and that they keep a record of the units and where they fit into the model the user wishes to construct. The units are : **input, mixed flow (mfr), plug flow (pfr), mixer/splitter (ms)** and **output.**

  input : an input unit is used to model a stream entering the process being modelled. Its parameter set consists of a flowrate history, a concentration history and associated scaling factor.

  The user must assign a name to each input. The input is an editable curve. A scaling factor can be added to the curve. Data can be entered from the keyboard as time and concentration, with each data set on a separate line and time and concentration separated by a space.

  Data can also be imported from a file made in a spreadsheet program. The file should contain only time and concentration, or time and flowrate, with each data set on a separate line, with spaces between data elements in each. This filename is typed into the space given for a name, after *F1* has been pressed.

  mixed flow (mfr) : the mixed flow (mfr) unit is a perfectly mixed vessel, as defined in Chapter 1, with an equation associated with it (Figure 4.11).

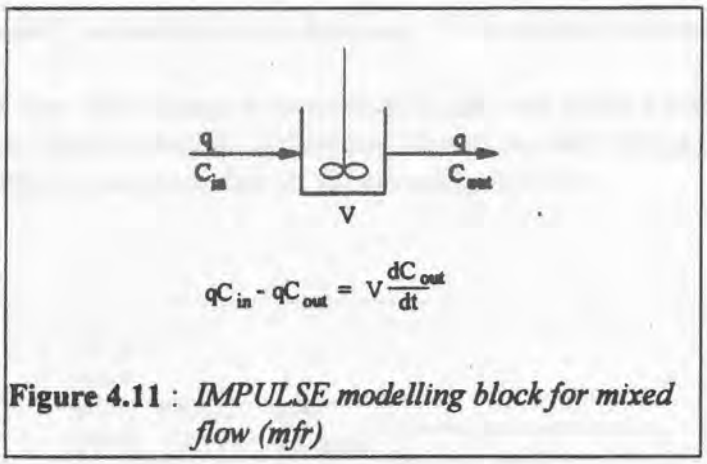


Figure 4.11 : *IMPULSE modelling block for mixed flow (mfr)*

where **q** is the volumetric flow through the mixed flow and **V** is the volume of the mixed flow.

The user must assign a unique name to each mfr, and guess a volume. The user must decide whether the volume should be held constant by **IMPULSE**, or whether it can be varied, as shown in Figure 4.12.

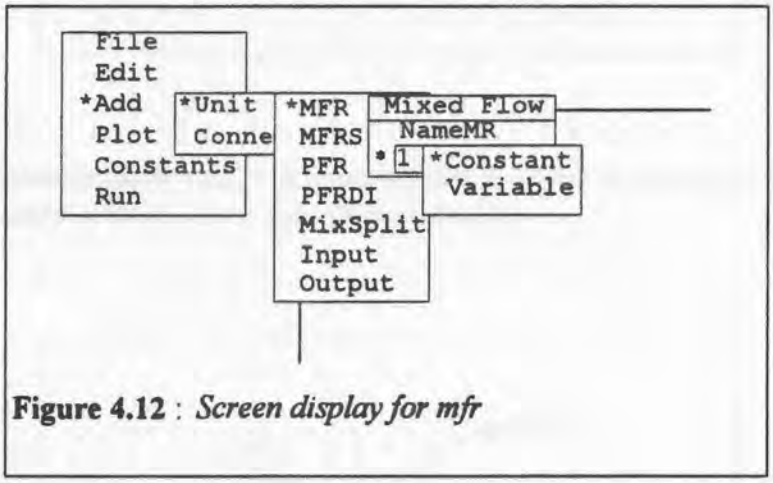


Figure 4.12 : *Screen display for mfr*

plug flow (pfr) : the plug flow (pfr) unit is a perfectly mixed vessel, as defined in Chapter 1, with an equation associated with it (Figure 4.13).

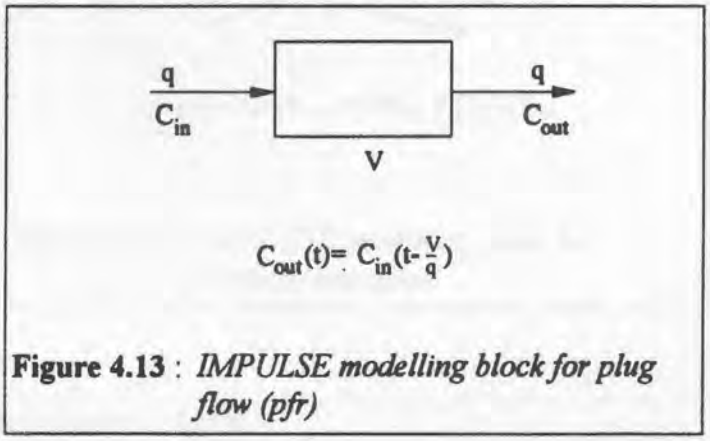


Figure 4.13 : *IMPULSE modelling block for plug flow (pfr)*

where **q** is the volumetric flow and **V** is the dead volume.

The user must assign a name to each pfr, and guess a dead volume. The user must decide whether the volume should be held constant by **IMPULSE**, or whether it can be varied, as shown in Figure 4.14.

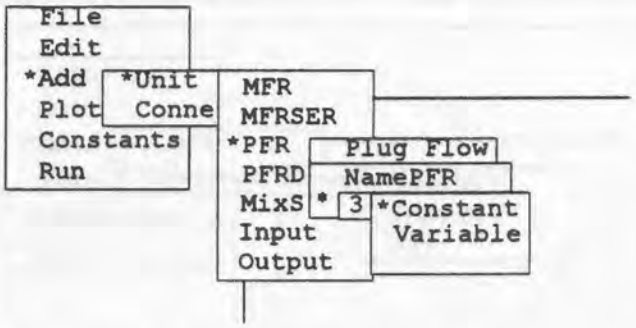
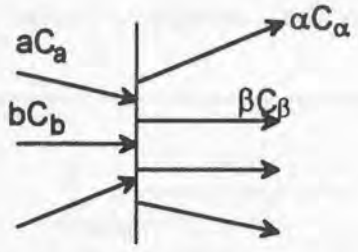


Figure 4.14 : *Screen display for pfr*

mixer/splitter (ms) : a mixer/splitter is added to the model whenever a stream needs to be joined or split (Figure 4.15).



$$aC_a + bC_b + \ldots = \alpha C_\alpha + \beta C_\beta + \ldots$$

Figure 4.15 : *IMPULSE modelling block for mixer/splitter (ms)*

where **a** , **b** , etc. are volumetric flows.

The user must assign a name and split fraction to each ms.

output : an output records the history of any flowrate and concentration. A name needs to be associated with this output for plotting purposes.

- **Connector** : allows the user to connect the units together in any way. A list of the units to be connected *FROM* is shown and the cursor can be moved to the desired unit using the arrow keys (Figure 4.16). A list of the units to be connected *TO* is shown and the cursor can be used to select the desired unit.

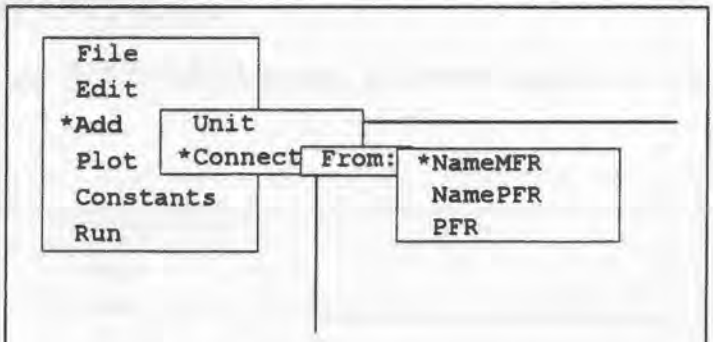


Figure 4.16 : *A list of possible units for connections*

Only the units possible are shown so, for example, the input will only be shown on the *FROM* submenu, as it has only one connection. An unit will be erased from the lists of possible options once the unit's maximum connection requirements are met. A mixer/splitter has no connection limitations, and will remain on both list. An output will only appear on the *TO* submenu as it has only one possible connection.

4.2.7 The PLOT option

By selecting the PLOT option, a submenu appears on the screen as shown in Figure 4.17.

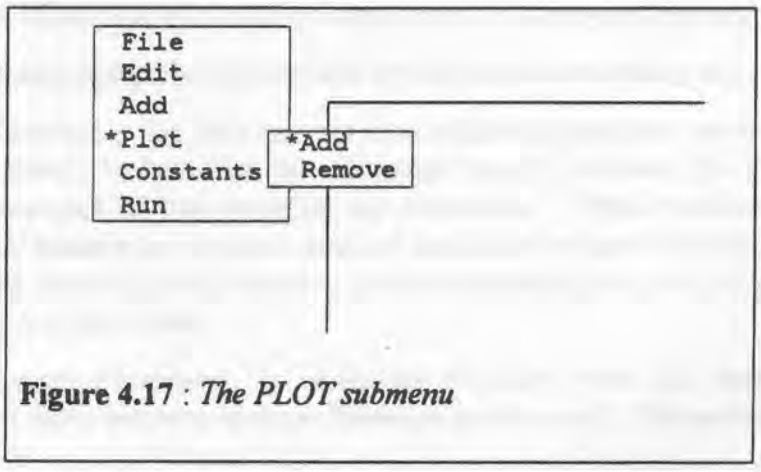


Figure 4.17 : *The PLOT submenu*

Moving the cursor to an option and pressing *Enter* selects that option. The PLOT option allows the user to determine what data sets are plotted on the screen. This is

useful if there are many data sets, or if the data sets have very different scales, so that it is difficult to see any one set.

- **Add** allows the user to add a data set to the plot that appears on the screen. A list of possible data sets will appear, and the cursor can be used to select a set.
- **Remove** allows the user to remove a data set from the plot that appears on the screen. A list of possible data sets will appear, and the cursor can be used to select a set.

4.2.8 The CONSTANTS option

By selecting the CONSTANTS option, a submenu appears on the screen as shown in Figure 4.18.

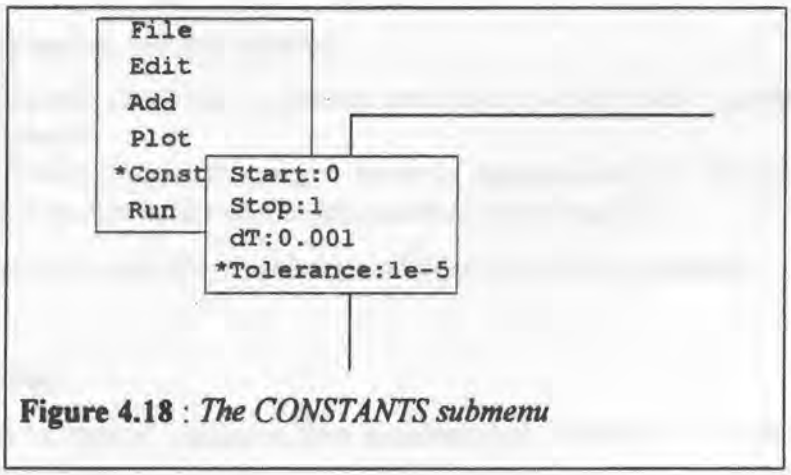


Figure 4.18 : *The CONSTANTS submenu*

Moving the cursor to an option and pressing *Enter* selects that option. The CONSTANTS option allows the user to determine the constants in the curve fitting.

- **Start** determines the relative time at which the curve fitting begins.
- **Stop** determines the relative time at which the curve fitting ends.
- **dT** determines the time interval over which the program iterates. Reasonably, this should be less than the minimum interval between the time values of any adjacent pair of data points on any date curve. With in these confines, this value should initially be chosen as large as possible to reduce computing time. Once the model curve fits the reference curve moderately, this can be reduced to give a more accurate result.
- **Tolerance** determines the maximum allowable error for flowrate convergence where there are non-constant flowrates in the model. The recommended setting is 1.0e-5.

4.2.9 The RUN option

By selecting the RUN option, a submenu appears on the screen as shown in Figure 4.19.

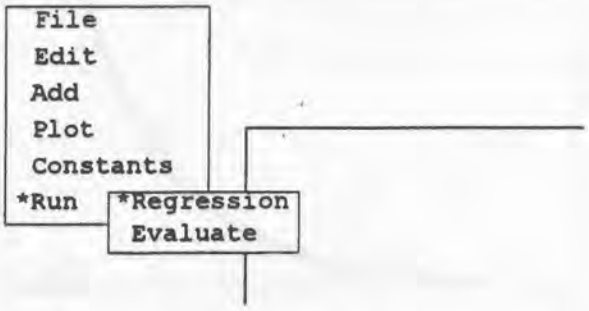


Figure 4.19 : *The RUN submenu*

Moving the cursor to an option and pressing *Enter* selects that option.

- **Regression** has two options :

  Regress starts the regression procedure on all model parameters specified as variable.
  Choose chooses the output curve to compare with the reference curve. There may be more than one output curve on some models.

- **Evaluate** starts the processing and the curve fitting procedure.

4.3 Examples

A number of typical residence time problems are presented to illustrate the program's capability.

4.3.1 Example 1

Figure 4.20 shows the tracer response curve for a reactor which is meant to behave as an ideal mixer. A spike of tracer was injected into the inlet line leading into the reactor, and the concentration was measured at the outlet of the reactor. The flow through the reactor was held constant during the experiment. Using **IMPULSE**, determine the model for the reactor and assess its performance.

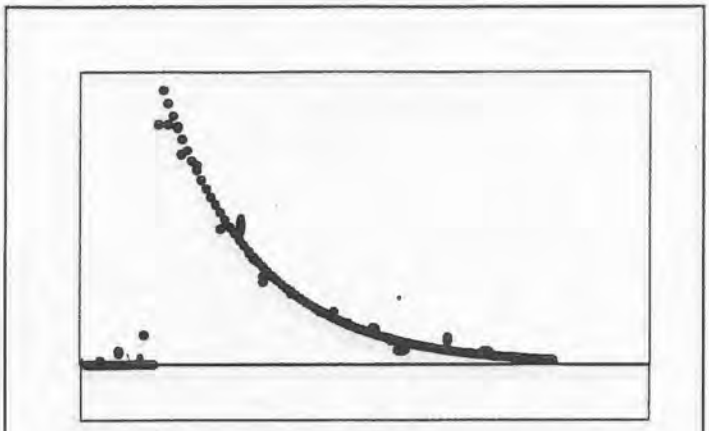


Figure 4.20 : *Raw data for example 1*

The delay before the tracer appears indicates an ideal plug flow region. The perfect exponential curve indicates an ideal mixed flow region. This is in series with the plug flow region. There appears to be no other flow characteristics. The quantity of dead space cannot be determined as there are no quantities given. The model is shown in Figure 4.21.

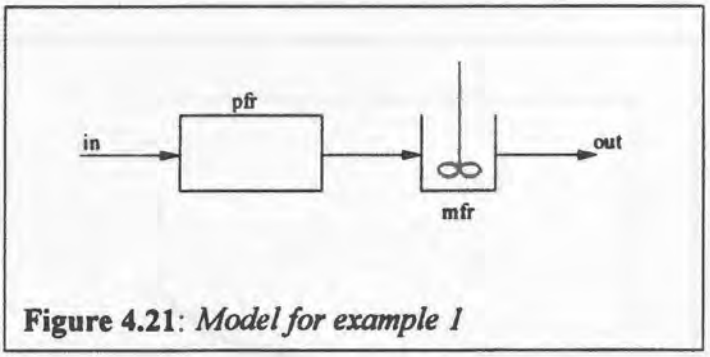


Figure 4.21: *Model for example 1*

The plug flow region in the model is explained by the inlet line to the rector. This delayed the tracer. The reactor operates as an ideal mixer. The modelling results are shown in Figure 4.22.

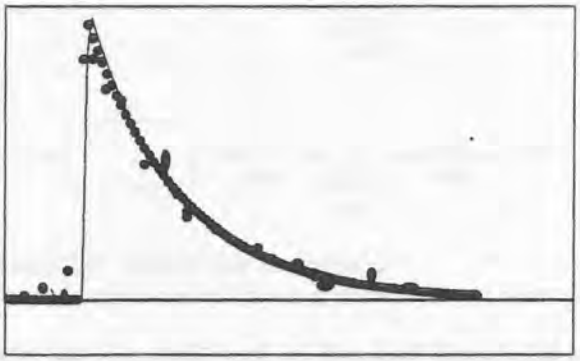


Figure 4.22 : *Result for example 1*

4.3.2 Example 2

A tracer was injected into a mixing vessel as there appeared to be a bypass over the vessel. The tracer response curve, from a spike of tracer injected into inlet line to the vessel, is given in Figure 4.23. Determine whether there is a bypass over the vessel, assuming flow was held constant during the experiment.

Figure 4.23 : *Raw data for example 2*

The delay before the tracer appears indicates a plug flow region. This is in series with a mixed flow region is indicated by the exponential curve. There is a bypass over the mixed flow region, but there is some mixing in the bypass, as the spike has an exponential character. The model is shown in Figure 4.24.

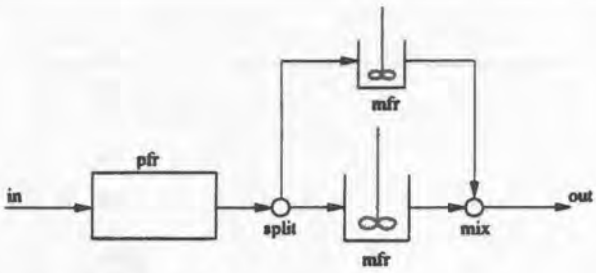


Figure 4.24 : *Model for example 2*

The plug flow region may be explained by the inlet line to the vessel. The vessel has a large ideal mixing zone by there is, however, a bypass on the vessel. The modelling results are shown in Figure 4.25.

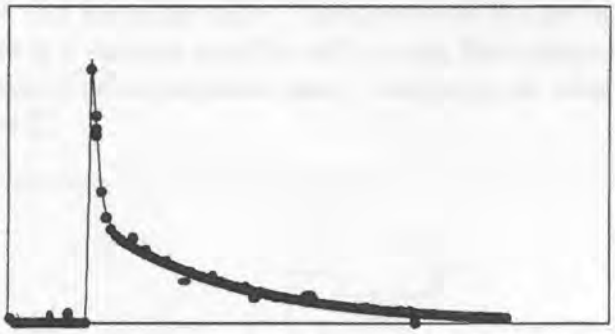


Figure 4.25 : *Results for example 2*

4.3.3 Example 3

A tracer was injected into the inlet of a system through to act as a plug flow vessel. The tracer response curve determined is shown in Figure 4.26. Determine the flow pattern for the system and whether the assumption of plug flow is correct.

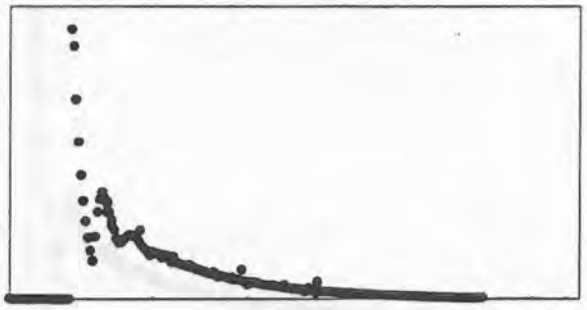


Figure 4. 26 : *Data for example 3*

The data indicated that there may be more than one plug flow region, from the delay before the tracer and from the slight `bumpiness' of the curve. The regular `bumps' indicate that there is a recycle, possibly with a plug flow delaying the `bumps' regularly. The overall shape is an exponential curve, indicating an ideal mixer. The model is shown in Figure 4.27.

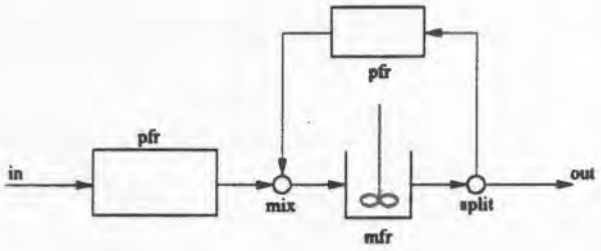


Figure 4.27 : *Model for example 3*

There is a large mixing region that is recycling in the system and the system has very little plug flow character. The modelling results are shown in Figure 4.28.

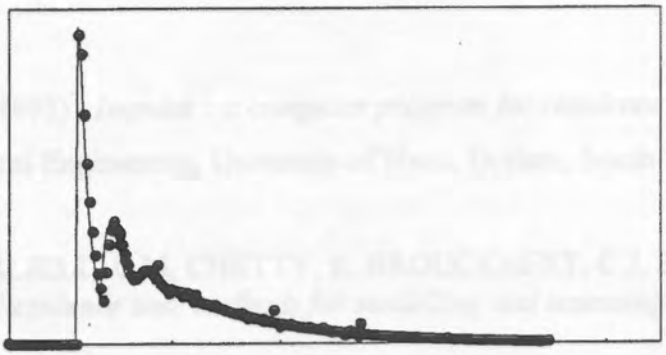


Figure 4.28 : *Results for example 3*

REFERENCES

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INFORMATION AND ERROR MESSAGES

- **Are You Sure That You Want To Exit? <Y> to exit :**

  This is displayed when the user presses the escape key from the main menu. When this message is displayed, pressing 'y' or 'Y' will exit the application, and return the user to the dos prompt, or any menu system that was used to invoke the program. Pressing of any other key will return the user to the main menu. Care should be taken to ensure that any work that is needed at a later stage is saved before exiting, as automatic saving of work on exit is not implemented.

- **Cannot Open File *<FILENAME>* :**

  There has been an error during the file open process. There may be a number of causes for this. The only cause specific to the package is if the file that is specified is not in the current working directory. All files MUST be in the directory that the package was invoked from. For any other causes, the user should consult a DOS manual or a network manual if the files are stored on a network drive.

- **Enter File Name :**

  This message appears during the file import process (for importing a set of points into an *'Editable Curve'* by pressing the 'F' key), during the 'File -> Save' process if the working file was not originally loaded from disk (i.e. created from scratch), or during the 'File -> Save As' process. Note that no path should be specified for the file... the file will be saved to the current working directory. (The directory that the package was invoked from).

- **Error Opening File : *<FILENAME>* :**

  See *'Cannot Open File <FILENAME>'*.

- **File Already Exists! Overwrite? <y/n> :**

  This message is displayed when the user requests a save for the model under development, and the specified save filename already exists. This message will not be seen if the current model was initially loaded from disk, altered and then saved using the 'save' option, rather than the 'save as' option.

- **No Valid Point Could Be Found In File *<FILENAME>* :**

  This occurs when the user is in an 'Editable Curve' and has selected a file from which to import data, where the specific file does not contain at least one numeric pair on a single line of ASCII text, separated by anything non-numerical.

- **Not Implemented Yet!! :**

  This message should never be seen by the user. If it is, the user is requested to contact the Pollution Research Group, to report it.

- **Press Any Key to Stop The Regression :**

  While in an regression procedure, this box is continually displayed. The regression information box will continuously update during this procedure, display the model iteration number. If the user presses a key, it is unlikely that the regression procedure will terminate immediately. This is often disturbing, but nevertheless necessary, in order to ensure that the set of parameters that remain after the user has requested a regression termination are better than the starting estimates.

- **Reduction Tolerance % :**

  This message is displayed, along with a numerical entry box when the user has selected the file import facility in an 'Editable Curve'. This figure is used for point filtering, and only really has to be used if the input file has more than about 100 points in it.

- **Running.. :**

  This message is displayed while the current model is being evaluated. As soon as it is no longer visible, the model calculations are complete. Users running simple models on fast machines may not see this message at all.

- **Saving : *<FILENAME>* :**

  This message is displayed whenever a file save has been requested and stays on the user display as long as the file writing process is in action. The file saving is complete as soon as the message disappears.

- **There Are Units That Still Need Input Connections :**

  Each unit in the package that is used for modelling has certain connection requirements, that must be satisfied. It does not, for example, make sense for a mixed flow reactor to have more than one input, but it does have to have the input. (It would be useless for modelling flow processes if it did not have a flow input!) If, for example, a mixed flow reactor was created, and did not have any connection going to it from another unit, this message will be displayed when the user tries to run the model. The connection requirements are presented in the table below.

Table A.1 : Unit Connection Requirements		
UNIT	INPUTS	OUTPUTS
MFR	1	1
MFRSER	1	1
PFR	1	1
PFRDISP	1	1
MIXSPLIT	At least 1	At least 1
INPUT	0	1
OUTPUT	1	0

- **There Are Units That Still Need Output Connections :**
  See the above message for details.

- **The Following Units Need Modification :**
  This message appears whenever one of the parameters specified in any of the units used in the current model is invalid, and a model run is requested. A list of the offending units will be displayed, and the user may alter them at this point, (a unit disappears off the list once all its parameters are valid) or the user can press the escape key to return to the menu system, and alter them using the *EDIT->UNIT* option. The most common causes of this message are listed in the table below, by unit type.

Table A.2 : Causes of Incorrect Unit Configuration	
UNIT	CHIEF CAUSE
MFR	The volume has been set to a value of zero or less.
MFRSER	The volume has been set to a value of zero or less. The number of series mixed flow reactors is less than or equal to zero.
PFR	The dead volume has been set to zero or less.
PFRDISP	The dead volume has been set to zero or less. The Peclet number is less than or equal to zero. The Peclet number is greater than 1500
MIXSPLIT	A split proportion has been specified with a negative value.
INPUT	One of the input profiles (flowrate or concentration) has a negative value of flowrate or concentration/
OUTPUT	-

- **The Unit Name (The First Line In The Box) Must Consist Of Non-Blank Characters :**

  The name of each unit MUST consist of a non-empty set of ASCII characters. Spaces and tabs are not counted, as they are blank, and cannot be readily seen by the user.

- **This Is Not A Valid 1.01 Beta Analyser File :**

  This message appears when the user is trying to load an invalid file. Note that the same file format has been used from version 1.01 to the present, 1.022. If the file is indeed an impulse file and will not load, then the file has probably been corrupted.

- **Unit Name Must Be Unique :**

  Each unit that is specified in the working set MUST have a unique name.

- **You Have Not Specified Any Regressable Parameters! :**

  This is displayed when a regression has been requested, but no model parameters (split proportions, volumes, peclet numbers, scaling factor etc.) have been set to *'variable'*.

- **You Haven't Chosen a Curve To Regress Against Yet! :**

  As there is a single reference curve (normally containing experimental data), and no restriction on the number of output units that may be specified, the user is required to select the output unit that is to be compared with the experimental data that is contained in the reference.

- **Your Delta Needs Adjustment :**

  Unfortunately, due to the silly memory restriction that were placed on DOS applications, no solution may have more than about 3000 integration intervals in it. The User must ensure that $\frac{Stop\,Time - Start\,Time}{Delta\,T} \leq 3000$. (These settings can be found in the 'Constants" menu.

- **Your Delta T Is Too Small**

  See above.

- **Your Flowrate Convergence Tolerance Is Too Small :**

  The flowrate convergence tolerance must be greater than or equal to 1.0e-6. This is necessary, to ensure that convergence is possible. (Round-off errors which are inherent in floating point calculations can accumulate in the system, and may stop the solution from converging if this number could be set to a smaller value. A recommended setting is 1.0e-5.

- **Your Start Time and Stop Time Need Adjusting :**

  This appears if the user has specified the stop time to be smaller than or equal to the start time. (This obviously does not make sense!)

How Do I?

- **Make A Curve?**

  Firstly, get into an *'Editable Curve'*. (Examples are : The reference [Edit ->Reference], an input unit concentration curve and an input flowrate curve). If no editing has taken place, the user will see a scale factor on the first line (initially set to 1), and a point on the second line (initially set to 0 0). (The first value is the time, and the second value is the property value at that time [concentration or flowrate, depending on which curve is being edited)].

  To **edit** any point that is already in the list, simply move the cursor to the point for alteration, and press enter. An editing box will appear, with the values in it. Simply type in the new pair of values, separated by spaces. When finished, simply press enter, and the point will be updated in the list.

  To **add** a new point, set the cursor next to any point that already exists, or to the blank line immediately below the past point in the list, and press *'INSERT'*. An editing box will appear, this initial abscissa and ordinate values of 0. Alter, if necessary, and press enter when complete. The new point will appear in the list. Points do NOT have to be placed in the list in any particular order. They will be sorted as soon as the user exits the *'Editable Curve'* edit box.

  To **remove** a point from the set, simply place the cursor next to the point for deletion, and press the 'DELETE' key.

- **Import Data Into An 'Editable Curve' From a Spreadsheet?**

  From the spreadsheet, use the ***'Print Range To File'*** option, or some equivalent (extract semantics vary from spreadsheet to spreadsheet). Make sure that you have only two columns of data selected for output, and that the time fields are in the FIRST column. Give the print file a name, and on exiting the spreadsheet, ensure that the file is in the Working directory when invoking IMPULSE.

  Once in IMPULSE, go into the *'Editable Curve'* where the exported data is to be put, and press the 'F1' key. You will be prompted for a file name. Simply enter the file name that you created from the spreadsheet. (This file MUST be in the current working director!!!). You will now be asked for a reduction tolerance percentage. If you do not want any points in the input file to be filtered out (removed), simply press the 'ESCAPE' key. If a percentage value of X percent deviation from a straight line between their immediate left right neighbours will be removed.

FREQUENTLY ASKED QUESTIONS

- **What Unit System Does IMPULSE Use?**

  There is no prescribed system of units in IMPULSE. The user may use any set of units that makes sense, as long as all the data entered by the user are in the same set of consistent units. (If volumes in cubic angstroms, masses in megarams and times in microseconds seem fit for an application for some reason or other, then all flowrates entered should be entered in megagrams per cubic angstrom). It is up to the user to remember what the unit set is that they have chosen to work in.

- **What Are The Limitations?**

  The number of integration intervals for any run of a model is limited to about 3000 or so. This should be more than sufficient for any model, but is an artificial restriction imposed due to the small amount of memory available to DOS applications.

- **Why Do My Results Look Odd?**

  There are a number of causes for this :

  1) As there is only a single viewpoint on the screen, all the curves that have been included in the list of curves to be displayed are automatically scaled, in order to display all of them simultaneously in their entirety. If one curve in the set has upper and low values of 100 and 0, respectively, and all other curves have a cumulative maximum and minimum of 1 and 0, respectively, the first curve can 'overpower' the other curves on the display. (They will virtually appear as straight lines on the bottom of the screen, as their upper and lower values pale in comparison with [100,0].

  2) The user has not specified flowrate and concentration curves over the specified simulation interval. ([start time, stop time]). Every point outside the time interval range that is given in an *'Editable Curve'* is considered zero.

  3) The DeltaT specified for the simulation is too small. (If, for example, the start time and stop time are set to 0 and 2, respectively, and the DeltaT is set to 1, only 3 integration intervals will be used!. This is not suitable for any half-descent simulation!).

- **How Do I Represent An Impulse (Spike) Tracer Input?**

  When doing this, the user must remember that concentrations are used for input, NOT masses. (The input unit should be thought of conceptually as a pipe entering the system, into which the tracer is injected). Therefore, the concentration which is attributed to the addition of a certain specified mass is dependent on the flowrate in the 'pipe'. The user should also realise that the addition of a specified mass has a certain, finite time associated with it. (The dirac delta so often used in mathematical modelling is an idealised situation, and cannot be physically realised in practice).

EXAMPLE :

Let us say, for example, that the steady addition of 5 kg of tracer to an input stream flowing at 10 m^3/s takes the experimenter 4 seconds. This means that the actual concentration of tracer in the input stream during this period is :

$conc = \frac{5kg}{10\frac{m^3}{s} * 4s} = 0.125\frac{kg}{m^3}$. Note that this concentration exists for the entire 4 second interval!

As linear interpolation is used internally between any two points in the *'Editable Curves'*, a point list looking like the following for the flowrate and concentration curves can be used (assuming that the simulation start time and stop time are 0 and 100 seconds, respectively) :

FLOWRATE		CONCENTRATION	
Time	Value	Time	Value
0	10	0	0
100	10	0.001	0.125
		4.001	0.0125
		4.002	0

- **Who Do I Contact If I Have a Query?**

The Pollution Research Group
Chemical Engineering Department
University of Natal
King George V Avenue
DURBAN
4001
South Africa

Fax : (+19) (+27) (+31) 260-1118
e-mail : baddock@che.und.ac.za
buckley@che.und.ac.za
brouckae@che.und.ac.za

APPENDIX

B

Equipment used

1. **Atomic absorption spectrophotometer**

   Varian AA-1475 series

2. **Spectrophotometer**

   Biochrom Ultrospec II

APPENDIX

C

Steps in preliminary calculations

Step 1

The first step is to convert all data into concentration-time data. In some cases, this step is not required as the data is already available as concentration-time data.

Step 2

If the background concentration is known (as a constant or for each data point) then this is subtracted from the concentration data.

Step 3

The tail of the response is extrapolated where necessary. The tail is assumed to be exponentially decaying, and an equation is fitted to the end of the known data. The equation is then used to determine tail data.

Step 4

Determine the area under the concentration-time response

$$area = \sum_0^n C_i \cdot (t_i - t_{i-1})$$

Step 5

Determine the area multiplied by the time

$$(area \cdot t_i) = \sum_0^n C_i \cdot t_i \cdot (t_i - t_{i-1})$$

Step 6

Determine the experimental variables

$$\bar{t} = \frac{(area \cdot t_i)}{area}$$

$$V\_pred = \bar{t} \cdot flow$$

$$mass_{out} = area \cdot flow$$

$$recovery_{tracer} = \frac{mass_{out}}{mass}$$

where :

$\bar{t}$ = realised mean residence time

V_pred = predicted volume of system

$flow$ = average flow through system

$mass$ = mass of tracer put into system

APPENDIX

D

Raw Data

D-1 Northern Waste Water Treatment Works

Experiment 2

tracer mass in	1 200 kg
digester volume	2 300 m^3

time (days)	conc (mg/l)	flow to both digesters (m3/day)
0,00	352	101
0,50	332	
1,00	322	108
1,50	348	
2,00	300	118
2,50	292	
3,00	282	127
3,50	304	
4,00	254	118
4,50	240	
5,00	282	122
5,50	272	
6,00	268	123
6,50	244	
7,00	210	125
7,50	224	
8,00	232	127
8,50	226	
9,00	212	118
9,50	222	
10,00	202	117
11,00	168	119
13,00	188	123
14,00	170	119
15,00	136	121
16,00	136	126
17,00	126	123
19,00	106	127
20,00	100	117
21,00	96	141
22,00	84	148
23,00	70	144
24,00	76	99
25,00	60	105
26,00	82	101
27,00	72	116
28,00	66	122

. *Experiment 3*

tracer mass in 800 kg

digester volume 2 300 m^3

time (days)	conc (mg/l)	flow to both digesters (m3/day)
0	294	92
0,042	381	
0,083	88	
0,125	80	
1,04	80	179
2,00	82	
3,00	81	
4,00	74	
5,00	70	133
6,00	69	130
7,00	74	128
8,00	66	130
9,00	66	134
10,00	59	156
11,00	49	152
12,00	41	120
13,00	47	57
14,00	51	123
15,00	48	109
16,00	45	112
17,00	43	191
18,00	39	111
19,00	39	144
20,00	42	116
21,00	38	126
22,00	39	125
23,00	33	140
24,00	33	168
25,00	31	149
26,00	29	187
38,00	23	124
41,00	20	105
48,00	19	126

D-2 Umbilo Waste Water Treatment Works

flow	1,091 m^3/min
tracer mass in	100,04 g
biofilter volume	36,45 m^3

time (min)	absorbance (nm)
3	0
4	0
4,5	0
5	0
5,5	0
6	0,005
6,5	0,003
7	0,014
7,5	0,021
7,75	0,019
8	0,029
8,25	0,036
8,5	0,04
8,75	0,038
9	0,048
9,5	0,049
9,75	0,05
10	0,052
10,25	0,064
10,5	0,061
10,75	0,062
11	0,067
11,25	0,074
11,75	0,065
12,25	0,075
13	0,068
13,5	0,077
14	0,081
14,5	0,076
15,5	0,073
16,5	0,083
18,5	0,075

time (min)	absorbance (nm)
20,5	0,077
22,5	0,076
24,5	0,071
29,5	0,057
34,5	0,044
40	0,04
50	0,034
60	0,024
90	0

D-3 Wiggins Water Treatment Evaluation Unit

Step-up experiment

flow	0,972 l/s
mixer volume	167 l

time	conc	time	conc	time	conc
0	0	330	0,2045	655	0,2347
5	0,0023	335	0,2073	660	0,239
10	0,0022	340	0,2056	665	0,2364
15	0,0001	345	0,2075	670	0,2386
20	0,011	350	0,2052	675	0,234
25	0,0135	355	0,2089	680	0,2407
30	0,0179	360	0,2115	685	0,2406
35	0,0254	365	0,2138	690	0,2388
40	0,0329	370	0,2094	695	0,2355
45	0,038	375	0,2122	700	0,2396
50	0,0496	380	0,2091	705	0,2376
55	0,0537	385	0,2136	710	0,2355
60	0,0593	390	0,2134	715	0,2384
65	0,068	395	0,2152	720	0,2385
70	0,0699	400	0,2166	725	0,2373
75	0,076	405	0,2184	730	0,2372
80	0,0806	410	0,2146	735	0,2354
85	0,0872	415	0,2152	740	0,2373
90	0,0911	420	0,2151	745	0,2359
95	0,0952	425	0,2178	750	0,2393
100	0,101	430	0,22	755	0,2385
105	0,1016	435	0,2188	760	0,2354
110	0,1079	440	0,2226	765	0,2316
115	0,1117	445	0,2222	770	0,2338
120	0,1151	450	0,2234	775	0,2321
125	0,1142	455	0,2215	780	0,2357
130	0,1226	460	0,2232	785	0,2329
135	0,1249	465	0,2225	790	0,2345
140	0,1297	470	0,223	795	0,2305
145	0,1329	475	0,2205	800	0,2341
150	0,1374	480	0,2247	805	0,2371
155	0,1405	485	0,2249	810	0,2349
160	0,1475	490	0,2288	815	0,2331
165	0,1493	495	0,2272	820	0,2341
170	0,1477	500	0,2263	825	0,2346
175	0,153	505	0,2259	830	0,2339

time	conc	time	conc	time	conc
180	0,1535	510	0,2262	835	0,2353
185	0,1578	515	0,2262	840	0,2347
190	0,1595	520	0,2237	845	0,2357
195	0,1628	525	0,2284	850	0,234
200	0,166	530	0,2277	855	0,2346
205	0,1664	535	0,2263	860	0,2372
210	0,1701	540	0,2279	865	0,2366
215	0,1699	545	0,2279	870	0,2367
220	0,1728	550	0,2301	875	0,2361
225	0,1716	555	0,2319	880	0,2358
230	0,1771	560	0,2293	885	0,2359
235	0,1792	565	0,2287	890	0,2343
240	0,181	570	0,2286	895	0,2343
245	0,1837	575	0,2304	900	0,2334
250	0,1872	580	0,2315	905	0,2329
255	0,1877	585	0,233	910	0,234
260	0,1864	590	0,2344	915	0,2356
265	0,1897	595	0,234	920	0,2367
270	0,1906	600	0,2346	925	0,2364
275	0,1891	605	0,2329	930	0,2369
280	0,1953	610	0,2363	935	0,2374
285	0,1985	615	0,2344	940	0,2363
290	0,196	620	0,2321	945	0,2366
295	0,1963	625	0,2374	950	0,2348
300	0,1984	630	0,2351	955	0,2337
305	0,1986	635	0,2355	960	0,2342
310	0,2016	640	0,2362	965	0,2363
315	0,2023	645	0,2397	970	0,2365
320	0,2014	650	0,2383	975	0,236
325	0,2032			980	0,2416

Step-down experiment

flow	0,972 l/s
mixer volume	167 l

time	conc	time	conc	time	conc
0	0,2188	290	0,0403	580	0,0125
5	0,2133	295	0,0421	585	0,0128
10	0,2092	300	0,0377	590	0,0145
15	0,2008	305	0,0358	595	0,013
20	0,1977	310	0,0363	600	0,012
25	0,1889	315	0,0355	605	0,0118
30	0,1891	320	0,0362	610	0,0133
35	0,1824	325	0,0317	615	0,01
40	0,1728	330	0,0299	620	0,0106
45	0,1684	335	0,0306	625	0,0125
50	0,1669	340	0,0287	630	0,0138
55	0,16	345	0,0324	635	0,0108
60	0,1533	350	0,0309	640	0,01
65	0,149	355	0,0275	645	0,0122
70	0,1444	360	0,028	650	0,0102
75	0,1431	365	0,0271	655	0,0084
80	0,1374	370	0,0261	660	0,0103
85	0,1356	375	0,0253	665	0,0107
90	0,1305	380	0,0246	670	0,0098
95	0,1254	385	0,0249	675	0,0095
100	0,1185	390	0,0242	680	0,0107
105	0,1156	395	0,0222	685	0,0091
110	0,1126	400	0,0221	690	0,0088
115	0,1107	405	0,0228	695	0,0087
120	0,1076	410	0,0186	700	0,0065
125	0,1019	415	0,0206	705	0,0102
130	0,0995	420	0,0181	710	0,0104
135	0,1002	425	0,02	715	0,0076
140	0,0974	430	0,0202	720	0,008
145	0,0948	435	0,0199	725	0,0063
150	0,0917	440	0,018	730	0,0082
155	0,092	445	0,0176	735	0,005
160	0,0888	450	0,0156	740	0,0095
165	0,0828	455	0,0155	745	0,0115
170	0,0838	460	0,0191	750	0,0092
175	0,0788	465	0,0158	755	0,0082

time	conc	time	conc	time	conc
180	0,0749	470	0,0156	760	0,0058
185	0,0728	475	0,0155	765	0,0058
190	0,0719	480	0,0158	770	0,0047
195	0,0671	485	0,0177	775	0,0082
200	0,0655	490	0,0177	780	0,0071
205	0,0647	495	0,0158	785	0,0057
210	0,0648	500	0,0141	790	0,0058
215	0,0603	505	0,0141	795	0,0059
220	0,0603	510	0,0162	800	0,0056
225	0,0563	515	0,0141	805	0,0055
230	0,0556	520	0,0143	810	0,0067
235	0,0554	525	0,0137	815	0,0079
240	0,0538	530	0,0152	820	0,0085
245	0,0531	535	0,0123	825	0,0068
250	0,0549	540	0,01	830	0,0079
255	0,0519	545	0,0125	835	0,0086
260	0,0493	550	0,0112	840	0,004
265	0,047	555	0,0151	845	0,0064
270	0,0461	560	0,0131	850	0,006
275	0,0452	565	0,013	855	0,0074
280	0,0415	570	0,0095	860	0,0069
285	0,0402	575	0,0102	865	0,0045