MODELLING ACTIVATED SLUDGE TREATMENT OF PETROLEUM AND PETROCHEMICAL WASTES

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Ph.D in Engineering

To my uncle, Thomas A. Porter, who as a civil engineer devoted his career
to preserving the waterways of Northern Ireland

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ABSTRACT

The objective of this study was to establish the general framework of a comprehensive dynamic mechanistic mathematical model for predicting the behaviour of an activated sludge plant treating petroleum/petrochemical industrial wastewaters. Specifically, the aim was to develop two activated sludge mechanistic models which predicted the behaviour of systems treating: (1) petroleum refinery wastewater, and (2) petrochemical refinery wastewater. The wastewater treatment plants at two industrial facilities in Ontario were used to develop these models.

A review of the literature identified that mechanistic models were not available for industrial activated sludge plants, but there was extensive information on the development and application of such models to municipal treatment systems i.e. the ASM1 model developed by the IAWPRC (Henze *et al.*, 1987). The development of models for the municipal systems served as a valuable resource for developing these models, but extensive differences between the two types of wastewaters meant that it could not be applied directly to predicting the behaviour of these systems.

The premise for developing these two industrial models was based on the fact that the types of contaminants treated in petroleum and petrochemical refineries have similar characteristics. Both types of systems are based on the processing of crude oil or its derivatives. Therefore, if the contaminants have similar properties, it was hypothesized that the removal mechanisms of the different compounds would also be similar. For example, removal processes such as volatilization, sulphur oxidation, degradation of oils and greases, and degradation of inhibitory compounds such as phenolics are characteristic of these industrial facilities. As a result it was possible to develop a model structure which would apply to the activated sludge treatment of various petroleum/petrochemical wastewaters. This study illustrates these points as they apply to the two selected facilities.

In general, development of a mechanistic model involved:

(1) Identifying model components; and,
(2) Identifying model processes.

Once these model elements were determined, the model was formulated into a mathematical structure. In terms of the development of an activated sludge mechanistic model the following steps were identified as necessary parts of the process and were applied to the development of each of the activated sludge models in this study:

Selection of model structure and complexity
Gathering of experimental data
Mathematical model formulation
Model calibration and verification

The first stage in the study was the development of the petroleum refinery model in order to establish the model structure. In an earlier study (Baker, 1993), an experimental programme designed especially to provide the data necessary for model development was conducted. Using this data the model structure was developed for activated sludge treatment of petroleum refinery wastewaters. Once the model structure was in place, the data were used to calibrate the model predictions to the known system behaviour monitored during the experimental programme. This involved determining values for the different stoichiometric and kinetic coefficients included in the model. By adjusting the values of the parameters until they match observed system behaviour, a single set of values was established which enabled the model to predict adequately system behaviour.

With the experience gained during development of the petroleum refinery model, development of the petrochemical model followed a different approach. The petroleum refinery model provided a structure on which to base the petrochemical model. Therefore, only limited experimentation was conducted to collect the necessary data to determine the important components and processes to include in the model. This experimental programme was performed at the petrochemical facility, and data collected during this study were supplemented with data monitored on the full-scale system. The core of the experimentation involved performing a series of batch tests in which activated sludge was mixed with individual influent streams and the response of the mixture with respect to OUR, filtered COD, and filtered TKN was measured over time. These tests provided data on the kinetic response of the petrochemical system. This data was used to calibrate the model to the behaviour of the petrochemical facility. The result was a model capable of predicting the response of the petrochemical system with reasonable accuracy.

A final stage of the study was to illustrate the advantages of having modelling tools of these systems. One key advantage is to be able to simulate system behaviour on a computer scale before testing operating strategies on a full-scale system. To illustrate a practical application of these models, the petrochemical model was used to determine those modes of operation which provided better system response in terms of effluent COD and VOC air emissions for this particular plant. A range of operating configurations and operating conditions were simulated in the model. Another application of activated sludge models which was not considered in this study was to assist in the design of new wastewater treatment systems.

In conclusion, this study developed two activated sludge models for the treatment of (1) the petroleum refinery system, and (2) the petrochemical refinery system. It illustrated the methodology required to develop models of these type of industrial wastewater treatment facilities. With the framework established for the treatment of petroleum based wastewaters, the development of a model for a different petroleum/petrochemical treatment system can be accomplished with limited experimentation. The approach applied to the development of the petrochemical activated sludge system model can be utilized. This was a valuable contribution of this work.

In achieving these objectives, the study also consolidated current knowledge on the response of these systems. As a result, a better understanding of system behaviour and the important removal mechanisms associated with treatment of petroleum/petrochemical wastewaters was attained. The differences between municipal wastewater treatment and petroleum based wastewater treatment became apparent during the course of the study and confirmed the need for separate models from the IAWPRC ASM1 model.

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GLOSSARY OF TERMS AND SYMBOLS

AT1 - first aeration tank in the petrochemical activated sludge system

AT2 - second aeration tank in the petrochemical activated sludge system

AT3 - third aeration tank in the petrochemical activated sludge system

AT4 - fourth aeration tank in the petrochemical activated sludge system

b - net endogenous decay rate constant for reactor volatile suspended solids, $[d^{-1}]$

b' - actual endogenous decay rate constant for reactor volatile suspended solids, $[d^{-1}]$

b_H - decay rate constant of active heterotrophic organisms, $[d^{-1}]$

b_N - death rate constant of active autotrophic organisms, $[d^{-1}]$

b_S - death rate constant of active sulphur oxidizing organisms, $[d^{-1}]$

BOD - biological oxygen demand

COD - chemical oxygen demand

DAF - Dissolved Air Flotation Unit in the wastewater treatment plant

DO - dissolved oxygen

f - net fraction of active heterotrophic mass which remains as endogenous residue, [gCOD endog. mass $(\text{gCOD active mass})^{-1}$]

f' - actual fraction of active heterotrophic mass which remains as endogenous residue, [gCOD endog. mass $(\text{gCOD active mass})^{-1}$]

f_{ch} - fraction of the total influent COD which are hydrocarbons

f_{cv} - COD:VSS ratio of mixed liquor volatile suspended solids, $[\text{gCOD}\ (\text{gVSS})^{-1}]$

$f_{cv,CH}$ - COD:VSS ratio of hydrocarbons, $[\text{gCOD}\ (\text{gVSS})^{-1}]$

$f_{cv,H}$ - COD:VSS ratio of mixed liquor volatile suspended solids, $[\text{gCOD}\ (\text{gVSS})^{-1}]$

$f_{cv,N}$ - COD:VSS ratio of nitrifying organisms, $[\text{gCOD}\ (\text{gVSS})^{-1}]$

$f_{cv,S}$ - COD:VSS ratio of sulphur oxidizing organisms, [gCOD $(gVSS)^{-1}$]

$f_{cv,X}$ - COD:VSS ratio of particulate organic material, [gCOD $(gVSS)^{-1}$]

f_{enm} - fraction of the total influent COD which is slowly biodegradable

f_E - fraction of active heterotrophic mass and other particulate material which remains as endogenous residue, [gCOD endog. mass (gCOD active $mass)^{-1}$]

$f_{Ep,H}$ - fraction of active heterotrophic mass which remains as endogenous residue, [gCOD endog. mass (gCOD active $mass)^{-1}$]

$f_{Ep,N}$ - fraction of active nitrifier organism mass which remains as endogenous residue, [gCOD endog. mass (gCOD active $mass)^{-1}$]

$f_{Ep,S}$ - fraction of active sulphur oxidizer mass which remains as endogenous residue, [gCOD endog. mass (gCOD active $mass)^{-1}$]

F/M - food-to-microorganism ratio, [gCOD/gVSS]

f_{maxCH} - maximum concentration adsorption sites available on mixed liquor suspended solids for the adsorption of hydrocarbon

f_m - fraction of the total influent COD which is mixed COD

f_n - TKN/VSS ratio of waste solids, [gN $gVSS^{-1}$]

f_{nh} - fraction of the total influent TKN which is ammonia

f_p - fraction of the total influent COD which is particulate

f_{ph} - fraction of the total influent COD which are phenolic compounds

f_{sr} - fraction of the total influent sulphur which is in the reduced form

f_{up} - fraction of the total influent COD which is unbiodegradable particulate

fus - fraction of the total influent COD which is unbiodegradable soluble

f_v - fraction of the total influent COD which are volatile organics

$f_{ZBH,N}$ - nitrogen content of the active mass of heterotrophic organisms, [gN $(gCOD)^{-1}$ in active organisms]

$f_{ZEH,N}$ - nitrogen content of the endogenous mass of heterotrophic organisms, [gN $(gCOD)^{-1}$ in endogenous residue]

$f_{ZBN,N}$ - nitrogen content of the active mass of nitrifying organisms, [gN $(gCOD)^{-1}$ in active organisms]

$f_{ZEN,N}$ - nitrogen content of the endogenous mass of nitrifying organisms, [gN $(gCOD)^{-1}$ in endogenous residue]

$f_{ZBS,N}$ - nitrogen content of the active mass of sulphur oxidizing organisms, [gN $(gCOD)^{-1}$ in active organisms]

$f_{ZES,N}$ - nitrogen content of the endogenous mass of sulphur oxidizing organisms, [gN $(gCOD)^{-1}$ in endogenous residue]

$f_{ZBH,P}$ - phosphorus content of the active mass of heterotrophic organisms, [gP $(gCOD)^{-1}$ in active organisms]

$f_{ZEH,P}$ - phosphorus content of the endogenous mass of heterotrophic organisms, [gP $(gCOD)^{-1}$ in endogenous residue]

$f_{ZBN,P}$ - phosphorus content of the active mass of nitrifying organisms, [gP $(gCOD)^{-1}$ in active organisms]

$f_{ZEN,P}$ - phosphorus content of the endogenous mass of nitrifying organisms, [gP $(gCOD)^{-1}$ in endogenous residue]

$f_{ZBS,P}$ - phosphorus content of the active mass of sulphur oxidizing organisms, [gP $(gCOD)^{-1}$ in active organisms]

$f_{ZES,P}$ - phosphorus content of the endogenous mass of sulphur oxidizing organisms, [gP $(gCOD)^{-1}$ in endogenous residue]

H - Henry's Law Coefficient

HRT - Hydraulic residence time, [d]

IAWPRC - International Association on Water Pollution Research and Control

K_A - adsorption rate for soluble hydrocarbons on volatile suspended solids, [m^3 (gCOD $d)^{-1}$]

K_H - maximum specific hydrolysis rate, [d^{-1}]

K_I - inhibition constant for growth of heterotrophs on phenolics, [gCOD m^{-3}]

k_La - mass transfer rate coefficient of a compound through a liquid film, [d^{-1}]

k_{Lav} - mass transfer rate coefficient of a volatile organic compound through a liquid film, [d^{-1}]

k_{LO2} - mass transfer rate coefficient of oxygen through a liquid film, [d^{-1}]

K_{LP} - soluble phosphorus limit in IAWPRC model switching function, [gP m^{-3}]

K_N - rate constant for ammonification of soluble organic nitrogen, [m^3 (gCOD $d)^{-1}$]

K_{NA} - ammonia limit in IAWPRC model switching function, [gN m^{-3}]

K_{NO} - nitrate limit in IAWPRC model switching function, [gN m^{-3}]

K_O - oxygen limit in IAWPRC model switching function, [gO m^{-3}]

K_{OH} - aerobic/anoxic growth limit in IAWPRC model switching function, [gO m^{-3}]

K_{RAA} - hydrolysis rate of an aliphatic amine, [m^3 (gCOD d)$^{-1}$]

K_R - rate constant for ammonification of soluble organic nitrogen, [m^3 (gCOD d)$^{-1}$]

K_s - half saturation coefficient for aerobic growth of heterotrophs, [gCOD m^{-3}]

K_{sAP} - half saturation coefficient for aerobic growth of heterotrophs on alcohol P, [gCOD m^{-3}]

K_{sCH} - half saturation coefficient for aerobic growth of heterotrophs on hydrocarbons, [gCOD m^{-3}]

K_{sM} - half saturation coefficient for aerobic growth of heterotrophs on mixed organic compounds, [gCOD m^{-3}]

K_{sNH} - half saturation coefficient for aerobic growth of nitrifiers, [gCOD m^{-3}]

K_{sPH} - half saturation coefficient for aerobic growth of heterotrophs on phenolics, [gCOD m^{-3}]

K_{sR} - sulphite oxidation rate of reduced sulphur to sulphate, [d^{-1}]

K_{sS} - half saturation coefficient for aerobic growth of sulphur oxidizers, [gCOD m^{-3}]

K_{sV} - half saturation coefficient for aerobic growth of heterotrophs on volatile organic compounds, [gCOD m^{-3}]

K_V - rate constant for the volatilization of volatile organics, [d^{-1}]

K_X - half saturation constant for hydrolysis, [gCOD (g COD)$^{-1}$]

L - litre

mg - milligram

MISA - Municipal and Industrial Strategy for Abatement

MLSS - mixed liquor suspended solids

MLVSS - mixed liquor volatile suspended solids

N - nitrogen

NH_3 - ammonia nitrogen

NO_3 - nitrate nitrogen

P - elemental phosphorus

PT - pretreatment tank in the petrochemical activated sludge system

O_t - total oxygen utilization rate, [mgO_2/L/h]

OUR - oxygen utilization rate, [mgO_2/L/h]

Q - influent wastewater flow rate, [L/day]

ρ - symbol denoting the overall reaction rate expression for a component in the IAWPRC model

RAS - return activated sludge

S - elemental sulphur

S_{AP} - concentration of soluble alcohol P COD, [g COD m^{-3}]

S_{AAP} - concentration of soluble aliphatic amine P COD, [g COD m^{-3}]

S_{CH} - concentration of soluble hydrocarbon COD, [g COD m^{-3}]

S_I - concentration of unbiodegradable soluble COD, [g COD m^{-3}]

S_M - concentration of mixed substrate biodegradable soluble COD, [g COD m^{-3}]

S_{NH} - concentration of ammonia nitrogen, [g N m^{-3}]

S_{NO} - concentration of nitrate nitrogen, [g N m^{-3}]

S_O - dissolved oxygen concentration, [g (-COD) m^{-3}]

S_{O3} - sulphite compounds

S_{ON} - concentration of soluble biodegradable organic nitrogen, [g N m^{-3}]

S_P - concentration of soluble phosphate, [g P m^{-3}]

S_{PH} - concentration of phenolic biodegradable soluble COD, [g COD m^{-3}]

SRT - solids retention time [days]

S_S - concentration of biodegradable soluble COD, [g COD m^{-3}]

S_{SO} - concentration of sulphate, [g S m^{-3}]

S_{SR} - concentration of reduced sulphur, [g S m^{-3}]

S_V - concentration of volatile biodegradable soluble COD, [g COD m^{-3}]

TKN - Total Kjeldahl nitrogen

TOC - total organic carbon

TSS - total suspended solids, [g TSS m^{-3}]

V - volume, [L]

VSS - volatile suspended solids

VOC - volatile organic compound

X_{CH} - concentration of adsorbed hydrocarbon substrate, [g COD m^{-3}]

X_I - particulate unbiodegradable matter, [g COD m^{-3}]

X_{ON} - concentration of particulate organic nitrogen, [g N m^{-3}]

X_S - concentration of slowly biodegradable substrate, [g COD m^{-3}]

X_V - mixed liquor volatile suspended solids concentration, [g COD m^{-3}]

Y - yield coefficient of microorganism on organic substrate, [g cell COD yield (g COD utilized)$^{-1}$]

Y_H - heterotrophic yield coefficient on COD, [g cell COD yield (g COD utilized)$^{-1}$]

Y_{hAP} - heterotrophic yield coefficient on alcohol P COD, [g cell COD yield (g COD utilized)$^{-1}$]

Y_{hCH} - heterotrophic yield coefficient on adsorbed hydrocarbon COD, [g cell COD yield (g COD utilized)$^{-1}$]

Y_{hM} - heterotrophic yield coefficient on mixed COD, [g cell COD yield (g COD utilized)$^{-1}$]

Y_{hPH} - heterotrophic yield coefficient on phenolic COD, [g cell COD yield (g COD utilized)$^{-1}$]

Y_{hV} - heterotrophic yield coefficient on volatile organic COD, [g cell COD yield (g COD utilized)$^{-1}$]

Y_m - heterotrophic yield coefficient on mixed COD, [g cell COD yield (g COD utilized)$^{-1}$]

Y_{mixed} - heterotrophic yield coefficient on mixed COD, [g cell COD yield (g COD utilized)$^{-1}$]

Y_N - nitrifier yield coefficient, [g cell COD yield (g N utilized)$^{-1}$]

Y_S - reduced sulphur oxidizer yield coefficient, [g cell COD yield (g S utilized)$^{-1}$]

q_X - sludge age, [d]

η_{grow} - correction factor for anoxic growth of heterotrophs

η_{sol} - correction factor for anoxic solubilization

μ_{hAP} - maximum specific growth rate of heterotrophic organisms on alcohol P COD, [d^{-1}]

μ_{hCH} - maximum specific growth rate of heterotrophic organisms on adsorbed hydrocarbon COD, [d^{-1}]

μ_{hM} - maximum specific growth rate of heterotrophic organisms on mixed COD, [d^{-1}]

μ_{maxM} - maximum specific growth rate of heterotrophic organisms on mixed COD, [d^{-1}]

μ_{hPH} - maximum specific growth rate of heterotrophic organisms on phenolic COD, $[d^{-1}]$

μ_{hV} - maximum specific growth rate of heterotrophic organisms volatile COD, $[d^{-1}]$

μ_N - maximum specific growth rate of nitrifying organisms, $[d^{-1}]$

μ_S - maximum specific growth rate of sulphur oxidizing organisms, $[d^{-1}]$

ρ - symbol denoting the process rate equations in the IAWPRC model

ν - symbol denoting the stoichiometric parameters in the IAWPRC model

Z_B - concentration of biomass in the reactor, [g cell COD m^{-3}]

Z_{BH} - active heterotrophic biomass, [g cell COD m^{-3}]

Z_{BN} - active nitrifier biomass, [g cell COD m^{-3}]

Z_{BS} - active sulphur oxidizing biomass, [g cell COD m^{-3}]

Z_E - endogenous mass, [g COD m^{-3}]

ψ - ratio of the transfer of a volatile organic compound to the transfer of oxygen across a liquid film

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CHAPTER ONE

INTRODUCTION

1.1 INTRODUCTION

Wastewater treatment facilities have received increased attention in the last decade with the promulgation of stricter water quality standards to control the effluent quality discharged from both municipal and industrial wastewater treatment facilities. For example, in Ontario industrial and municipal discharges are controlled by the Ministry of the Environment and Energy's Municipal and Industrial Strategy for Abatement (MISA) Regulations (MOEE, 1988, 1989) whereby failure to meet established water quality standards is punishable by law. Industrial facilities have been identified as primary targets in this legislation due to the toxicity of many of the contaminants potentially discharged in these wastewaters. Petroleum and petrochemical refineries are amongst the first group of industries to have stricter guidelines imposed on their effluent quality because of the large volumes of wastewater generated (Laffly, 1990; Putnam, 1990). To ensure compliance with water quality regulations such as those outlined in MISA, the petroleum and petrochemical refineries have had to look at optimizing the operation of their wastewater treatment facilities, and in some instances extend existing systems with new treatment processes. Efforts to optimize and design a system are greatly improved with a thorough understanding of the behaviour of the system and the influence of various operating conditions on the response of the unit. With this understanding it is easier to implement the necessary steps to prevent the discharge of poor quality effluent. It is this goal which initiated the following research on petroleum refinery and petrochemical refinery wastewater treatment modelling.

Wastewaters generated in petroleum and petrochemical refineries have similar characteristics since both systems deal with the refining of crude oil feedstock. In the case of the petroleum refinery, crude oil is refined into products which can be utilised directly or sent to petrochemical refineries. In the petrochemical refinery the feedstock is processed further into a range of petrochemical products. Therefore, the main differences between petroleum refinery and petrochemical wastewaters are the specific contaminants present. Also, petrochemical facilities produce different products depending on their operation, and as a result, the specific composition of the petrochemical wastewaters tend to vary even from facility to facility. The pollutants in the petrochemical refinery wastewaters, however, have similar chemical properties to the petroleum refinery wastewaters since both are generated from the processing of hydrocarbons.

As would be expected, oils, greases, and other hydrocarbon contaminants such as C-H compounds, phenolics, alcohols and amines account for a significant portion of the organic pollutant load in the wastewaters. The processing stages in the refineries may also produce pollutants such as ammonia, and reduced sulphur based compounds. This mixture of compounds must be removed from the effluent before safe discharge to the receiving waters.

Treatment of the processing effluent generated from petroleum/petrochemical refineries generally involves several sequential steps, and these steps are often similar due to the similar characteristics of the wastewaters. Each stage is designed to remove one or more of the contaminants which have been identified in the wastewaters generated in these facilities. The wastewaters initially receive primary treatment. This may involve removal of oils and greases in API separators (gravity based settling system) or dissolved air flotation (DAF) units, air or steam stripping of compounds such as ammonia and sulphides, or pH control. The exact nature of these primary treatment stages is highly dependent on the characteristics of the specific wastewater. Having been processed through primary treatment, the wastewater proceeds to secondary treatment which is generally a biological process, often an activated sludge system. This unit is responsible for removing the bulk of the organics in the wastewater and provides the important function of reducing the levels of toxins in the effluent. Finally, a tertiary treatment stage consisting of a carbon adsorption column or a filtration unit may be included as a final polishing step to further improve effluent quality.

Although each treatment process is important, the secondary treatment stage is critical to successful wastewater treatment since it has the greatest impact on the reduction of contaminants to low levels. It is also the most complex unit and the most difficult to operate and control. Understanding this stage of the treatment process is a key element in optimizing the performance of the wastewater treatment system and attaining the treatment objectives. As a result, the activated sludge system of a petroleum/ petrochemical wastewater treatment facility will be the focal point of this research.

One approach which has been used widely in the field of science and engineering for gaining an understanding of overall system behaviour is to develop a mathematical model of the system of concern. Developing a model simultaneously addresses two complementary purposes. Firstly, to formulate a model the different elements of the system must be studied. For example, in a chemical system there are different reactions which must be understood independently before they can be included in an overall model of the system. Therefore, as the model is developed, insight into the behaviour of various individual components in the system is obtained and the controlling elements of system behaviour are identified. As a result the model building procedure itself initiates an understanding of system behaviour. Secondly, as each element in the system is studied and modelled, it can be combined with other elements to form a comprehensive mathematical model. Initial model development may only consider key elements of the system in order to reduce its complexity, but as each component or process of the system is better understood the model complexity can be increased and the ability of the model to predict system response improved. With a comprehensive working model in place the behaviour of the system under different operating conditions can be estimated initially using the model without having to impact the actual system. Only feasible operating conditions need be tested on an actual system thereby minimizing system upset. In summary, model development initiates system understanding by forcing the individual elements of the system to be studied and provides a tool which can be used for optimization of the overall process behaviour.

As an example which is pertinent to this research, modelling efforts in *municipal* wastewater treatment have demonstrated that a dynamic model which predicts the behaviour of the activated sludge unit is a very powerful tool. The IAWPRC (International Association of Water Pollution Research and Control) Model No.1 (ASM1) for activated sludge treatment of municipal wastewater is a mechanistic model that has been used extensively and successfully in the design, control and optimization of activated sludge systems (Grady, 1989). Use of this model for predicting the behaviour of the activated sludge systems treating municipal wastewaters has been shown to serve a number of specific functions; for example:

- The model can be used to improve design of an activated sludge system, given information on influent wastewater characteristics. A range of process configurations and operational strategies can be evaluated rapidly.

- The model can be used as an aid in the control of the activated sludge system to produce high quality effluent on a consistent basis. By running the model under time-varying influent conditions the appropriate operating conditions and control strategies can be identified and corrective measures can be suggested. This assists in optimizing the performance of the system.

- The dynamic model can be used as a tool for training of plant operating personnel. The model can be used to simulate system behaviour under different conditions to illustrate how changes in process parameters impact plant performance. This approach facilitates an understanding of what parameters to change and the magnitude of the changes required to correct particular problems which arise during process operation.

The advantages of a model which emulates the benefits of the IAWPRC ASM1 model, but for activated sludge systems treating petroleum or petrochemical refinery wastewaters, are evident from the above discussion. However, an extensive review of the literature on petroleum refinery wastewater treatment by this author (Baker, 1993) identified the following situation :

- A dynamic mathematical model specifically structured and developed for describing the behaviour of an activated sludge plant treating petroleum or petrochemical refinery wastewater was not available. [In a number of instances minor adaptations of the IAWPRC model have been applied for these systems e.g. Yuan (1994)].

- Past studies conducted on refinery biological wastewater treatment have been directed mainly at determining contaminant concentrations in the effluent and identifying processes occurring in the system. Incomplete information was available on the stoichiometry and kinetics of the individual processes that occur within the activated sludge unit; specifically, how the processes interact to impact the overall system behaviour in terms of factors such as sludge production, oxygen requirements, and so on. The lack of a complete set of data for model formulation was addressed in Baker (1993). In that study experiments were conducted to obtain the information required for model development for an activated sludge system treating petroleum refinery wastewaters.

In summary, without comprehensive data it has not been possible to develop a dynamic mechanistic mathematical model of the petroleum or petrochemical refinery activated sludge system.

1.2 OBJECTIVE

The objective of this research was to establish the general framework of a comprehensive dynamic mechanistic mathematical model for predicting the behaviour of an activated sludge plant treating petroleum/petrochemical type industrial wastewaters. Specifically, the aim was to develop two mechanistic models which predicted the behaviour of activated sludge systems treating: (1) petroleum refinery wastewater and, (2) petrochemical refinery wastewaters. This development was directed at the wastewater treatment systems of two large Ontario industrial facilities processing these two types of wastewater.

The premise on which this objective was based is that petroleum and petrochemical wastewaters exhibit similar behaviour patterns when treated in an activated sludge system due to the similar characteristics of the compounds which must be removed from these wastewaters. Therefore, the models developed for the treatment of petroleum refinery and petrochemical refinery wastewaters likely should be very similar. However, these compounds are significantly different to those found in municipal wastewaters. This meant that a different model was required from that which currently exists for activated sludge treatment of municipal wastewaters (ASM1). Development of the IAWPRC model for municipal systems served as a valuable resource in achieving the above objective, however. Based on this experience, the following approach was utilized for developing models for activated sludge treatment of petroleum and petrochemical refinery wastewaters.

- **Literature Review:** The purpose of conducting the literature review was to survey work which has been completed in this field of research to establish the current knowledge base and identify any deficiencies. For example, in this study information was required on model development for activated sludge systems, specifically any experience with modelling the treatment of petroleum and petrochemical refinery wastewaters. The literature identified previous successes with model development for activated sludge systems and identified the stages required in the development of similar models to the ones reported. In the current situation, it also confirmed that a model designed to predict the behaviour of activated sludge systems treating petroleum and petrochemical wastewaters did not exist. Complementing the experience on model development with information reported on the behaviour of the petroleum and petrochemical wastewaters enabled a procedure to be established for accomplishing the objectives. The literature review is presented in Chapter 2. From the review a methodology for model development was established.

- **Development of the Model for the Petroleum Refinery Activated Sludge System:** The second stage of the study was to initiate development of the specific activated sludge system models. The availability of a comprehensive database on the behaviour of an activated sludge system treating petroleum refinery wastewaters (Baker, 1993) provided the necessary information to proceed with development of a mathematical model representing activated sludge treatment of petroleum refinery wastewaters. The data was collected on continuous flow laboratory-scale activated sludge systems operating under both constant loading and dynamic loading conditions (Baker, 1993). Operation of these systems provided extensive information on the stoichiometry and kinetics of these systems. Model development is presented in Chapter 3 and calibration of the model is described in Chapter 4.

- **Development of the Model for the Petrochemical Refinery Activated Sludge System:** The next stage in the study was to develop a second activated sludge model for predicting system behaviour when treating petrochemical wastewaters. The rationale behind this step was to illustrate the similarities in the behaviour of the two systems despite the fact that the specific compounds treated in each system are significantly different. The approach had to be different for developing this model since extensive experimental data was not already available. Chapters 5 and 6 describe the limited experimental programme which was required and the form of the model developed to represent the behaviour of an activated sludge system treating petrochemical wastewater.

- **Application of the Petrochemical Activated Sludge Model:** The aim of the final stage in the study was to illustrate the advantages of having an activated sludge modelling tool. The petrochemical model was used in the study. As outlined in Chapter 7, this element of the approach served to illustrate how modelling system behaviour can be used as an optimisation tool for evaluating changes to full-scale operation.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

The objective of this study was to develop two activated sludge mechanistic models for the treatment of petroleum refinery and petrochemical refinery wastewaters. Part of this aim was to illustrate that, due to the similarities in the nature of the wastewaters treated in these systems, a similar model structure could be applied to the development of the two activated sludge models. Having illustrated the applicability of the model structure to both systems, the format could be applied to the development of activated sludge models treating other petroleum and petrochemical refinery wastewaters. The literature review was conducted with these overall objectives in mind and is presented in four parts.

Section 2.2 of the literature review discusses previous experience with modelling of biological wastewater treatment systems and the benefits of having such models. The next section (2.3) identifies the similarities and differences between activated sludge systems treating municipal wastewaters and those treating petroleum/petrochemical wastewaters. This justified the need to develop separate models for the latter. The steps required to develop activated sludge models, therefore needed to be determined. The success of mechanistic models developed and applied to activated sludge systems treating municipal wastewaters was deemed a valuable resource for determining an approach for developing models for the petroleum based applications. This is discussed in Section 2.4. Finally, experience with modelling on petroleum/petrochemical systems is presented in Section 2.5 to provide background on the nature of processes occurring in these activated sludge plants.

Together these tasks provided insight into the process of developing a dynamic mechanistic model capable of predicting the behaviour of an activated sludge plant treating petroleum or petrochemical refinery wastewaters. Out of this review a specific approach for developing a mechanistic model for activated sludge systems treating these wastewaters could be formulated. This included identifying any experimentation required for formulating and developing the model.

2.2 MODELLING IN BIOLOGICAL WASTEWATER TREATMENT

2.2.1 Biological Wastewater Treatment

The process of developing a model initially requires the identification of a particular system to be modelled. Before proceeding with the discussion on modelling these systems, a brief overview of the principles of activated sludge treatment will be provided. This identifies the exact nature of the system which is being considered.

The system which required modelling was identified as the biological treatment system of a petroleum or petrochemical refinery wastewater. This is one of the most difficult and complex processes to control and optimize in a wastewater treatment scheme because of the range of processes occurring within the system, many of them interactive in nature. One of the more common types of biological treatment systems used in industrial wastewater treatment is an activated sludge system and as a result, was the specific system chosen for model development.

In terms of its role in a wastewater treatment plant, an activated sludge plant, like all biological systems, is primarily responsible for the removal of organic compounds. The organic material is removed by the action of microorganisms using the organic contaminants as a food and energy source. Nitrogen and phosphorus compounds also are utilized in these processes. In addition to removal of organic matter, biological action in an activated sludge system also contributes to the removal of certain inorganic compounds like nitrogen and sulphur through a different series of reactions. The bacteria performing these reactions are called chemo-autotrophs and utilize inorganic compounds as their energy source and carbon dioxide as their carbon source to synthesize new cells. Growth of microorganisms in the system also is accompanied by natural death and decay processes. These processes produce particulate byproducts referred to as endogenous residue which contribute to the solids concentration in the activated sludge reactor. These reactions all contribute to the overall ability of the activated sludge system to reduce the potential oxygen demand and nutrient loadings discharged to the receiving waters. The system also reduces toxicity in the effluent streams. Without this type of biological process unit the low concentrations sighted in the water quality objectives would be difficult to achieve.

Activated sludge systems generally consist of: (1) a series of CSTR's in which biological degradation of the contaminants results in the growth of biomass, and (2) a clarification unit for the removal of suspended solids from the treated effluent. Some of the settled biomass is recycled to the bioreactor to maintain the concentration of organisms in the system; this stream is termed the return activated sludge recycle (RAS). Accumulated solids are removed from the system via a wastage (WAS) stream, usually from the RAS recycle. This stream controls the length of time the organisms remain in the system i.e. sludge age. The sludge age influences the type and diversity of organisms which exist in the mixed liquor. Organisms with lower growth rates can survive at longer sludge ages, but wash out of the system at shorter sludge ages. The longer the sludge age the more diverse the organism type. This improves the ability of the organism mass to degrade organic material in the wastewater, especially those compounds which are more resistant to biodegradation and compounds adsorbed on the sludge mass. As a result, sludge age is the main control variable in these systems. Figure 2.1 schematically illustrates the setup of the activated sludge system receiving wastewaters.

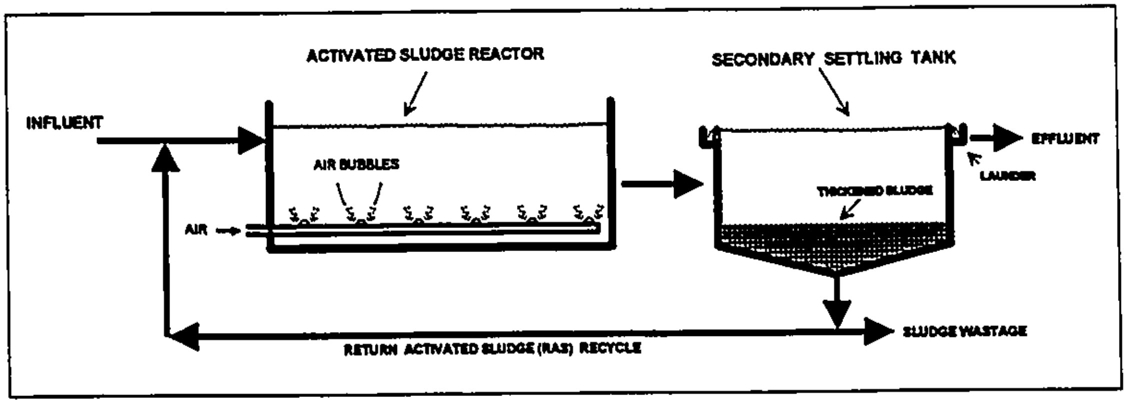

Figure 2.1 Schematic Diagram of Aerobic Activated Sludge System Configuration.

Unlike the primary treatment processes which are designed to remove one specific type of contaminant generally on the basis of some physical phenomena, the biological process is responsible for removing a large number of compounds all with different chemical characteristics. To do this there are several different removal processes occurring simultaneously within the system. Optimizing this array of processes is what makes operation and control of the refinery activated sludge system so complex. This system forms the basis of the modelling problem in this study.

2.2.2 Stochastic *versus* Mechanistic Models

As identified in the introduction, a common approach which has been used widely in the field of science and engineering for gaining an understanding of overall system behaviour is to develop a mathematical model of the system of concern. With the mathematical structure in place, the models can be used as a tool in many working situations (Grady, 1989). A model can be used as a conceptual framework in research areas to extend knowledge by building and testing different hypotheses. In systems where there are many interactive processes, it is especially important to have a structure in which to determine the possible outcomes of different operating scenarios. A model also can be used by a designer to identify the best alternatives by enabling different systems and system variables to be considered. Optimization of system design could be based on performance or cost, or both. Furthermore, a model can be used to determine the potential impact of changes in process operation or design modifications on the desired outcome i.e. wastewater treatment system models can be used by regulators to determine the effect of stricter water quality standards on the cost of operation. Application of the model in operational situations enables an operator to test a range of input and operational conditions in order to develop a control strategy without impacting the actual system. In other words, it provides direction on what course of action to pursue given certain events. It also can be used as a learning tool in educational situations to explore the interrelationships in a system and to explore new ideas. These examples illustrate the significant benefits achieved by having a model of the particular system of interest.

In mathematical modelling of any system there are two main approaches that can be used: (1) stochastic modelling, or (2) deterministic/mechanistic modelling. Both types of models were considered initially for application to an activated sludge system. A stochastic model is an empirical input/output model which does not consider the processes occurring within the system. Stochastic models are derived directly from dynamic input/output data collected on the process using the methods of time series or frequency analysis. This type of model provides a simple representation of the process response to measured or known input disturbances in addition to the effect of measurement noise and unmeasured process disturbances which are present during the collection of the data. A stochastic modelling approach can thus provide information on the relative contribution of known input perturbations and unmeasured process disturbances on observed variations in the process output. A disadvantage of this approach is that the resulting models are highly system specific as well as operating region specific. That is, a stochastic model developed for one particular system over one particular operating region cannot be applied to a different system directly and may not be valid for a different operating point in the same process.

By way of an example, stochastic models have been developed in an effort to explain the behaviour of municipal wastewater treatment systems (MacGregor, 1973; Berthouex *et al.*, ,1978, 1975 *a,b*). This approach has met with limited success, however i.e. it was difficult to establish an input/output pattern of system behaviour. Debelek and Sims (1981) also had difficulty using stochastic models to represent an industrial activated sludge system. Stochastic models have been found to describe effectively the influent flow and loading patterns to the treatment plant using a time-series approach. However, problems arise when attempting to model the input/output relationships between different parameters across the biological treatment system. Development of these models in order to estimate organics removal across the aeration basins proved difficult since in many cases there is not a significant difference in effluent quality despite varying influent concentrations of organic material. The noise component of the stochastic model accounted for the majority of the variation. This is the result of the systems operating below capacity which ensures essentially complete removal of the biodegradable organic material. In this situation a stochastic model does not adequately represent the behaviour of the system. However, combining both deterministic and stochastic elements produces time series models which provide better estimates of the system relationships (Novotny *et al.*, 1991).

On the other hand, input/output relationships often can be developed more readily for nutrient removals such as nitrogen and phosphorus across an activated sludge plant because these tend to exhibit more variation in effluent quality. Adeyemi (1979) successfully modelled total phosphorus removal using stochastic methods. Therefore, if the selected parameters do vary significantly between influent and effluent quality a stochastic representation may provide useful insight into system behaviour. However, as indicated above, a stochastic model only applies to the system of concern and the specific mode of operation being studied. It cannot be applied readily to another activated sludge system or to a very different operating strategy for the plant. Furthermore, it is difficult to relate the wastewater parameters to the operating parameters in order to establish and optimize operating strategies. Therefore, for activated sludge applications the use of stochastic models for describing the relationships between influent and effluent quality and the operational variables is considered to be limited.

The alternate type of model is a mechanistic model. A deterministic mechanistic model relates the inputs to the system to the outputs through a set of process rate equations which mathematically mimic the actual processes or transformations occurring within the system of interest. Generally, a mechanistic model of a wastewater treatment system embraces two main characteristics :

(1) The components (or compounds) in the influent waste and in the biological system which are of interest to the modeller.
(2) The processes (biological and physical) occurring within the system and the manner in which these influence the component concentrations.

The model should track the fate of the model components. To do this it is necessary to quantify the influence of the processes on the model components. That is, each process incorporated in the model requires a mathematical description of (1) the reaction rate, and (2) the reaction stoichiometry. These characteristics emphasize the marked differences between a stochastic modelling approach versus a mechanistic one.

An advantage of deterministic models over stochastic models is that the former are more transportable to other systems and may be valid for a wider region of process operation. This is related to the fact that the processes occurring in the reactor will behave in a similar manner in different systems. Development of mechanistic models usually results in a greatly improved understanding of the detailed phenomena occurring in the process. A mechanistic approach also provides the flexibility for testing alternate process configurations. The current trend within wastewater treatment is to use mechanistic models for predicting the behaviour of activated sludge systems.

An example of the application of a mechanistic process model used in wastewater treatment is the International Association of Water Pollution Research and Control (IAWPRC) Model No.1 (ASM1) for the activated sludge treatment of municipal wastewaters. The advantages of this model to both designers and operators in the design, operation, and control of these systems (Henze *et al.*, 1987) were identified in Chapter 1. It is a dynamic mechanistic model based on understanding the transformations occurring within the system, and the stoichiometry and kinetics of the biological reactions. Its dynamic nature enables system response to the variable inputs of flow and water quality often typical of full scale facilities to be predicted. Details of the IAWPRC model will be discussed later in this chapter as it provided a starting point for model formulation of the petrochemical model.

In summary, therefore, the advantages of the mechanistic model support its choice over a stochastic model when possible. Although development of mechanistic models often requires a more extensive effort, once formulated, these provide a good understanding of the actual events occurring in the system and can be readily applied to new systems once the basic structure is in place.

2.2.3 Modelling of Municipal Wastewater Treatment Systems and the ASM1 Model

A key concern in conducting this literature review was to identify previous use of mathematical models for the understanding and optimizing of system behaviour in the operation of activated sludge systems. As indicated earlier, most of the modelling efforts for activated sludge systems have been directed towards municipal wastewater treatment (Dold & Marais, 1985; Billing & Dold, 1988 *a,b,c*; Dold *et al.*, 1980; Ekama *et al.*, 1980; Gaudy & Kincannon, 1977*a* and 1977*b;* Ramalo, 1978). The International Association of Water Pollution Research and Control (IAWPRC) made a concentrated effort over the last two decades to develop a mathematical model which predicts the response of municipal activated sludge systems to various influent and operating conditions. The driving force was to combine the work of many researchers into a single consensus model which could be used in design, operation, and optimization of these systems. As a result a task group was established with the aim of developing the simplest mechanistically based deterministic model capable of simulating the behaviour of municipal activated sludge systems. The result of their efforts is the IAWPRC ASM1 model summarized by Henze *et al.* (1987).

To provide some background, development of the IAWPRC model evolved largely from work during the 1970's of G.v.R. Marais and his coworkers at the University of Capetown (Marais & Ekama, 1976) and J.F.Andrews and coworkers at the University of Houston and Rice University (Blackwell, 1971; Clift & Andrews, 1981; Stenstrom, 1976). This work in itself was the summation of the efforts of many researchers over the years as discussed by Dold & Marais (1984) in their report to the 2nd meeting of the IAWPRC Task Group. In brief, it was identified in Dold & Marais (1984) that there had been four stages of model development since World War II. These were (1) experimental empirical models, (2) aerobic models for constant flow and load, (3) aerobic space-time dynamic models, and (4) anaerobic-anoxic-aerobic space-time dynamic models. The IAWPRC model was the next stage in this development and it consolidated the information contained in the other models. The following processes were identified as occurring in municipal activated sludge systems and were incorporated in the IAWPRC Model No.1:

- Carbonaceous removal due to the action of microorganisms. The biodegradable portion of the influent is converted to new cell mass in this process. The strength of the organic matter is defined in terms of its electron equivalence, or in practical terms, its chemical oxygen demand.
- Hydrolysis of biodegradable particulate COD after it has been adsorbed onto the sludge.
- Enmeshing of unbiodegradable particulate COD into the sludge for removal in the waste sludge stream.
- Discharge of soluble unbiodegradable COD with the effluent stream.
- Decay of the organisms in the system using the death-regeneration theory.
- Conversion of organic nitrogen to ammonia.
- Nitrification of free and saline ammonia to nitrate.

- Denitrification for the conversion of nitrate to nitrogen gas. This process, where nitrate acts in place of oxygen as a terminal electron acceptor is termed anoxic growth.

Using previous work reported in the literature, the initial IAWPRC model represented each of these reactions by a mathematical equation. As more information was collected on the behaviour of the activated sludge systems more accurate representations of these reactions and their kinetic constants have been determined. Therefore, development of the IAWPRC model is a continuous process where the mathematical equations are constantly being refined to reflect new information. The model has also served as a guide for developing more comprehensive models of activated sludge systems. An example of this situation is the development of a mechanistic model to predict the behaviour of biological phosphorus removal in activated sludge systems (Marais & Dold, 1985; Dold, 1990a).

Without going into detail, the ASM1 model for municipal activated sludge treatment is illustrated in the matrix presented in Table 2.1. This table lists the different compounds included in the activated sludge model across the top of the table and the processes occurring in the system down the left hand side. The rate equations used to represent these processes are listed on the right hand side, and the stoichiometry of the different reactions is evident in the body of the matrix. This table illustrates the type of mechanistic model required to represent an activated sludge system.

In summary, the development of the IAWPRC ASM1 model for activated sludge systems treating municipal wastewaters has provided valuable insight into the behaviour of these systems and the mathematical representations of the different reactions occurring in the reactors. The model has been analysed by various experts in the field (Dold & Marais, 1984 and 1985; Grady, 1989) and as improvements have evolved it has become the standard in the industry.

Table 2.1: Model Matrix for Municipal Activated Sludge System (ASM1)

COMPONENT	1	2	3	4	5	6	7	8	9	10	11	12	13	
PROCESS	Z_{BH}	X_E	X_{BA}	X_S	X_I	X_{ND}	S_S	S_{NH}	S_{ON}	S_{NO}	S_{ALK}	S_I	S_O	PROCESS RATE EQUATIONS, ρ i
1 Aerobic growth of heterotrophs on S_S	1						$-\frac{1}{Y_H}$				$-\frac{f_N}{14}$		$\frac{-(1-Y_H)}{Y_H}$	$\mu_H \cdot \frac{S_S}{K_s + S_S} \cdot Z_{BH} \cdot \frac{S_O}{K_{OH} + S_O}$
2 Anoxic growth of heterotrophs on S_S	1						$-\frac{1}{Y_H}$	$-f_N$		$\frac{-(1-Y_H)}{2.86 Y_H}$	$\frac{-(1-Y_H)}{14 \cdot 2.86\, Y_H} - \frac{f_N}{14}$			$\eta_{grow} \cdot \mu_H \cdot \frac{S_S}{K_s + S_S} \cdot Z_{BH} \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}}$
3 Decay of heterotrophs	-1	f_E		$1 - f_E$		$f_{EN} - f_E f_{EN}$		$-f_N$						$b_H \cdot Z_{BH}$
4 Hydrolysis of X_S				-1			1							$K_H \cdot \frac{X_S/Z_{BH}}{K_X + X_S/Z_{BH}} \cdot Z_{BH} \cdot \left(\frac{S_O}{K_{OH} + S_O} + \eta_{sol} \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}}\right)$
5 Hydrolysis of particulate organic N									1					$K_{Hn} \cdot X_{ON}/X_S$
6 Ammonification								1	-1		$\frac{1}{14}$			$K_R \cdot S_{ON} \cdot Z_{BH}$
7 Autotrophic growth			1					$-f_N - \frac{1}{Y_A}$		$1/Y_N$	$-\frac{f_N}{14} - 1/7 \cdot Y_N$		$\frac{-(4.57 - Y_N)}{Y_N}$	$\mu_N \cdot \frac{S_{NH}}{K_{sNH} + S_{NH}} \cdot Z_{BN} \cdot \frac{S_O}{K_{OH} + S_O}$
8 Autotrophic decay		f_E	-1	$1 - f_E$		$f_{EN} - f_E f_{EN}$								$b_N \cdot Z_{BN}$

2.3 SIMILARITIES AND DIFFERENCES BETWEEN THE MUNICIPAL AND PETROLEUM/PETROCHEMICAL ACTIVATED SLUDGE SYSTEMS

2.3.1 Similarities in the Modelling of Municipal Activated Sludge Systems and Petroleum Based Activated Sludge Systems

Identifying key principles in municipal treatment systems and their respective models aids in the understanding of the petroleum and petrochemical refinery activated sludge systems and simplifies efforts to develop models of their behaviour. The following discussion will present those elements of the IAWPRC Model No.1 which can assist in the development of the petroleum based systems. The approach used to develop the IAWPRC model will then be considered in detail in Section 2.4. This provided the rationale behind the approach to this study.

Many of the basic processes used to model the treatment of municipal wastewater apply to the petroleum and petrochemical refinery applications with some modification. For example, biological growth and decay of heterotrophs and autotrophs occurs in activated sludge systems regardless of the nature of the wastewater. As a result, in the IAWPRC model biodegradation of organic material in both aerobic and anoxic environments, and nitrification of ammonia are the main removal mechanisms included in the model. Monod growth kinetics are used to model the conversion of soluble organic substrate into heterotrophic biomass and the conversion of ammonia nitrogen into nitrate via growth of autotrophic biomass. The stoichiometry and kinetics of the processes may differ for the petroleum based applications since the wastewater characteristics are very different from municipal wastewater, but the appropriate values can be determined for the particular wastewater system. The basic principles of microorganism growth continue to apply. These observations reflect the similarities between the two systems and indicate the nature of some of the mathematical expressions which can be used to represent the different processes.

The structure developed to present the activated sludge model treating municipal wastewaters also provided an effective approach for presenting the model of any activated sludge system. The IAWPRC model was presented in a matrix format (Billing & Dold, 1988). Any changes or additions made to the removal mechanisms in the model or comparison of the IAWPRC model with other models is simplified by tabulating the model in this fashion. This format allows each individual process in the overall scheme to be considered separately.

The points described above give a general overview of those elements of the IAWPRC Model No.1 for municipal activated sludge systems which are applicable to the industrial applications. Again, they serve as a starting point for this modelling problem.

2.3.2 Differences in the Modelling of Municipal Activated Sludge Systems and Petroleum Based Activated Sludge Systems

A review of the literature (Baker, 1993) revealed that efforts to develop such a comprehensive model which emulated the benefits of the IAWPRC model for municipal treatment were minimal in the activated sludge treatment of petroleum and petrochemical refinery wastewaters. Furthermore, due to the differences between municipal and petroleum based wastewaters, the model developed for municipal applications cannot be applied directly to petroleum and petrochemical wastewaters. These differences will be highlighted throughout the project, but to put the work into context a list of the main differences in the treatment of the two different types of wastewaters is summarized. The differences include:

- The presence of hydrocarbons have a major influence on the response of these activated sludge systems. The compounds tend to be adsorbed onto the sludge which extends their influence on the oxygen usage in the system i.e. these contaminants degrade slowly. Also, reports have indicated that the degradation of hydrocarbons tends to result in lower yields of microorganisms and higher oxygen consumption rates than for growth on municipal wastewaters (Humphrey, 1970; Payne, 1970; McKenna & Kallio, 1965). One possible explanation for this observation is the initial requirement for oxygen and energy in converting the hydrocarbon to a fatty acid which then can be utilized in the normal energy pathways in an organism (citric acid cycle, oxidative phosphorylation) (Van der Linden & Thijsse, 1965; McKenna & Kallio, 1965).

Hydrocarbons can influence the settling properties of the sludge in the clarifiers and may increase the apparent decay rate of organisms. Since these compounds have a direct impact on several aspects of system performance it is important that a model of these systems incorporates the hydrocarbon component directly into the model structure.

- The presence of significant concentrations of volatile organic compounds (VOC's) in the industrial wastewaters has a significant influence on the solids concentration and oxygen consumed in the aeration tanks in the system. A portion of the influent COD of these compounds may be oxidized by the organisms whereas the remaining portion is stripped. The division in the response behaviour depends on the relative kinetics of the two processes. Defining the contribution of the different removal processes is important for determining system response. VOC's are not as critical to the overall response of a municipal activated sludge system because the concentration in the influent generally is low. However, VOC emissions may become more important as increased emphasis is placed on air quality.
- Compounds such as phenolics, which exhibit inhibitory growth kinetics in sufficient quantities have been identified in these wastewaters. Transient spike loadings of these compounds are not uncommon and the resulting high concentrations can have a negative impact on the effluent quality. Modelling efforts should include this inhibitory effect on growth or the system capabilities may be grossly overestimated (Rozich, 1983, 1985).
- Reduced sulphur compounds have been identified in petroleum/petrochemical wastewaters and can have a major impact on oxygen demand in the system. These generally are not considered in municipal systems since they do not appear in sufficient quantities. In Baker (1993) the potential impact on oxygen consumption in a petroleum refinery was observed. For the treatment of wastewaters generated during the processing of certain crude oils, reduced sulphur compounds could be the major consumer of oxygen in the activated sludge plant.
- A larger portion of the organic matter in petroleum refinery wastewaters is soluble compared to municipal wastewaters. Therefore, the process of hydrolysis/solubilization of particulate organic matter is less important than for municipal systems.

- In municipal wastewaters the organic material generally is comprised of a large number of different compounds each at low concentration. The opposite often is true for industrial wastewaters where the majority of the influent organic matter is derived from a limited number of compounds each at significant concentration. For municipal wastewaters it has been found acceptable to group the compounds into surrogate components; for example, soluble and particulate, with no distinction between the individual compounds. This is not necessarily possible or appropriate for industrial wastes where system behaviour may be impacted significantly by a single compound. For example, the hydrolysis of an aliphatic amine to a carbon compound and ammonia. In order to monitor adequately system behaviour these compounds must be tracked specifically.

These points illustrate the major differences between activated sludge systems treating municipal versus petroleum based wastewaters. Treatment of these compounds results in a number of removal processes which must be included in modelling efforts of the industrial systems which have been neglected in the IAWPRC model for municipal systems. The significant differences prevent direct application of the ASM1 Model to predicting the response of industrial systems. However, these differences do not negate the fact that the model for municipal wastewater treatment is adaptable for developing models of other wastewater treatment systems. Using the experience gained during the development of the model describing the behaviour of an activated sludge system treating municipal wastewaters, a comparable model also can be developed for the petroleum or petrochemical refinery wastewater treatment systems by including the issues just described. In summary, the IAWPRC model for municipal wastewater treatment served as a valuable resource during the development of a model which can be applied to petroleum based activated sludge systems. With such a model these facilities also can benefit from having a comprehensive dynamic model which predicts system behaviour.

2.4 STEPS IN MODEL DEVELOPMENT

As indicated, development of the IAWPRC model for the activated sludge treatment of municipal wastewaters suggested an effective approach for building activated sludge models and identified key elements of system behaviour in this study. The approach implemented by the IAWPRC task group will be presented in the following discussion to establish a methodology for developing the models for the petroleum based systems.

A mechanistic model for municipal activated sludge systems was developed in order to address the problem of predicting the changing concentrations of certain compounds with time within the system (possibly multiple reactors) under constant and dynamic input conditions. These transformations result from a combination of different processes. The mathematical model, therefore, had to represent this range of processes which act on the many components in the wastewater and influence both the response within the system and the effluent quality. In order to develop such a model two major questions needed to be considered at the outset:

(1) What compounds of interest should be included in the model?
(2) What are the processes acting on these compounds, and what are the stoichiometry and kinetics of the processes?

Generally, the compounds of interest in any activated sludge system include the contaminants to be removed from the wastewaters and the biological components conducting the degradation processes. Since there are many different types of compounds and organisms in these systems a practical method of selecting and representing groups of these components needs to be established to simplify the model to a practical form. It is important that the components to be tracked in the system reflect the nature of the influent wastewater and the composition of the biomass in the activated sludge reactor. This selection is critical during initial stages of model development.

Experience gained during development of the IAWPRC model provided insight into the selection of the model components. It also provided information on the complexity of the model to develop in the initial stages. Ideally, a model of any treatment process should account for the fate of each individual compound in the wastewater since the principal concern in operating these systems is to ensure that the effluent concentrations of specific compounds are below certain limits. However, wastewaters consists of a wide range of individual chemical compounds. To develop a model which initially accounts for all these individual compounds would be extremely complex. Therefore, in the first instance a simplified approach must be taken where: (1) only major groups of compounds are considered (e.g. total biodegradable soluble COD rather than individual compounds), and (2) the concentrations of these groups are measured in terms of some bulk parameter such as Chemical Oxygen Demand (COD). This approach was adopted by the IAWPRC Task Group in modelling of municipal treatment systems. That is, initially model development was based on measurements of bulk parameters such as total influent COD, but as the understanding of the processes improved, the models have been refined to discriminate between different fractions of COD and to include the occurrence of nitrogen and phosphorus removal mechanisms in the activated sludge. This approach assisted in identifying the type and number of components to include in the initial model development of petroleum based systems.

Inherent in the above discussion is the importance of characterizing the wastewater during the initial model development stages. This was identified during the development of the IAWPRC model and extends into the petroleum based application. For industrial systems, the fate of certain specific compounds and groups of compounds within the wastewater may need to be considered in some instances. Therefore, the sole use of bulk parameters in models of municipal systems may not be appropriate for all industrial applications. In any case, the decision to study the pathway of any particular contaminant either as a bulk parameter or individually depends on identifying its presence in the incoming wastewater. Characterization of the wastewater is therefore, an integral part of developing the model of any activated sludge system as was illustrated in the development of the IAWPRC model for municipal systems. It must be a key consideration in developing an experimental programme to determine the data requirements for model formulation.

In terms of the system processes the biological interactions are central to the activated sludge system, although other removal mechanisms including physicochemical processes also have to be considered. These processes then act on the various compounds present in the wastewaters to generate a specified mass of microorganisms and to produce effluent of a particular quality. The rate equations proposed for these processes are key to enabling the model to predict effectively the wastewater effluent quality and system parameters. As a result, development of these rate equations and determination of the stoichiometry of the reactions in a municipal activated sludge system were critical to a successful predictive model of system response (Henze *et al.*, 1987). This remains true for the petroleum based application.

With the required data the mechanistic models can be formulated and then calibrated to predict the specific behaviour of the activated sludge system of interest. In general, two forms of data are required:

(1) Steady state operating data from continuous flow systems: Ideally the systems should be operated over a range of sludge ages. This data provides the basis for calibrating certain stoichiometric parameters, which in turn enables prediction of parameters such as sludge production and oxygen demand.

(2) Dynamic system response data either from continuous flow systems under time-varying loading or from batch tests. This data enables evaluation of kinetic formulations and kinetic parameters

Previous research studies on the processes occurring in these systems can assist in determining the appropriate model formulations. This stage in model development establishes the mathematical relationships between influent characteristics, system processes, system operating parameters, and the overall system response in terms of effluent quality. Once the mathematical structure is in place the coefficients in the model equations can be determined using the experimental database. This is accomplished by direct measurement and by adjusting the model parameters until model predictions match actual experimental results. Determining the model coefficients calibrates the model and constitutes a critical element in model development. The extent of success depends largely on the extent of the database.

This brief overview describes the overall procedure used by the IAWPRC task group in collecting and utilizing data for developing the model of the municipal activated sludge system. Sufficient data describing the system of concern is critical to model development. Therefore, if such data is not available, suitable experiments need to be performed to obtain the information. With the necessary database, model development for an activated sludge system treating petroleum or petrochemical wastewaters can proceed.

In summary, development of the model framework to emulate the approach that was successfully applied in the development of the IAWPRC activated sludge model for municipal systems involved four specific tasks :

- **Selection of model structure and complexity:** The first stage of any model development requires consideration of the desired model structure and complexity. This involves identification of (1) the model components (compounds) of concern, and (2) the processes which act upon these components in the system. The numbers of processes and components selected for consideration in the model determines the complexity of the mechanistic model. This identification procedure is applied to establish a structure for a model appropriate to the activated sludge system of interest.

- **Gathering of experimental data:** Development of a mathematical model requires data on the behaviour of the activated sludge system so that the system equations can be developed to produce outputs which match the actual events occurring in the system. Available data in the literature or current plant operating data can be used for this purpose, or if this is insufficient, an experimental programme can be designed to obtain the necessary information. The development of the IAWPRC model for activated sludge systems treating municipal wastewaters provides an example of the type of data necessary for model development and the types of experimentation required to obtain this information.

- **Mathematical model formulation:** The results of the experimental studies or operating data are used to develop a system of equations which mathematically represent the response of the activated sludge system i.e. a mathematical model. This involves determining stoichiometric expressions to describe the effects of particular reactions on the masses of compounds and kinetic expressions to determine the rate-concentration dependence. When used in conjunction with the influent wastewater quality and the reactor configuration of the system, these equations are used to calculate a mass balance equation over each reactor for each compound of concern. These mass balances generate a set of simultaneous non-linear differential equations which form the basis for simulating the behaviour of the activated sludge treatment system.

- **Model calibration and verification:** The final stage of model development is to calibrate the model using the experimental data. Any stoichiometric or kinetic parameters not directly measured during the experiments are determined during the calibration process. By comparing the predictions determined from the calibrated model to actual observations measured on the laboratory or full scale system, the success of the model development exercise is evaluated. Comparison of the calibrated model with another set of observed data aids in verifying the ability of the model to predict system behaviour under a different set of conditions. This verification stage is an important step in model validation. During this process a sensitivity analysis also should be conducted to determine how a change in the value of a given model parameter impacts model predictions.

The outline above indicates the general approach required to formulate a dynamic model of an activated sludge plant. As a result of the success of the IAWPRC modelling approach, it will be used as a basis on which to approach the modelling of activated sludge systems treating petroleum/petrochemical wastewaters.

2.4.1 Summary

Experience gained in modelling municipal treatment systems provided guidance in (1) choosing the parameters to be measured during experiments on the refinery systems, and (2) designing the experimental programmes needed to provide the data for model development, and (3) presenting the model structure in a useful fashion. These concepts were applied in the development of the model describing treatment of petroleum based wastewaters.

2.5 EXPERIENCE WITH ACTIVATED SLUDGE SYSTEMS TREATING PETROLEUM AND PETROCHEMICAL WASTEWATERS

A review of past experience with activated sludge systems treating petroleum and petrochemical wastewaters provides insight into the type of compounds commonly found in these wastewaters and the type of behaviour to expect. The following discussion identifies the compounds which are characteristic of these systems. It also presents typical behaviour of these systems which assists in determining the important removal mechanisms. Finally, experience with modelling the different removal mechanisms are reviewed.

2.5.1 Composition of Petroleum and Petrochemical Refinery Wastewaters

2.5.1.1 Petroleum Wastewaters

A detailed description of the contaminants typically found in petroleum refinery wastewater was given in Baker (1993) along with the results of the wastewater characterization study conducted on the Imperial Oil Refinery at Nanticoke, Ontario. To identify the components which should be considered in model development, the review is summarized.

The petroleum refining process is a very complex operation which produces a highly contaminated wastewater. Organic compounds such as hydrocarbons (C-H compounds) are typical of these wastewaters. A major component of the organic material, therefore, is related to residual oils and greases from the processing units. For the most part these constitute the "insoluble" organic portion of the wastewater chemical/biological oxygen demand (COD/BOD). However, very small particles of oils and greases are effectively soluble in water and contribute to the soluble organic fraction of the wastewater. Aromatic compounds such as benzene and toluene also have been identified and contribute to the volatile organic emissions from these systems. A range of phenolic compounds derived principally from sour waters from the distillation and cracking units also have been detected. Certain organic compounds in these wastewaters are refractory in nature and result in a "non-biodegradable" organic component.

The principal inorganic components in the wastewater are nitrogen and sulphur due to the presence of these compounds in crude oil. These are transformed during processing into the ammonia and sulphides found in the waste streams. A sour crude oil contains greater quantities of nitrogen and sulphur than a sweet crude. This may be reflected in higher concentrations of ammonia and sulphides in the wastewaters generated from sour crude oil. The combination of these waste streams results in the complex refinery effluent which must be effectively treated before discharge to receiving waters.

In terms of specific toxic organic compounds, short chain carboxylic acids, naphthenic acids, and various substituted aromatics (volatile aromatics and PAH'S) (Sun *et al.*, 1987) are the groups of toxic organics which generally have been found. However, of the extensive number of contaminants listed on the EPA Priority Pollutant List eighty percent were either not detected or only rarely detected in petroleum refinery effluent wastewater (Maynard, 1990). Several other studies and reviews of refinery wastewater characteristics support these observations (PACE, 1987; API, 1984). As a result of this work it has been suggested (Maynard, 1990) that only a limited list of parameters need be monitored to demonstrate that the system is controlling toxic chemicals. These were:

(1) Volatile organic compounds of benzene, toluene, ethylbenzene, xylenes;
(2) Conventional parameters of TOC/COD/BOD, oil/grease, suspended solids;
(3) Total Phenolics[•];
(4) Nutrients - nitrate and ammonia;
(5) Metals - copper, zinc, chromium (if used in the refinery).

This suggestion is valuable in assessing the components to include in a model of these activated sludge systems in order to achieve a model of reasonable complexity.

[•] In the petroleum refinery sector, phenolic compounds or "phenolics" are measured using a specific method, the 4-AAP analytical test procedure developed by the EPA. This analytical procedure analyses for selected unsubstituted and substituted phenolic compounds. It should not be confused with the measurements of the specific compound, phenol. For instance, under the MISA monitoring program for the petroleum refining section, both "phenolics (4AAP)" and "phenol" were reported, the former in mg/L and the latter in µg/L.

Table 2.2 (from Rebhun & Galil, 1988*a*) lists the composition of a typical waste stream entering a petroleum refinery biological treatment plant and compares this to values which have been reported in the literature. Since the wastewater characteristics depend on the nature of the crude oil and operations in the refinery, the consequence is a range of potential values. Included in Table 2.2 are the effluent quality values after biological treatment.

Table 2.2: Examples of Concentrations of Refinery Wastewater Pollutants Before and After Biological Treatment (after Rebhun & Galil, 1988*a*).
[Concentrations in units of mg L^{-1}]

COMPONENT	*INFLUENT*		*EFFLUENT*	
	R & G	*Literature*	*R & G*	*Literature*
pH	8.14	6.2 - 10.6	7.85	6.7 - 7.9
Total suspended solids	98	15 - 85	47	6 - 112
Volatile susp. solids	65		26	
COD - Total	625	140 - 3340	230	80 - 300
COD - Soluble	443		165	
BOD - Total	268	7 - 230	19	4 - 100
BOD - Soluble	143		7	
Hydrocarbons	40	23 - 200	4.8	0.5 - 9.0
Ammonia (as N)	21	0 - 120	13	0 - 43
Chlorides		19 - 1080		
Sulphides		0 - 38		

2.5.1.2 Petrochemical Wastewaters

The petrochemical industry is extremely diverse and as a result the wastewaters it produces are highly varied depending on the product being produced at a given facility. Therefore, it is extremely difficult to identify specific compounds which may be present in a wastewater without knowing what it produces. For example (Nemerow & Desgupta, 1991), a synthetic rubber manufacturer may use styrene and butadiene in the processing units so contamination of the effluent with these compounds would be expected. Another facility may use large amounts of phenolics for processing resulting in high effluent phenolics values. In general terms, however, the wastewaters generated in petrochemical facilities have the following characteristics (Nemerow & Desgupta, 1991; Goettems *et al.*, 1988; Huber, 1988; Okawa, 1988):

- High concentration of COD;
- High total dissolved solids;
- Oils and greases;
- Compounds inhibitory to biological treatment (i.e. phenolics) often in high concentrations;
- Insufficient nitrogen and/or phosphorus for organism growth is common;
- High frequency of spills resulting in spike loadings to treatment plants;
- Product revision in the processing trains which causes variations in waste characteristics.

These general characteristics provide guidance for the types of compounds to consider when studying a particular petrochemical facility. The specific contaminants would have to be determined for the given wastewater treatment system. Since many of the compounds are derived from petroleum products it is expected that the behaviour of the different compounds during biological treatment is similar.

2.5.2 Behaviour of Petroleum and Petrochemical Activated Sludge Systems

A significant amount of the research conducted on the processes occurring in activated sludge systems treating petroleum based wastewaters has been on petroleum refineries. A limited number of studies have been performed on petrochemical facilities, and of those reported, the emphasis has been on determining system performance. Therefore, the emphasis in the following discussion will be on the petroleum refinery activated sludge systems. Reviewing past experience assisted in determining the key removal processes to include when developing the models.

A summary of previous experience with petroleum refinery activated sludge systems is outlined below to highlight the major points. This summary is based on an extensive review of the literature by Baker (1993) and the results of experiments conducted on a laboratory scale activated sludge system treating petroleum refinery wastewater detailed in the same report. Detailed discussion of the following points can be found in that report.

- In the overall treatment scheme the major portion of soluble organics removed from the wastewater occurs in the activated sludge system.
- The bulk of the soluble organics are removed through biological degradation. System performance is discussed in terms of parameters characteristic of biological systems e.g. oxygen utilization, chemical oxygen demand, and sludge production, etc.
- In addition to biodegradation, other removal mechanisms were identified as contributing to the overall removal of contaminants. These include biosorption and stripping processes. Some research has been directed at quantifying the contribution of each of these removal mechanisms.
- In terms of efficiency of organics removal and reduction in toxicity levels, activated sludge systems generally have proven successful. Nevertheless, certain operational problems have been identified.
- A major operational concern evident from the literature is the presence of oils and greases in the wastewater. Higher influent concentrations are thought to have a negative impact on sludge settling. Ineffective settling in the clarifiers may result in increased solids in the effluent.
- Nitrification of ammonia to nitrate has been identified in many of these systems when nitrogen is present in sufficient quantities. This reduces the toxicity of the wastewater to receiving waters.
- Oxidation of reduced sulphur compounds contributes to the oxygen demand of the activated sludge system. In some cases, it is the major oxygen consumer in the system.

Along with the above characteristics which describe the general functioning of the biological system the literature also contains information on quantifying the fate and influence of certain toxic contaminants in refinery wastewater. The following aspects have been highlighted in a number of studies.

- Biological nitrification has been found to be very susceptible to inhibition by toxic compounds found in the wastewater.
- The removal mechanisms of a number of toxic organics like phenolics, benzenes, and ethylbenzenes have been studied. In certain cases the principal removal mechanism has been identified as volatilization (e.g. benzene and

ethylbenzene). In other cases biological degradation is the primary removal mechanism (e.g. phenol). Adsorption has been shown to have minimal influence in these systems for the compounds considered. The impact of other toxic compounds and their associated removal mechanisms requires further study to fully understand their influence on the system.

- The removal of phenolics has received special attention due to the inhibitory effect these compounds have on the biodegradation process and on nitrification. Some research has been directed at determining the removal pattern and the kinetics of the phenol removal process.

In summarizing all the past experience with refinery activated sludge systems, it was evident that the studies conducted previously can be grouped into two categories. Studies conducted at one level complement the findings at the other level to provide a better understanding of process behaviour.

- One category of available information is concerned with *performance* of the refinery activated sludge system. That is, the capacity of the system to remove contaminants, quantified either in terms of bulk parameters such as chemical oxygen demand (COD) or concentrations of specific compounds. As noted, the concern with specific compounds is that water quality standards require that concentration limits for certain compounds are met. However, information on specific compounds is inadequate for proper control of the biological reactor. The concentrations of the individual compounds are small and as a result do not provide a basis for establishing reactor size, sludge ages, and hydraulic retention times required for the initial design and control of the reactor. This necessitates quantification of bulk parameters such as COD in order for overall operating parameters such as sludge production and oxygen utilization rates to be determined. The result is that quantification of both bulk parameters and specific compounds are required to improve system operation.
- The second category of the studies has been targeted at a more complex level of the biological system; that is, establishing *removal mechanisms* of bulk and specific contaminants in the wastewater including kinetics and stoichiometry. This type of information is vital to fully understanding why the process

> behaves as it does. Predictions of the removal rate of the substrate can be made, as well as how much a particular contaminant is inhibiting growth of the organisms. Studies conducted on ammonia and phenol removals are examples of the work on inhibitory compounds. The efforts to establish kinetic constants for the various biodegradation reactions are critical for predicting the response of the system. Quantification of the kinetic constants in the volatilization and biosorption processes also are necessary. Most of the research conducted to date has only considered the individual processes and much work still has to be conducted in this area to understand fully the removal mechanisms. The missing element in this previous work is the combination of all the removal processes into one predictive modelling tool.

This previous experience with refinery activated sludge systems was useful for gaining an understanding of their behaviour. This was extremely advantageous in formulating a comprehensive mathematical model of all the processes occurring in the petroleum based activated sludge systems. Advancements in modelling many of these processes is now presented.

2.5.3 Modelling of the Processes in Petroleum and Petrochemical Activated Sludge Systems

With the desire to improve the understanding of the processes in biological treatment of petroleum based wastewaters, advances have been made in modelling the individual removal processes. This work was very valuable in building a predictive mathematical model to describe the response of a petroleum/petrochemical refinery activated sludge system. It provided insight into the type of equations which should be used in a mathematical model and quantified many of the reaction coefficients of specific contaminants.

Growth of organisms on non-toxic components in the petroleum based wastewaters generally was assumed to behave in a similar manner to organism growth in municipal systems. Therefore, growth was assumed to follow Monod growth kinetics and modelled accordingly (Monod, 1942). However, as indicated in Section 2.3.1, despite the applicability of the Monod relationship, the actual model coefficients may vary between the two types of systems i.e. municipal *versus* petroleum. For example, the rates of degradation may vary depending on the characteristics of the compounds. Also, the yield coefficients of the growth mechanisms may vary between the contaminants in municipal and petroleum based wastewaters. One explanation for this difference involves the conversion of hydrocarbon compounds characteristic of petroleum wastewaters to fatty acids. The fatty acids then are used in the energy cycles of the microorganism. This original transformation to a fatty acid utilizes oxygen and energy resulting in the lower yields of organisms on hydrocarbon COD which have been reported (Payne, 1970; Ertola *et al.*, 1965). The mechanism involved in the hydrocarbon metabolism does not influence the form of the Monod kinetics, but must be considered when evaluating the coefficients associated with the reaction. This is important to realize when developing the models of the petroleum based activated sludge systems. This example also illustrates the influence of influent characteristics on system performance.

The removal processes of particular concern in the activated sludge treatment of petroleum and petrochemical wastewaters are those involving toxic organic compounds which are often inhibitory to organism growth (i.e. phenolics), and those involving volatile organic compounds which may be stripped from the aeration tanks (benzene). These processes are not as critical to the behaviour of municipal activated sludge systems, and as a result, are not included in models of these systems. The behaviour of the toxic and volatile organic compounds is emphasized in the following discussion.

Initial efforts to model the fate of compounds found in many chemical and petroleum industry wastewaters assumed first order reaction equations for biodegradation, stripping, and adsorption mechanisms. The scope of much of this research was to identify the fate of the compounds in these systems (Gaudy *et al.*, 1963; Stover & Kincannon, 1982; Weber *et al.*, 1987). These studies identified the processes which controlled the removal of a given compound and quantified the impact of the combined processes on the kinetic constants. For example, Stover & Kincannon (1982) determined values for the biokinetic and stripping constants in terms of BOD, TOC, and COD for a system treating a number of toxic compounds. The studies revealed the impact of stripping when determining the values of the biokinetic constants. If stripping was not a significant removal mechanism then the kinetic constants remained unchanged. This was the case for the behaviour of phenol in a bench-scale system, whereas the kinetic constants for benzene changed due to the impact of stripping. Adsorption of compounds to the biomass was found to be significant for only a limited number of compounds so in general was not included in subsequent modelling efforts. Weber *et al.* (1987) also conducted research to determine the kinetic coefficients of stripping, biosorption and biodegradation and again found that biosorption was not a major removal mechanism except for the compound lindane. More mathematically complex fate models of organic compounds have been reported more recently (Berglund & Whipple, 1987; Govind & Dobbs, 1991; Melcer, 1993), but the emphasis remains on determining the relative fate of the organic compound in the treatment plant. All these studies illustrated the key removal mechanisms which control the removal of toxic compounds from activated sludge systems and provided estimates of the kinetic constants to expect from these systems.

Other studies have looked specifically at modelling the biological removal of toxic organic compounds such as phenol (Andrews, 1968; Pawlowsky & Howell, 1973; Rozich *et al.*, 1983, 1985; Gaudy *et al.*, 1986; Rebhun & Galil, 1988; Godrej & Sherrard, 1988). As an extension to the studies completed by Rozich and Gaudy (1985) on phenol behaviour, Gaudy *et al.* (1988) performed studies on the degradation of 2,4-dinitrophenol and orthochlorophenol. The consensus of all these research efforts indicated that the Haldane relationship (Haldane, 1930) best represented the growth rate, μ of organisms on inhibitory substrates:

$$\mu = \frac{\mu_{max} S}{K_s + S + S^2 / K_I} \qquad (2.1)$$

where μ_{max} = the maximum growth rate,
S = the concentration of substrate,
K_S = the half-saturation constant, and
K_I = the inhibition constant.

Rozich *et al.* (1983,1985) confirmed the results of many of the earlier works which indicated the importance of modelling toxic organic compounds, including phenol, using the Haldane equation rather than Monod kinetics. Although at low phenol concentrations the Monod equation adequately satisfied the process kinetics for organism growth, it allowed for operating ranges which would lead to system failure during the treatment of high concentrations of inhibitory substrate. The Haldane equation predicted more accurately the response of the system to shock phenol loads and the critical operating conditions which would lead to system failure. Rozich *et al.* (1985) tabulates the range of kinetic constants to expect when modelling the growth of phenolics using the Haldane equation. These are as follows: μ_{max}, range = 0.08-0.36 h^{-1}, mean = 0.19 h^{-1}; K_S, range = 1.3-266 mg/L, mean = 75 mg/L; K_I, range = 66-1463 mg/L, mean 449 mg/L.

The kinetic constants established in the above studies at steady-state conditions also were used to analyse the predictive nature of the model equations under transient loading conditions. The inhibition models were not as successful under the transient loadings. The problem of predicting the behaviour of phenolic degradation under transient loadings may be a function of the characteristics of a transient system rather than the inhibitory nature of phenolics. The studies of Rozich and Gaudy (1985) found discrepancies in the transient model predictions which were comparable to problems associated with model predictions of a system treating transient loads of non-toxic substrates. Both model types do not consider the biological changes which occur in a system during any shock load. The models do not account for a lag in growth response to a changing influent condition, or a reserve capability of the system to handle the shock. The latter factor is believed to a be characteristic of systems operating at low growth rates. Furthermore, the shock load may cause the actual organism population to change depending on their ability to respond to the feed. Since biokinetic constants used in these models are dependent on both the substrate and the type of organism, the constants acting during the shock load may be different than those operating during a transient load. In a non-toxic system all of these growth phenomena may occur, but only in the toxic system do they lead to system failure as a result of reaching the critical growth rate, μ^*. Further study is required in this area for both toxic and non-toxic contaminants to draw any firm conclusions.

The important fact to be realized from these observations is that the kinetic constants established in any modelling efforts are not absolute, but rather indicate the general tendencies of a system. Generally, all the above studies conducted on the degradation of phenolics indicate that these compounds are an important concern in the activated sludge process when considering the behaviour of these systems. All the growth and operational phenomena noted in these studies should be kept in mind when modelling the petroleum and petrochemical activated sludge systems.

The other removal mechanism which has been identified as important for the removal of organic compounds from petroleum and petrochemical wastewaters is stripping. Stripping refers to the mass loss of volatile compounds in aerated turbulent vessels, and is differentiated from volatilization which is the transfer of compounds from a quiescent surface (Melcer *et al.*, 1993). Generally, stripping is modelled using a first order rate equation of the form (Melcer *et al.*, 1993; Matter-Mueller *et al.*, 1981; Munz & Roberts, 1989; Gaudy *et al.*, 1963; Engelbrecht *et al.*, 1961):

$$r_v = K_V C, \tag{2.2}$$

where r_v = the rate of stripping from the system,
K_V = the volatilization rate constant, and
C = the concentration of the volatile organic compound.

Although the form of this equation is simple, the critical element in its ability to predict the stripping rate of an organic compound from the activated sludge systems is quantifying the rate constant K_V. Studies have shown that K_V is dependent on temperature, unit air flow rate and tank geometry (Gaudy *et al.*, 1961, 1963). In order to estimate the impact of these physical parameters on the stripping rate, researchers have developed relationships based on mass transfer theory for determining the stripping rate constant in activated sludge systems depending on the characteristics of the compound being stripped (Hseih *et al.*, 1994; Munz & Roberts, 1989; Roberts *et al.*, 1984; Matter-Mueller *et al.*, 1981). Equations have been developed which apply to both surface and bubble aeration. Development of the equations which apply to bubble aeration are described in Appendix 7. These relationships enable estimates of the stripping rate constants to be determined for a given activated sludge system.

The above discussion highlights research which has been conducted on the removal mechanisms which are characteristic of activated sludge systems treating petroleum and petrochemical wastewaters. The influence of these processes on the behaviour of these treatment systems means that any modelling efforts of these facilities must include equations which represent the different mechanisms. The discussion identifies mathematical formulations which have been used successfully in previous research and were of valuable in developing the models of the petroleum based activated sludge systems.

2.6 SUMMARY OF LITERATURE REVIEW

A key finding of this literature review was confirmation that there has been minimal effort directed at developing a comprehensive model which predicts the behaviour of activated sludge systems treating petroleum and petrochemical wastewaters. Therefore, this review of the literature concentrated on identifying the requirements for developing a mechanistic model for these systems. Information was collected on: (1) modelling activated sludge treatment, and more specifically, (2) treatment of petroleum and petrochemical refinery wastewaters.

Previous experience with modelling activated sludge systems treating municipal wastewaters (IAWPRC model) served as a valuable resource for identifying the data requirements for developing such a model and identifying an effective approach for formulating the mathematical equations. It was identified that model formulation initially involves three main stages :

- Identification of the system to be modelled,
- Identification of the system components, and
- Identification of the model processes.

With the basic structure in place the mathematical equations are developed to represent the different processes, and the parameters in the model equations evaluated using experimental data. This results in a mechanistic model representing the behaviour of the activated sludge system.

In order to develop the equations necessary to describe the petroleum and petrochemical wastewater treatment systems, a review of the literature of these systems was conducted. It identified the nature of the influent streams these activated sludge systems must handle along with the processes which impact system behaviour. It was confirmed that biodegradation of non-toxic and toxic (inhibitory) compounds, biosorption of oils and greases, stripping, nitrification, and sulphur oxidation are all important removal mechanisms in these systems. Having identified the key removal mechanisms, experience with modelling these processes was reviewed. This provided guidance for the type of mathematical formulation to use in developing the model.

In summary, the aim of reviewing the literature was to consolidate past experience with (1) modelling activated sludge systems, and (2) the behaviour of the petroleum based activated sludge systems. The outcome was an effective approach for developing a model for the petroleum and petrochemical application. Previous experience maximized the ability to develop an effective tool for design and optimization of these systems.

2.7 RESEARCH OBJECTIVES AND APPROACH

Completion of the literature review enabled a detailed approach to be developed for attaining the desired objectives of the study. As indicated in Chapter 1, the objective of this research was to develop two models for activated sludge systems treating wastewaters from petroleum refineries or petrochemical facilities in order to predict system behaviour. As a result of this objective, a framework for activated sludge models treating petroleum/petrochemical wastewaters would be established.

Wastewaters generated in petroleum/petrochemical facilities have similar characteristics, but are quite different from municipal wastewaters. Similarly, the processes treating these wastewaters are comparable, but different from municipal systems. Therefore, it should be possible to develop a model structure for this general classification of wastewater which can be tailored to the specific system of concern. However, because of the differences between municipal and industrial wastewaters, the model is likely very different from the IAWPRC ASM1 model for municipal systems.

The approach taken in this study was first to develop a model for petroleum refinery wastewater treatment. In a second stage the petroleum refinery model was adapted for application to a petrochemical refinery wastewater. This sequenced approach was adopted primarily because of the nature of the wastewaters. The composition of petroleum refinery wastewater is more consistent from plant to plant than is the case with petrochemical wastes. The specific contaminants present in petroleum wastewaters remain fairly uniform although concentrations may vary. This consistency enabled the major components and the processes governing system response to be identified and the general framework of the model to be established.

Data for development of the petroleum refinery model was available from an earlier study Baker (1993). This comprised data from (1) a continuous flow laboratory scale activated sludge system operated with constant and time-varying inputs, and at different sludge ages; and (2) a range of batch tests.

The development of the activated sludge model treating petrochemical facility wastewaters used a different approach. The model framework established for activated sludge treatment of refinery wastewaters was applied to the petrochemical operation. The main difference between petroleum refinery and petrochemical wastewaters is the specific contaminants present. The pollutants in the wastewaters, however have similar chemical characteristics to the refinery wastewaters since both are generated during the processing of hydrocarbons. The mechanisms required to treat these wastewaters, therefore, are likely similar. Therefore, the aim was to apply the model structure used to model the petroleum refinery to the petrochemical activated sludge system with a few minor modifications.

In order to develop the activated sludge model for the treatment of petrochemical wastewaters experimental data was required. This information was attained in two forms. The full-scale operation of the plant provided data on the operation of a continuous flow system. Using long term averages of influent flow rates and quality, along with effluent quality and operating conditions an understanding of system performance could be developed. To supplement data from the full-scale operation, a limited number of batch experiments were conducted to characterize and quantify certain kinetic rates. Batch tests involved mixing influent streams with activated sludge from the full-scale plant and monitoring the response of the mixture over a selected period of time. These two sources of data generated sufficient information for the model to be calibrated and validated.

This approach was much faster than the development of the initial petroleum refinery model. The aim of using this approach in this section of the study was to illustrate the ability of the procedure to generate a calibrated model. If successful, it would provide a method for calibrating any petroleum/petrochemical activated sludge system with relative expediency.

The final stage in the model development of these industrial activated sludge systems was to illustrate the use of these models for studying potential operating strategies. The activated sludge model developed for predicting the behaviour of petrochemical systems was utilized in a simulator which models the entire system configuration. Different operating strategies were tested in the simulation model to identify which mode of operation was likely to provide the best treatment performance. This procedure confirmed the benefits of having a model of the activated sludge system and how it can be utilized to optimize system behaviour.

2.7.1 Selection of Case Studies

Development of the mechanistic models of activated sludge systems treating petroleum based industrial wastewaters involved selection of two case studies:

(1) Petroleum - Imperial Oil Petroleum Refinery, Nanticoke, Ontario
(2) Petrochemical - Petrochemical Facility, Sarnia, Ontario.

Using wastewater from full scale facilities for model development provided a realistic basis for model development. The broad range of contaminants present in a "real" wastewater would be very difficult to simulate in a "synthetic feed." Therefore, with the latter, interactions which may occur between compounds in a wastewater would not be accounted for in the model development process. Using actual wastewater also provided a more realistic view of the variability of contaminants present in the wastewater over time and how the operation of the activated sludge system is impacted by this variability. By developing an activated sludge model based on the treatment of actual wastewaters the predictive capacity of the model is more likely to reflect the true response of the system to a given set of operating and influent conditions.

The choice of wastewater from the Imperial Oil Petroleum Refinery, Nanticoke for model development was a result of an ongoing efforts between McMaster University and Imperial Oil to achieve a better understanding of industrial wastewater treatment. In this coordinated effort, it was considered desirable that part of this overall study would be to carefully study and optimize the behaviour of the activated sludge system operating at the Nanticoke facility. As a result it became an important element in the development of the activated sludge model for treatment of industrial wastewaters. For purposes of model development, the refinery wastewater was used for the extensive experimental program due to the proximity of the facility to the laboratories at McMaster (Baker, 1993). Experimental requirements necessitated that wastewater be collected from the Nanticoke plant every two to three weeks. The experimental results using this wastewater served in the initial model formulation stage.

Activated sludge treatment of a second type of petroleum based industrial wastewater was necessary to test the applicability of the formulated model to a different system. Since the nature of the pollutants in these different types of wastewaters are a result of processing petroleum related compounds, the mechanisms involved in removing them from the wastewater treatment system should be very similar. This hypothesis needed to be tested, however, by applying the model to a petrochemical facility. The choice for this research as a second test case was a result of negotiations between McMaster University, the Wastewater Technology Centre, and the petrochemical facility to address the operation of the activated sludge plant used at their Sarnia site. Again, the aim was to develop a better understanding of process behaviour so the operation of the system could be improved to meet the necessary water quality criteria.

Development of the activated sludge models for industrial wastewater treatment utilized the wastewater and operating data from both of these full-scale facilities to identify and quantify the removal mechanisms of different contaminants present in these wastewaters. These two facilities represent a broad range of processing operations and therefore, generate wastewaters with a range of characteristics. As a result the applicability of the activated sludge model to different petroleum based wastewaters was considered.

The following chapters explain the development of the activated sludge models for treating petroleum and petrochemical wastewaters. Chapter 3 describes the formulation of the activated sludge model to describe the behaviour of the petroleum refinery systems. Chapter 4 reviews the experimental program completed by Baker (1993) on refinery wastewaters and how this data was used to determine the stoichiometric and kinetic constants in the activated sludge model treating petroleum refinery wastewaters. Chapter 5 discusses the development of the activated sludge model for a petrochemical facility. Calibration of the model constants and the experiments conducted to assist with this process are outlined in Chapter 6. Application of the petrochemical model for analysing system behaviour and optimizing operation of the system is described in Chapter 7. Finally, Chapter 8 draws conclusions from the research and suggests areas which require further investigation.

CHAPTER 3

DEVELOPMENT OF A MECHANISTIC MODEL FOR ACTIVATED SLUDGE TREATMENT OF PETROLEUM REFINERY WASTEWATERS

3.1 INTRODUCTION

The objective of modelling is to be able to predict the response of a system during exposure to a particular set of conditions. For an activated sludge system these "conditions" refer to the operating mode (recycle rates, DO levels in reactors, sludge age, etc.) and the influent loading (flow rate and composition). For this system, the concern is being able to predict the changes in concentration of certain components of interest within the bioreactor and in the effluent, and the associated impact on parameters such as oxygen utilization rate and the total mass of suspended solids. In this Chapter, the aim is to present a model capable of predicting the behaviour for an activated sludge system treating petroleum refinery wastewaters.

In Section 2.4 of the literature review, four specific steps were identified for developing and testing mechanistic models of activated sludge systems. Identification of these tasks was based on the experience gained during the development of the ASM1 model for municipal wastewater treatment. This same approach has been applied in this study to the development of the activated sludge model for the treatment of petroleum refinery wastewaters. The four steps are:

- Selection of model structure and complexity;
- Gathering of experimental data;
- Mathematical model formulation; and,
- Model calibration and verification.

Application of the first three stages of model development to the activated sludge system treating petroleum refinery wastewaters is now discussed in more detail. Model calibration and verification is addressed in Chapter 4.

3.2 SELECTION OF MODEL STRUCTURE AND COMPLEXITY

The required complexity of a model depends largely on the objectives for model use. For example, if the objective for an activated sludge model is to predict only sludge production, then likely a single COD component can adequately represent the influent wastewater quality. If however, the model should be able to predict the effluent concentration of a compound such as phenolics, then it would be necessary to separate phenolics as a second influent component. Furthermore, if the model should predict nitrification behaviour then it would be necessary to include at least ammonia as a further influent component and possibly organic nitrogen, and also nitrate as a model component. In this manner, as the objectives and requirements of the model are expanded, so the model complexity increases due to the inclusion of additional components and processes. However, for any level of complexity the aim should be to develop the simplest model structure which satisfies the objectives.

In this study the objective was to develop a mechanistic model with the capacity to predict the following system parameters:

(1) Sludge production;
(2) Oxygen demand;
(3) Dynamic oxygen response; and,
(4) Effluent concentrations of selected parameters such as phenolics. [Interest in specific components generally is motivated by regulatory requirements].

With the objectives established, the components and processes included in the activated sludge model treating petroleum refinery wastewaters were selected and are described in Sections 3.4 and 3.5, respectively. Establishing the desired model complexity also influences the parameters which must be measured in the experimental programme in order to collect all the necessary data for model development. These are identified and discussed in Section 3.3

3.3 DATA REQUIREMENTS FOR MODEL DEVELOPMENT

One key point highlighted in the development of the IAWPRC model is the importance of having available a comprehensive database which represents the relationships between the changing contaminant concentrations and system operating conditions. These data are required to identify compounds which influence system behaviour and to identify the different mechanisms which act on these compounds in the system. In terms of model development, this information provides the basis for relating the model predictions to observed results for known operating parameters.

Specific data requirements for developing an activated sludge model have been identified in previous studies (Dold, 1984; Billing and Dold, 1988; Dold and Marais, 1984). In those studies it was indicated that ideally, information should be available for a number of operating scenarios and under both steady state and dynamic loading conditions. Data are required (1) on steady state or constant loading response to aid in determining the stoichiometry of the reactions occurring in the system, and (2) on dynamic operating conditions to aid in determining the kinetics of the processes and to establish rate parameters. To supplement this data, batch tests may also be required. As an example, determining the decay rate of organisms in a system is facilitated by a batch test which monitors the decline in oxygen consumption of a sludge sample over a period of several days. In an earlier study this author (Baker, 1993) identified that a comprehensive database was not available for activated sludge model development for treatment of petroleum refinery wastewaters. As part of that study, an experimental programme was conducted to generate the database necessary for model development. The experiments were divided into three parts:

1. Constant loading experiments;
2. Dynamic loading experiments; and,
3. Batch tests.

This experimental programme is discussed in detail in Baker (1993) so only a brief overview is presented here.

The experiments conducted on the activated sludge treatment of petroleum refinery wastewaters involved operating a number of single reactor continuous-flow bench-scale activated sludge systems. The systems treated wastewater collected from the Imperial Oil Refinery at Nanticoke, Ontario. Using a "real" wastewater rather than a synthetic substitute ensured more realistic monitoring of the conditions which control the behaviour of these activated sludge systems. The wastewater was collected at bi-weekly intervals during the laboratory study. Over the course of operation, both steady state and dynamic influent flow loading patterns were imposed on systems operated at different sludge ages. Batch tests were performed on separate samples of influent wastewater and activated sludge to supplement the information collected on the continuous flow systems.

As an example of the type of information collected on these continuous flow systems, Figure 3.1 illustrates the results of one of the dynamic loading experiments for a system operated at a sludge age of 5 days. Each day influent was fed to this system for 12 hours and then the feed was stopped for the following 12 hours. The changes in OUR, COD, and TKN over a single cycle of this feed pattern are shown in Figure 3.1. By monitoring the changes in system parameters information can be discerned on the kinetics of the different removal processes. For example, the changes in TKN and nitrate concentrations reflected the use of nitrogen by the organisms and the nitrification behaviour. Over the 12 hour feed period TKN accumulated in the system and the nitrate concentration decreased. This response reflected the nitrification capacity of the system under these operating conditions. The kinetic coefficients associated with these processes can be determined by matching model predictions with observed results. In this fashion the results of the different tests enable the model parameters to be quantified.

To have a complete set of data for model development, experiments were conducted over a range of system operating conditions. Since the principle operating variable in any activated sludge system is sludge age (SRT), initial experiments were concerned with analyzing the system behaviour over a range of SRT's. The system was operated under constant loading conditions for sludge ages of 10 and 20 days, and then was operated under dynamic loading conditions for sludge ages of 5 and 20 days. This database

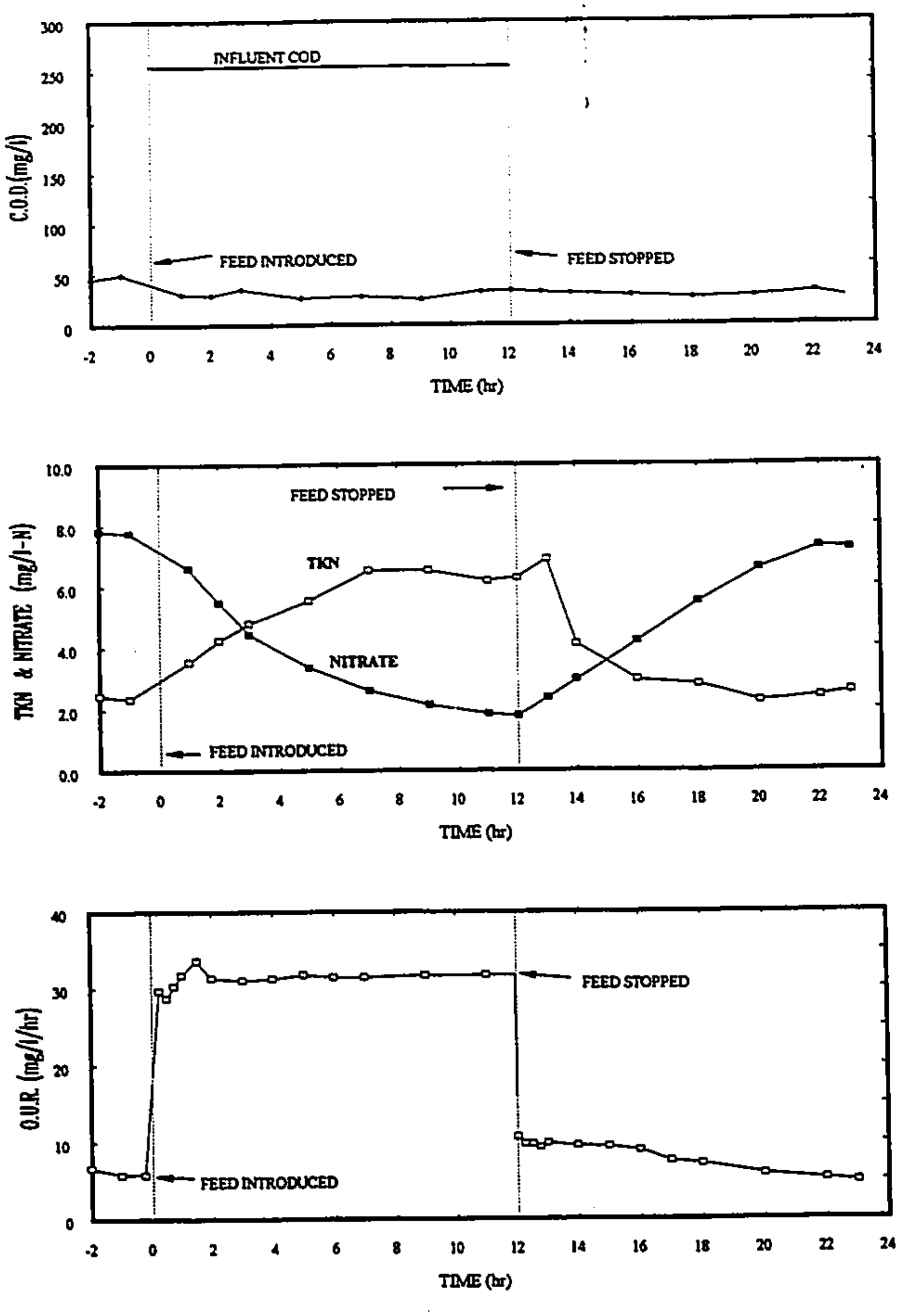

Figure 3.1: Response observed in the laboratory activated sludge system operated under square-wave influent flow and COD loading at a sludge age of 5 days. [Influent COD = 255 mg COD L^{-1}; influent TKN = 13.3 mg N L^{-1}].

enabled a model structure to be determined for activated sludge systems treating petroleum refinery wastewaters.

The following information was determined for each mode of operation in order to collect data for different operating conditions.

Constant Loading Operation of the System

- Influent quality (organic and nitrogen components)
- Effluent quality (organic and nitrogen components, VSS)
- Oxygen utilization rates
- Sludge production (total and volatile suspended solids)
- Sludge age (accounting for loss of solids in the effluent)

Dynamic Input Operation of the System

- Influent quality (organic and nitrogen components)
- Changes in concentration of the organic and nitrogen components in the reactor over the duration of the dynamic input
- Changes in the oxygen utilization rate over the duration of the dynamic input
- Sludge production (total and volatile suspended solids)
- Sludge age (accounting for loss of solids in the effluent)

Data collected on the continuous flow systems were supplemented with a number of batch experiments. These were:

- Influent characterization tests,
- Organism decay rate tests, and
- Volatilization rate tests.

All this information provided the necessary data to develop a model structure for an activated sludge treatment plant treating petroleum refinery wastewaters. The data also was used to calibrate the model to predict the behaviour of these systems. With the required data, the next stage of model development involved confirmation of the model components and processes to incorporate in the model structure. The following sections address these tasks.

3.4 MODEL COMPONENTS

Before identifying the specific components included in the model, the methodology used to represent the different types of compounds should be established. The model uses the notation established in the IAWPRC model. Biomass components are represented by the symbol Z_i. Soluble components in the model are identified by the symbol S_i and particulate components by the symbol X_i. Subscripts are utilized to identify different components. In the model the concentrations of the model components are expressed in units of "mg/L". For the different components the following mass basis was used:

Soluble organic components	COD
Particulate organic and biomass components	COD
Nitrogen-containing components	Elemental N
Sulphur-containing components	Elemental S

In the model predictions of the biomass, concentrations are expressed in units of "mgCOD/L." However, in the experimental study concentrations of particulate organic matter (active biomass, endogenous residue, etc.) were quantified in terms of volatile suspended solids i.e. mg VSS/L. These are converted to an equivalent COD basis in the IAWPRC model. To convert the observed concentrations from a VSS basis to the equivalent COD basis, a ratio of the milligrams COD of the sludge for each milligram VSS is utilized. This converts model predictions of these concentrations in units of mgCOD/L to units of mg VSS/L. The COD/VSS ratio factor was determined experimentally for the petroleum refinery activated sludge.

The following sections describe the rationale for selecting the different components which were included in the activated sludge model of the petroleum refinery wastewaters.

3.4.1 Biomass Components

Activated sludge systems contain different types of organisms which perform various functions. In the case of the petroleum refinery system, initially it was envisaged that the model should include two biomass components:

(1) Heterotrophic biomass (Z_{BH}) resulting from growth on the influent organic material COD; and,

(2) Autotrophic nitrifying organisms (Z_{BN}) for monitoring the nitrification behaviour.

However, in the course of the experimental study (Baker, 1993) it was identified that oxidation of reduced sulphur compounds played an important role in the oxygen utilization rate response in the system. Measurement of the influent and effluent sulphate concentrations in the system indicated that a significant concentration of sulphate was formed in the process due to the oxidation of reduced sulphur compounds. In some instances, as much as 200-300 mg/L of sulphate as SO_4 was being produced in the system. The result of this process was a significant increase in the oxygen requirements of the system. Since oxygen requirements are a key concern in the operation of these systems, it was important to include such a significant consumer of oxygen in the model. As a result, sulphur oxidizers (Z_{BS}) were included as a third biomass component in the model.

The above biomass components refer to active organisms. However, along with growth in the system, organisms also undergo decay. The decay process is discussed later in the Chapter, but for purposes of establishing model components it is necessary to indicate that death of organisms results in an endogenous mass which cannot be degraded, but contributes to the volatile solids concentration in the system. This endogenous mass is represented by the symbol Z_E. These four classifications constitute the biomass components of the petroleum refinery activated sludge model.

3.4.2 Organic Components

Characterization of the organic components in the influent wastewater is a critical element in modelling any activated sludge system (Dold, 1984; Gibson & Dold, 1990) since the behaviour of the system depends on exactly what the organisms are degrading and in what quantities. The organic component of the petroleum refinery wastewater consists of a composite mixture of many different compounds. Due to the number of compounds present, it was essential that a bulk parameter such as COD was utilized to quantify the carbonaceous component. This simplifies the ability to monitor the transformations of the different compounds. Within the total influent COD, however, it was necessary to distinguish a number of different components when formulating the system model. Each compound or group of compounds selected for modelling purposes influences the behaviour of the treatment system in a different manner due to the transformations associated with it. Therefore, an understanding of the types of compounds to expect in these wastewaters and the types of processes they undergo are important for determining the appropriate organic components to include in the model.

As shown in Fig. 3.2, the first division of the influent organic content was into biodegradable and unbiodegradable portions. The biodegradable fraction contributes to the growth of organisms while the unbiodegradable portion remains unchanged in the system. Within each category, further fractionation into various soluble and particulate components was necessary. This characterization or fractionation of the total influent COD for modelling purposes was based on four factors: (1) measurements on the influent wastewater (reported in Chapter 4); (2) experience gained during the experimental program; (3) experience gained during the model calibration phase; and (4) an interest or need to track the fate of specific compounds (or related groups of compounds) in the system e.g. phenolics.

The majority of the influent COD was in the soluble form, accounting for about 90 percent of the influent organic content (Baker, 1993). Experiments indicated that most of this COD was readily biodegradable in nature, although some slowly biodegradable material was present. In terms of the model components, the total influent biodegradable COD was separated into four groups of soluble organic components, plus a biodegradable particulate component. These categories accounted for the influent components which had the greatest influence on system behaviour.

The four soluble biodegradable organic components incorporated in the model are as follows.

Phenolics (S_{PH}): Incorporation of a phenolic COD component in the petroleum refinery model is driven largely by the fact that phenolics is a regulated parameter. As a result, the activated sludge facility must successfully reduce the levels of phenolics in the effluent to below a specified concentration. Modelling efforts of these systems needed to include phenolics removal to assist in determining if the system is removing phenolics and indicate any potential problem scenarios with phenolics removal.

Volatile organics (S_V): Volatile organic compounds (VOC's) can account for nearly 20 percent of the influent COD in some instances and have a significant influence on system behaviour. Firstly, VOC 's are stripped from the activated sludge system and contribute to the air emissions from these facilities. Concern about air quality has increased the importance of determining the organic loading to the atmosphere. Secondly, when COD is stripped from the system it is no longer available for organism growth. Therefore, the amount stripped from the aeration basins influences the amount of oxygen consumed and the mass of organisms formed. In developing a model of these refinery systems it was important to track the fate of these volatile compounds.

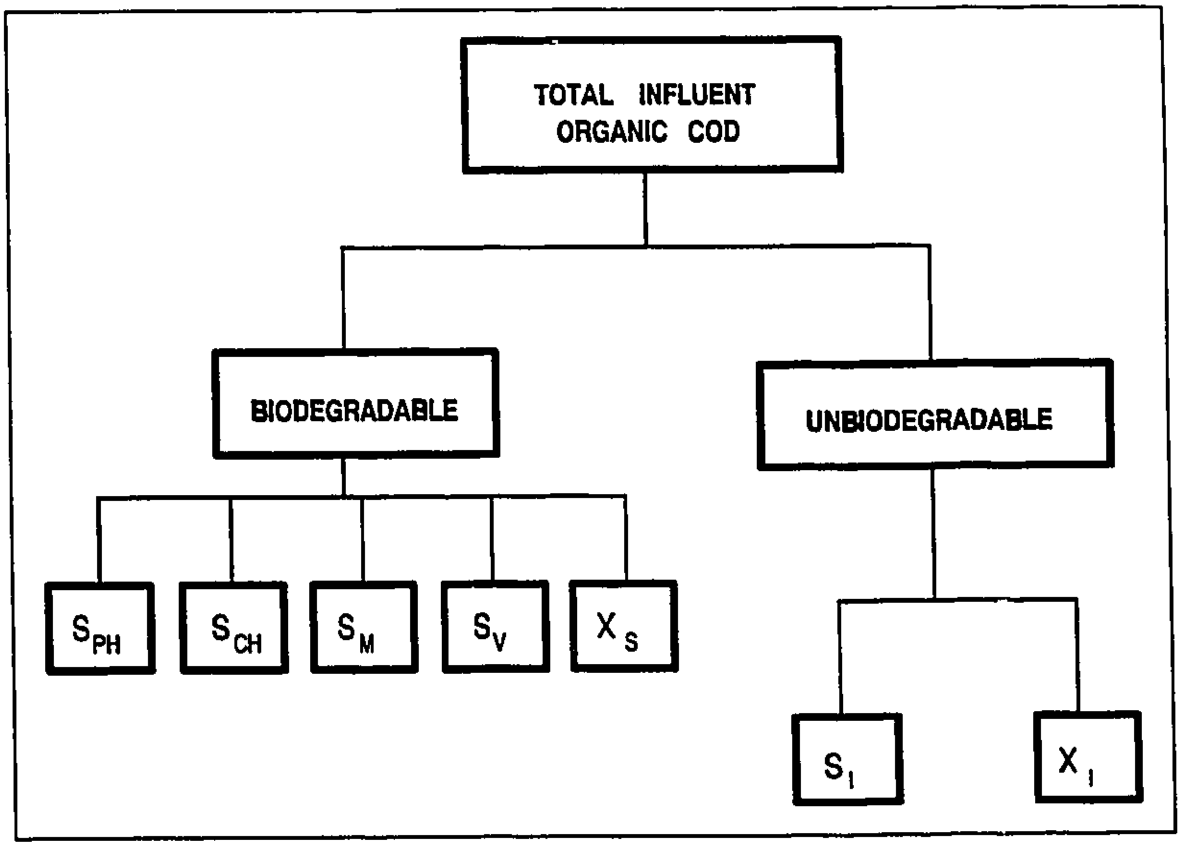

Figure 3.2: Petroleum Refinery Wastewater Characterization of the Total Influent Chemical Oxygen Demand.

Hydrocarbons (S_{CH}): Due to the processing of crude oil in the petroleum refinery, hydrocarbon COD in the form C/H compounds is an expected contributor to the organic content of the influent wastewater. Hydrocarbon COD is generally pseudo-soluble material, composed of large molecules partially miscible in the aqueous phase. In developing the model, it was hypothesized that the hydrocarbon COD is adsorbed onto the sludge mass, and subsequently is hydrolysed and then used by the organisms. This influences the oxygen utilization pattern associated with growth on this COD fraction by delaying the time that the oxygen is required for growth processes. These processes need to be monitored in a model of these systems. In terms of model representation, adsorption changes the form of the influent hydrocarbon COD from the soluble form (S_{CH}) to a particulate form (X_{CH}). Hence, two model components are required to account for this material.

Mixed organic compounds (S_M): The final category of influent biodegradable COD was included to account for the large number of compounds in the petroleum refinery wastewater which are present in small concentrations. To include each of these compounds individually in the model would generate an extremely cumbersome model. Instead these compounds are lumped together into one fraction and referred to as mixed COD. This COD fraction accounts for all the influent COD which cannot be categorized into any of the other model components.

As indicated, the four categories of soluble biodegradable COD constitute the majority of the influent COD. However, to completely specify the characteristics of the influent three other categories of COD had to be included:

(1) Slowly biodegradable particulate COD (X_S);
(2) Particulate unbiodegradable COD (X_I); and,
(3) Soluble unbiodegradable COD (S_I).

Slowly biodegradable particulate COD (X_S) was present in very small quantities in the influent, but should be specified to account for those situations which may generate larger concentrations of this particulate fraction. Furthermore, particulate substrate is generated in the activated sludge system itself via the degradation of organisms so this component needed to be included in the model to account for this internal process.

The unbiodegradable COD fraction of the influent consists of both particulate (X_I) and soluble forms (S_I). Each fraction influences the system in a different manner. The particulate unbiodegradable fraction may be present in the influent, but only in small quantities. It is enmeshed in the sludge as it enters the system and is removed with the wastage stream. However, the soluble unbiodegradable fraction remains in the liquid phase and contributes to the effluent COD concentration. As a result, it was important to include this fraction as a model component in order to predict properly the total effluent COD concentration.

Each of the above compounds were considered to be key contributors in determining the response of the petroleum refinery activated sludge system and therefore, needed to be included in the model developed to mimic its behaviour. Figure 3.2 illustrates the breakdown of the influent into these fractions. The actual fractions of these various components were determined for the wastewater being treated during the experimental study. The specific fractions of each component may vary from plant to plant and therefore, need to be quantified for the given petroleum refinery.

3.4.3 Nitrogen Components

Nitrogen compounds have been identified as having an important influence on the behaviour of activated sludge systems for a number of reasons. Firstly, nitrogen is required for organism growth. If present in insufficient levels, organism growth behaviour will be affected. Secondly, excess ammonia nitrogen must be removed from the wastewater to reduce the toxicity of the effluent to fish populations. This may be accomplished through nitrification of the ammonia to nitrate.

Three different nitrogen components were incorporated in the petroleum refinery activated sludge system model. These are free and saline ammonia nitrogen (S_{NH}), soluble organic nitrogen (S_{ON}), and nitrate nitrogen (S_{NO}). The influent wastewater usually contains only the first two classifications (Figure 3.3). The ammonia nitrogen serves as a source of nitrogen for the growth of biomass, and as the substrate for the autotrophic organisms. The organic nitrogen is converted to ammonia nitrogen, at which time it is either utilized for organism growth, or nitrified to nitrate.

The third classification of nitrogen, nitrate (S_{NO}), was incorporated as a model component to account for nitrate production through the biological process of nitrification. Since this process occurs in the reactor, the presence of nitrate generally is limited to the reactor and the effluent. This component actually combines the measurements of both nitrite and nitrate since the nitrification process is a combination of two reactions in series. The conversion of ammonia to nitrite is normally considered to be the rate limiting step so for purposes of the model a single reaction to the nitrate form was assumed with negligible impact on the accuracy of the model.

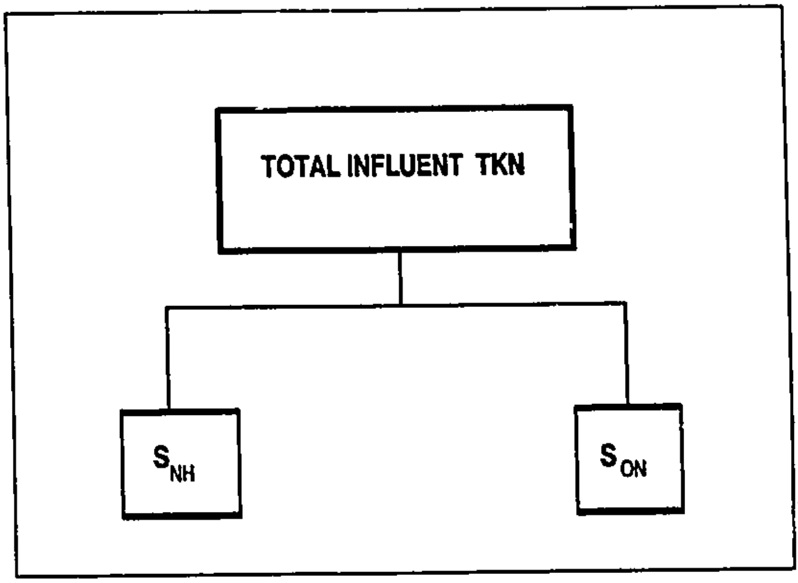

Figure 3.3: Petroleum Refinery Wastewater Characterization of the Total Influent Kjeldahl Nitrogen.

3.4.4 Sulphur-Containing Components

Sulphur compounds appear in the wastewaters from a petroleum refinery due to the presence of sulphur in the crude oil. The levels to expect in the wastewaters, therefore, relate to the sulphur content of the crude. For example, sour crude oil contains significant levels of sulphur which may result in a high sulphur content in the wastewater. Sweet crude oil contains much less sulphur and as a result, the concentration of sulphur compounds in the wastewater often is minimal. As indicated in the discussion on biomass components, experimentation indicated that the presence of sulphur compounds had a significant impact on the oxygen utilization rate of the activated sludge system in the experimental study. The sulphur containing species in the influent were being converted to sulphate in the activated sludge plant and in the process consuming large quantities of oxygen. In some instances up to 300 mg/L of sulphate as SO_4 was being generated in the process.

Two types of sulphur species were considered in the model; these are reduced sulphur species (S_{SR}) and sulphate sulphur (S_{SO}). Reduced sulphur in the influent is oxidized to sulphate in the activated sludge process, while any sulphate in the influent simply passes through the system unchanged. Figure 3.4 illustrates the breakdown of sulphur species in the influent wastewater.

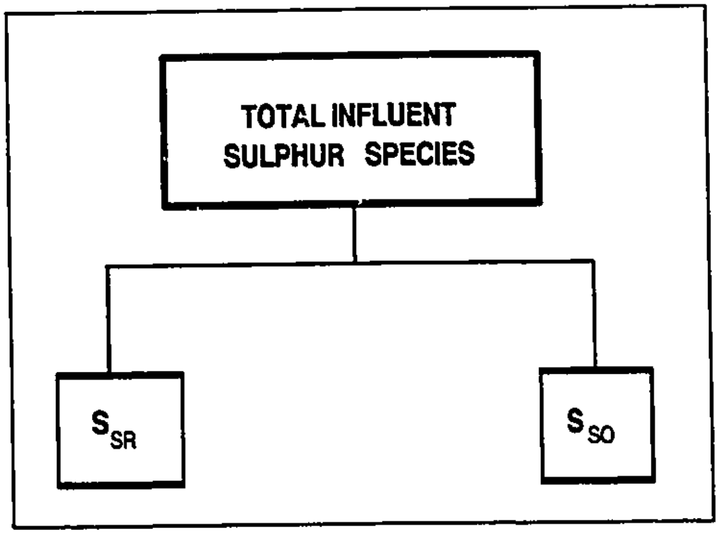

Figure 3.4: Petroleum Refinery Wastewater Characterization of the Total Influent Sulphur Species.

3.4.5 Miscellaneous

In the activated sludge system phosphorus is required for the synthesis of organism mass in the growth process. Usually, refinery wastewaters are deficient in phosphorus, and some form of soluble phosphate is added to the influent wastewater upstream of the activated sludge system. In many instances, the effluent phosphorus concentration must be maintained below a specified level for regulatory reasons. Therefore, it is important that phosphorus is not added in excess. Soluble phosphate (S_P) was incorporated as a model component to enable prediction of the amount of phosphorus required for organism growth for a given set of operating and influent conditions. This will aid model users in correctly estimating the amount of phosphorus which should be added to the influent wastewater to satisfy the system demand while still meeting effluent standards.

One other important component specified in the model is the dissolved oxygen concentration, S_O. Oxygen is crucial for growth of organisms in an aerobic system. The oxygen concentration usually is controlled at a setpoint level by the operator of the system. However, as with municipal systems, including the dissolved oxygen concentration in the model enables calculation of the oxygen utilization rate in the system. This parameter influences the aeration requirements of the treatment facility. Therefore, since information is desired on the oxygen consumed in the process, S_O was an important parameter to include in the model.

3.4.6 Summary of Model Components

The above discussion identified the different components involved in the development of the activated sludge model for petroleum refinery wastewaters. Table 3.1 summarizes the 19 components together with symbols and units. The concentration of each of these individual components is monitored in the model.

Table 3.1: Definition of Component Symbols in the Petroleum Refinery Activated Sludge Model.

COMP.	SYMBOL	DEFINITION	UNITS
1	Z_{BH}	Active heterotrophic biomass	g cell COD m^{-3}
2	Z_{BN}	Active nitrifier biomass	g cell COD m^{-3}
3	Z_{BS}	Active S oxidizing biomass	g cell COD m^{-3}
4	Z_E	Endogenous mass	g COD m^{-3}
5	X_S	Slowly biodegradable substrate	g COD m^{-3}
6	X_{CH}	Adsorbed hydrocarbon substrate	g COD m^{-3}
7	X_I	Particulate unbiodegradable matter	g COD m^{-3}
8	S_{PH}	Phenolic biodegradable soluble COD	g COD m^{-3}
9	S_M	Mixed substrate biodegradable soluble COD	g COD m^{-3}
10	S_V	Volatile biodegradable soluble COD	g COD m^{-3}
11	S_{CH}	Soluble hydrocarbon COD	g COD m^{-3}
12	S_{NH}	Ammonia nitrogen	g N m^{-3}
13	S_{ON}	Soluble biodegradable organic nitrogen	g N m^{-3}
14	S_{NO}	Nitrate nitrogen	g N m^{-3}
15	S_{SR}	Reduced sulphur	g S m^{-3}
16	S_{SO}	Sulphate	g S m^{-3}
17	S_P	Soluble phosphate	g P m^{-3}
18	S_I	Unbiodegradable soluble substrate	g COD m^{-3}
19	S_O	Oxygen	g (-COD) m^{-3}

3.5 THE MODEL PROCESSES

The next stage in model formulation was to determine processes which significantly influence system behaviour and to include these in the model. Again, the bench scale study treating petroleum refinery wastewater served as a basis for determining the key processes.

There were a number of different mechanisms occurring within the petroleum refinery activated sludge system which can be classified as either biological or physicochemical in nature. The results of the experimentation supported observations reported in the literature on the behaviour of these systems (Baker, 1993). The following processes were considered to be key mechanisms in determining the behaviour of an activated sludge system treating petroleum refinery wastewaters:

- Aerobic growth of heterotrophs on mixed organic components
- Aerobic growth of heterotrophs on volatile organic components
- Aerobic growth of heterotrophs on phenolics
- Aerobic growth of heterotrophs on adsorbed hydrocarbons
- Decay of heterotrophs
- Hydrolysis of hydrocarbons and other particulate COD
- Adsorption of hydrocarbons onto sludge mass
- Volatilization of volatile organic compounds
- Ammonification of organic nitrogen to ammonia
- Nitrification of ammonia (i.e. growth of nitrifiers)
- Oxidation of reduced sulphur compounds (i.e. growth of the sulphur oxidizers)
- Decay of nitrifiers and sulphur oxidizers

The experimental system used to generate data for model development was an *aerated* activated sludge process, similar to full-scale applications for refinery wastewater treatment. From the literature it would appear that inclusion of *unaerated* zones in these refinery systems has not been evaluated. However, to account for this possibility in future application of the model, the model structure was adapted. This necessitated inclusion of four anoxic growth processes to parallel each of the aerobic growth processes. It is stressed that this aspect of behaviour in unaerated reactors has not been investigated in this study.

Previous studies have considered many of the mechanisms listed above, and as a result, kinetic expressions have been proposed to represent these processes. The following section identifies the reactions incorporated in the petroleum refinery activated sludge model and describes the form of the rate equations used in the model to represent each process. The complete process model is summarized in Tables 3.2 and 3.3 in Section 3.6.

Aerobic Growth of Heterotrophs on Mixed and Volatile COD:

Heterotrophic organisms utilize many different types of soluble organic substrate for growth, with the rate of growth and the yield of organism mass associated with the particular compound dependent on its characteristics. These characteristics need to be specified for the COD components being considered in the model. As the biomass yield for the growth process (Y) changes, so the electron acceptor demand (1-Y) changes. Hence, in an aerobic system the amount of oxygen, S_O, consumed in the growth process varies depending on the organic source. However, the actual form of the growth mechanism on the different organic compounds is assumed to be the same. In the petroleum refinery activated sludge system growth on mixed COD (S_M) and volatile organic COD (S_V) was modelled using the Monod expression for biological growth. The Monod equation for soluble COD is based on the bulk concentration of COD i.e. mass of the organic compound of concern per unit of system volume. The form of this equation for growth on mixed COD is as follows:

$$\rho_3 = \mu_{hM} * \frac{S_M}{K_{sM} + S_M} * Z_{BH} * \text{AirYes} * \text{NH}_3\text{Yes} * \text{PO}_4\text{Yes} \qquad (3.1)$$

A similar equation was assumed for growth on volatile organic COD (S_V), where S_M is substituted by S_V, and μ_{hV} and K_{sV} are the kinetic parameters associated with growth on volatile organic compounds.

Along with the Monod equation, a series of "switching" functions were attached to the rate equation to reduce the process rate to zero when there is no oxygen in the system or when the system is deficient in nutrients required for growth i.e. ammonia nitrogen and phosphorus. The specifics of these switching functions are described in Section 3.6.1.

Aerobic Growth of Heterotrophs on Phenolic COD:

Heterotrophic organisms are susceptible to inhibition effects when degrading phenolic compounds (S_{PH}). Current understanding is that the presence of phenolics slows the ability of the organism to degrade the organic and that this effect increases with increasing concentration. For low concentrations the specific growth rate increases as concentration of the inhibitory organic increases. However, a point is reached where the increased inhibition outweighs the increased growth rate, and there is a decline in specific growth rate for further concentration increases. The literature reports (Rozich, 1983, 1985) the development of the Haldane equation for describing this inhibition phenomenon. It is a modified version of the Monod equation and reduces to the Monod equation when the concentration of phenolics drops below inhibitory levels. The form of the Haldane equation used in the petroleum refinery model to describe the behaviour of heterotrophs treating phenolic compounds is indicated in Equation 3.2:

$$\rho_1 = \mu_{hPH} * \frac{S_{PH}}{K_{sPH} + S_{PH} + \frac{S_{PH}^2}{K_I}} * Z_{BH} * \mathrm{AirYes} * \mathrm{NH_3Yes} * \mathrm{PO_4Yes} \tag{3.2}$$

Switching functions were added to the growth equation in the event that oxygen or nutrient deficiencies occur in the system.

Aerobic Growth of Heterotrophs on Hydrocarbon COD:

As noted in the description on heterotrophic growth on soluble COD, it was assumed that heterotrophs utilize soluble substrate directly. The fate of the hydrocarbon COD component (S_{CH}) was handled somewhat differently in the model as indicated in the discussion presenting the model components. This material is complex in nature and the molecules are large. In the model it was assumed that the molecules of hydrocarbon COD are too large to be used directly and must be broken into smaller units before utilization for growth. It was hypothesized that hydrocarbon COD is adsorbed onto the biomass and the adsorbed compound then is hydrolysed to smaller units prior to being utilized for growth. The soluble hydrocarbon (S_{CH}) then acts as a particulate form of COD and takes on the symbol X_{CH} in the model. Therefore, the growth behaviour on hydrocarbon COD is dependent on the concentration of adsorbed COD rather than the concentration in the liquid phase. For this reason growth on hydrocarbon COD was represented using the Monod expression, but with one major modification. Instead of growth being a function of the bulk concentration of the soluble COD, the Monod equation was expressed as a function of the surface concentration of the hydrocarbon COD on the heterotrophic biomass. This concentration is estimated as X_{CH}/Z_{BH}, the concentration of adsorbed hydrocarbon COD per unit mass of heterotrophs. The form of this growth equation is shown in Equation 3.3:

$$\rho_7 = \mu_{hCH} * \frac{\frac{X_{CH}}{Z_{BH}}}{K_{sCH} + \frac{X_{CH}}{Z_{BH}}} * Z_{BH} * \mathrm{AirYes} * \mathrm{NH_3Yes} * \mathrm{PO_4Yes} \qquad (3.3)$$

Switching functions were added to the growth expression which force the growth rate to zero in the absence of oxygen or limiting quantities of ammonia nitrogen or phosphorus.

Anoxic Growth of Heterotrophs:

Anoxic growth of heterotrophs was not considered in this research, but anoxic growth equations were included in the model for completeness. The form of the expressions used in the petroleum refinery activated sludge model were equivalent to the expressions used for municipal activated sludge systems (Billing & Dold, 1988). The expression is based on the assumption that only a fraction of the heterotrophs can utilize an alternative electron acceptor such as nitrate instead of oxygen, but that growth of this portion follows Monod kinetics. Therefore, the rate equation for anoxic growth is simply the Monod expression multiplied by a factor η_{grow}, which represents the fraction of heterotrophs capable of utilizing COD under anoxic conditions. The same correction factor was assumed for the four groups of readily biodegradable COD in the petroleum refinery system since anoxic conditions were not studied specifically in this work. As an example, anoxic growth on mixed COD is represented by the following equation:

$$\rho_4 = \eta_{grow} * \mu_{hM} * \frac{S_M}{K_{sM} + S_M} * Z_{BH} * \mathrm{AirNo} * \mathrm{NO_3Yes} * \mathrm{NH_3Yes} * \mathrm{PO_4Yes} \qquad (3.4)$$

Switching functions for oxygen, ammonia nitrogen, and phosphorus were included in the rate expression. If the oxygen concentration is too high the anoxic growth would cease. Insufficient levels of the two nutrients also limit anoxic growth. A switching function for nitrate concentration also was included in the rate expression so that if nitrate, as well as oxygen, is absent from the system, the anoxic growth rate would decrease to zero.

Decay of Heterotrophs:

Decay of microorganisms in the petroleum refinery activated sludge system was modelled using the "death-regeneration" hypothesis introduced in the IAWPRC model (Billing and Dold, 1988). The hypothesis proposed that the organisms die at a constant rate in the reactor and generate a non-biodegradable fraction ($f_{Ep,H}$) which contributes to the endogenous residue (Z_E), while the remaining fraction ($1-f_{Ep.H}$) adds to the mass of slowly biodegradable substrate (X_S) already present in the reactor. This organic fraction contributes to biological growth. This proposed behaviour results in a cycling of organic material within the activated sludge system.

The net decay rate represents the difference between the rate at which the organisms die and the rate at which new organisms grow from the released slowly biodegradable COD. This rate was determined in the experimental programme and suggested that decay is a first order process. The actual form of the decay rate expression used in the model refers to the overall decay rate of the organisms (the relationship between these two values is outlined in Appendix 3). It also was assumed to follow first order kinetics with respect to the concentration of heterotrophs in the activated sludge system with b_H representing the overall decay rate:

$$\rho_9 = b_H * Z_{BH} \tag{3.5}$$

The model assumes that in the decay process there is release of nitrogen (as soluble organic nitrogen, S_{ON}) and phosphorus (as soluble phosphate, S_P) in parallel with the release of organic material.

Hydrolysis of Particulate COD:

Along with biodegradable soluble COD in the influent, there is also a biodegradable particulate fraction (X_S). This material undergoes a different removal process than soluble COD components. Similar to the assumptions made in developing the IAWPRC model, the biodegradable particulate COD in the petroleum refinery influents was assumed to be enmeshed in the sludge mass upon entering the reactor. Before this material can be used by the biomass it has to be broken down extracellularly by enzymes produced by the microorganisms. The breakdown process produces readily biodegradable soluble substrate which can be used for biological growth.

To model this hydrolysis/solubilization process, similar methods to those used for development of the IAWPRC model (ASM1) were applied. Levenspiel's surface reaction kinetics theory was utilized (Levenspiel, 1972). The rate of hydrolysis was based on the surface concentration of particulate COD rather than the bulk liquid concentration of COD utilized in the simple form of the Monod equation. The surface concentration was estimated by dividing the concentration of particulate COD (X_S) by the concentration of biomass (Z_{BH}) in the reactor. The term X_S/Z_{BH} replaces S_S in the Monod equation. This form of this equation is illustrated in Equation 3.6:

$$\rho_{10} = K_H * \frac{\frac{X_S}{Z_{BH}}}{K_X + \frac{X_S}{Z_{BH}}} * Z_{BH} * (\text{AirYes} + \eta_{sol} * \text{AirNo} * \text{NO}_3\text{Yes}) \qquad (3.6)$$

Included with the rate equation were switching functions which decrease the hydrolysis to zero if there is no oxygen in the system, or decrease the rate if only nitrate is available. The assumption is that not all heterotrophs are capable of hydrolysis under anoxic conditions.

Adsorption of Hydrocarbon COD:

As suggested, the hypothesis for hydrocarbon COD (S_{CH}) is that it is adsorbed onto the biomass prior to being utilized, converting it to the X_{CH} form. It must be hydrolysed before utilization in the growth process. The size and complexity of these molecules may result in the biomass being coated with hydrocarbon so the potential for more adsorption is decreased or is stopped all together. Therefore, the rate of adsorption likely changes depending on the hydrocarbon concentration already adsorbed on the biomass. In order to account for this type of behaviour an adsorption process was included in the model of these petroleum refinery wastewater treatment systems.

The rate of adsorption of hydrocarbon onto the biomass was assumed to follow first order kinetics with respect to the bulk concentration of hydrocarbon COD (S_{CH}) in the system and the concentration of heterotrophs (Z_{BH}). A driving force term was included in the model equation to account for the impact of the number of available adsorption sites. The rate of adsorption is decreased as the number of available sites diminishes. This driving force term was expressed as f_{maxCH} - X_{CH}/Z_{BH}, where X_{CH}/Z_{BH} accounts for the hydrocarbon material already adsorbed on the sludge. Equation 3.7 represents the adsorption process:

$$\rho_{11} = K_A * \left\{ f_{maxCH} - \frac{X_{CH}}{Z_{BH}} \right\} * S_{CH} * Z_{BH} \tag{3.7}$$

Volatilization of Volatile Organic COD:

The volatilization of volatile organic compounds (S_V) from the wastewater was modelled using a first order equation (Equation 3.8) with respect to the concentration of soluble volatile organic COD:

$$\rho_{12} = K_V * S_V \tag{3.8}$$

Experimentation confirmed that a first order representation adequately predicted the stripping of VOC's from an aerated batch of raw petroleum refinery wastewater (Baker, 1993). Other work with volatile compounds also assumed a first order stripping constant (Mueller *et al.*, 1985; Robert *et al.*, 1984).

Ammonification:

It was envisaged that a relatively small portion of the influent TKN would be in the form of soluble organic nitrogen (S_{ON}) as opposed to ammonia (S_{NH}). Also, the model assumed that soluble organic nitrogen is generated through organism decay. Therefore, a process was incorporated in the model for conversion of organic nitrogen to ammonia.

The process was modelled as a first order rate equation in terms of the concentration of organic nitrogen. The expression rate also was assumed first order with respect to the concentration of heterotrophs in the system. Equation 3.9 represents the ammonification process:

$$\rho_{13} = K_N * S_{ON} * Z_{BH} \qquad (3.9)$$

Nitrifier Growth:

Autotrophic growth of nitrifiers (Z_{BN}) is important for the conversion of excess ammonia to nitrate in these industrial systems. Growth of nitrifiers was expressed in terms of Monod kinetics with respect to the bulk concentration of ammonia in the reactor (Equation 3.10):

$$\rho_{14} = \mu_N * \frac{S_{NH}}{K_{sNH} + S_{NH}} * Z_{BN} * \text{AirYes} * \text{PO}_4\text{Yes} \qquad (3.10)$$

The kinetic equation included two switching functions which decrease the nitrifier growth rate to zero if insufficient levels of oxygen and phosphate are present in the system.

Nitrifier Decay:

The decay of nitrifiers was assumed to proceed in a similar manner to the decay of heterotrophs. The expression for decay was presented in the form of a first order rate equation with respect to the concentration of nitrifiers in the system (Equation 3.11):

$$\rho_{15} = b_N * Z_{BN} \qquad (3.11)$$

Sulphur Oxidizer Growth:

Sulphur oxidizers (Z_{BS}) serve to minimize the impact of reduced sulphur compounds on receiving waters by converting them to sulphate species. Sulphur oxidizer growth was expressed as the Monod equation for biological growth with respect to the bulk concentration of reduced sulphur species in the activated sludge system (Equation 3.12):

$$\rho_{16} = \mu_S * \frac{S_{SR}}{K_{sS} + S_{SR}} * Z_{BS} * \text{AirYes} * \text{NH}_3\text{Yes} * \text{PO}_4\text{Yes} \qquad (3.12)$$

The rate of sulphur oxidizer growth is reduced to zero using switching functions if the levels of oxygen, ammonia, or phosphorus in the system are insufficient to sustain growth.

Sulphur Oxidizer Decay:

Similar to the decay of heterotrophs and nitrifiers, death of sulphur oxidizers was modelled as a first order process with respect to the concentration of the sulphur oxidizers in the reactor:

$$\rho_{17} = b_S * Z_{BS} \qquad (3.13).$$

3.5.1 Summary

Each of the processes described above contributes to the overall behaviour of the petroleum refinery activated sludge system. These kinetic equations constitute the reaction terms in the petroleum refinery model. The next stage in model development was to relate the model components and processes in a mathematical structure which reflected the stoichiometry of the processes. The following section describes how these elements were combined to generate the overall mechanistic model.

3.6 THE PETROLEUM REFINERY ACTIVATED SLUDGE SYSTEM MODEL REPRESENTATION

The method for representing the activated sludge system treating petroleum refinery wastewaters is the same as that used by the IAWPRC task group for the treatment of municipal wastewaters. The model is presented in a matrix format which clearly presents the compounds, processes, and reaction terms incorporated in the model. It is flexible and easy to understand and allows the model structure to be changed easily. The model matrix is also very easily converted to computer code for the simulation stage of model development. The matrix format will be reviewed briefly.

The matrix representation of the petroleum refinery activated sludge model is presented in Tables 3.2 and 3.3. Across the top of the matrix the i components of interest in the model, which were discussed above, are listed in symbol form. The 17 different biological and physical reactions occurring within the reactor are tabulated down the left hand side of the table. The actual rate equations which govern the reactions are tabulated down the right hand side of the table and are given the symbol ρ_j. The subscript j denotes the biological or physical process the rate equation represents. The kinetic parameters used in the rate equations are listed in Table 3.5. Finally, the body of the matrix (Table 3.2, Parts 1, 2 & 3) contains the stoichiometric coefficients, ν_{ij}, defining the mass action relationship between the components in the individual processes. The stoichiometric parameters are listed in Table 3.4.

It should be noted that in Tables 3.4 and 3.5 numerical values are specified for the stoichiometric and kinetic parameters. These values were determined in the model calibration phase described later in Chapter 4.

The following conventions were utilized in the model:

- In the table of stoichiometric coefficients a reaction which consumes the component is negative while a reaction which produces the component is positive.
- The growth coefficients were normalized with respect to biomass concentration. As an example, the stoichiometric coefficients for growth of Z_B (concentration of the heterotrophs) and utilization of S_S (soluble substrate) are 1 and -1/Y rather than Y and -1. That is, the rate equations are written in terms of biomass growth rate rather than substrate utilization rate with units of mg cell COD growth (mg substrate COD utilized)$^{-1}$.
- All concentrations of model components relating to biomass or organic substrate are expressed in terms of COD equivalents which simplifies many of the stoichiometric coefficients. This provides a check on the continuity of the matrix since the sum of the stoichiometric coefficients across any row in the matrix must equal zero.

Using this format the mechanistic model was formulated easily. Multiplication of the rate equation by the stoichiometric coefficient determines the impact of the given process on the particular model component. The combined impact of each of these model processes on each of the model components formed the mechanistic model of this system.

3.6.1 Switching Functions

Switching functions were a tool introduced during development of the IAWPRC municipal activated sludge model. These are a mechanism used to switch off a particular rate equation if the conditions necessary for the reaction are not present in the system at that time. A switching function is best explained through an example. In an aerobic system, aerobic growth of heterotrophs requires the presence of oxygen as an electron acceptor and sufficient levels of nitrogen and phosphorus to sustain growth. If insufficient oxygen is present in the reactor the heterotrophs cannot grow. Therefore, the rate equation expressing this growth situation should decrease to zero. This scenario can be represented mathematically using a Monod-type expression added to the growth equation such that as the oxygen concentration in the system approaches zero, the function approaches zero and the process rate also is "forced" to zero. If the oxygen concentration is sufficient the function value is close to unity so the growth equation is not effected. The form of the switching function for oxygen is:

$$\frac{S_O}{K_O + S_O} \tag{3.14}$$

where S_O is the concentration of dissolved oxygen, and K_O is the switching constant of small magnitude e.g. 0.1 mgO/L. This expression is continuous which helps to avoid numerical instability problems yet produces the "on" and "off" switching effect desired.

As certain processes are turned off by a particular condition another process may be switched on. The two processes are linked by multiplying the corresponding two reaction expressions by the appropriate switching functions. Aerobic and anoxic growth of heterotrophs is used as an example to illustrate the mathematics (Billing & Dold, 1988):

$$\text{Observed } \rho_{\text{aerobic}} = \rho_{\text{aerobic}} * \frac{S_O}{K_O + S_O} \tag{3.15}$$

$$\text{Observed } \rho_{\text{anoxic}} = \rho_{\text{anoxic}} * \left\{1 - \frac{S_O}{K_O + S_O}\right\} \tag{3.16}$$

$$= \quad \rho_{anoxic} \quad * \quad \frac{K_O}{K_O + S_O} \qquad (3.17)$$

With this mathematical setup the reactor switches from one reaction to another depending on the selection of K_O. Since the value of K_O actually determines the switching point, care in its selection is important. In this scenario K_O impacts the model predictions rather than simply serving as a mathematical function.

The advantage of using switching functions in the petroleum refinery application was that the same model can be used to predict the performance of the activated sludge system under different operating environments i.e. aerobic or anoxic. Such a model is much more flexible and powerful. Table 3.6 lists the switching function parameters and specifies the corresponding symbol and value used in the model. The switching function equations used in the model are defined in Table 3.7.

3.6.2 Incorporation of the Mechanistic Model in a Simulator

The mechanistic model is the set of process rate equations which act on the various model components and the associated stoichiometric relationships. However, in order to simulate the actual response of an activated sludge system, the mechanistic model must be integrated into a simulation model of the system. This involves being able to specify the reactor configuration (i.e. number and size of reactors), flow patterns (i.e. recycle flows, wastage rate), and influent wastewater quality for a particular activated sludge system. This information is combined with the governing mechanistic model to calculate mass balances over each reactor for each model component. The general form of the mass balance equation is the fundamental expression :

$$\left\{\begin{matrix}\text{Rate}\\\text{of}\\\text{Accumulation}\end{matrix}\right\} = \left\{\begin{matrix}\text{Rate}\\\text{of}\\\text{Input}\end{matrix}\right\} - \left\{\begin{matrix}\text{Rate}\\\text{of}\\\text{Output}\end{matrix}\right\} + \left\{\begin{matrix}\text{Production}\\\text{Rate}\\\text{by}\\\text{Reaction}\end{matrix}\right\} \qquad (3.18)$$

The input and output terms in the mass balance equations refer to the convection terms which depend on the system configuration and flow patterns. The reaction term is the combination of the removal mechanisms and growth reactions applicable to the compound of interest in the mechanistic model. The mass balances (state equations) quantify the behaviour of each compound in the system by relating the dependent variables (compounds and microorganisms) to the independent variables (reactor volume, etc.). These form a set of simultaneous non-linear differential equations which characterize the behaviour of the activated sludge system. In this fashion, the changing concentrations of the compounds in the system are related to the transport (input and output) and reaction processes occurring within the system. Solving this system of equations quantifies the concentrations of the different model components with respect to space (different reactors) and time (for a time-varying input). Since a mechanistic model such as that presented here is very complex, simulation of system behaviour generally demands computer implementation of the model.

In summary, development of a model which describes the behaviour of an activated sludge system involves two stages: (1) formulating the mechanistic model which identifies the model components to be tracked and describes the processes occurring within the system; and, (2) simulating the behaviour of a particular system within which the model is operating.

3.7 SUMMARY OF MODEL DEVELOPMENT FOR PETROLEUM REFINERY ACTIVATED SLUDGE SYSTEM

This Chapter has described the development of a mechanistic model for an activated sludge system treating petroleum refinery wastewaters. The next stage in model development was to calibrate the model. This involved matching model predictions to the response of the laboratory scale activated sludge systems. Calibration of the model involved assigning values to the stoichiometric and kinetic coefficients for model processes. The results of this step are reported in Chapter 4.

Table 3.2: Model Matrix for Petroleum Refinery Wastewater Treatment Model (Part 1).

	COMPONENT	1	2	3	4	5	6	7
	PROCESS	Z_{BH}	Z_{BN}	Z_{BS}	Z_E	X_S	X_{CH}	X_I
1	Aerobic growth of heterotrophs on S_{PH}	1						
2	Anoxic growth of heterotrophs on S_{PH}	1						
3	Aerobic growth of heterotrophs on S_M	1						
4	Anoxic growth of heterotrophs on S_M	1						
5	Aerobic growth of heterotrophs on S_V	1						
6	Anoxic growth of heterotrophs on S_V	1						
7	Aerobic growth of heterotrophs on X_{CH}	1					$\frac{-1}{Y_{hCH}}$	
8	Anoxic growth of heterotrophs on X_{CH}	1					$\frac{-1}{Y_{hCH}}$	
9	Decay of heterotrophs	-1			$f_{Ep,H}$	$1 - f_{Ep,H}$		
10	Hydrolysis of X_S					-1		
11	Adsorption of S_{CH}						1	
12	Volatilization of S_V							
13	Ammonification							
14	Nitrifier growth		1					
15	Nitrifier decay		-1		$f_{Ep,N}$	$1 - f_{Ep,N}$		
16	S Oxidizer growth			1				
17	S Oxidizer decay			-1	$f_{Ep,S}$	$1 - f_{Ep,S}$		

Table 3.2: Model Matrix for Petroleum Refinery Wastewater Treatment Model (Part 2).

	COMPONENT	8	9	10	11	12	13
	PROCESS	S_{PH}	S_M	S_V	S_{CH}	S_{NH}	S_{ON}
1	Aerobic growth of heterotrophs on S_{PH}	$\frac{-1}{Y_{hPH}}$				$-f_{ZBH,N}$	
2	Anoxic growth of heterotrophs on S_{PH}	$\frac{-1}{Y_{hPH}}$				$-f_{ZBH,N}$	
3	Aerobic growth of heterotrophs on S_M		$\frac{-1}{Y_{hM}}$			$-f_{ZBH,N}$	
4	Anoxic growth of heterotrophs on S_M		$\frac{-1}{Y_{hM}}$			$-f_{ZBH,N}$	
5	Aerobic growth of heterotrophs on S_V			$\frac{-1}{Y_{hV}}$		$-f_{ZBH,N}$	
6	Anoxic growth of heterotrophs on S_V			$\frac{-1}{Y_{hV}}$		$-f_{ZBH,N}$	
7	Aerobic growth of heterotrophs on X_{CH}					$-f_{ZBH,N}$	
8	Anoxic growth of heterotrophs on X_{CH}					$-f_{ZBH,N}$	
9	Decay of heterotrophs						$f_{ZBH,N}$ $-f_{Ep,H} \cdot f_{ZEH,N}$
10	Hydrolysis of X_S		1				
11	Adsorption of S_{CH}				-1		
12	Volatilization of S_V			-1			
13	Ammonification					1	-1
14	Nitrifier growth					$-1/Y_N$ $-f_{ZBN,N}$	
15	Nitrifier decay						$f_{ZBN,N}$ $-f_{Ep,N} \cdot f_{ZEN,N}$
16	S Oxidizer growth					$-f_{ZBS,N}$	
17	S Oxidizer decay						$f_{ZBS,N}$ $-f_{Ep,S} \cdot f_{ZES,N}$

Table 3.2: Model Matrix for Petroleum Refinery Wastewater Treatment Model (Part 3).

	COMPONENT	14	15	16	17	18	19
	PROCESS	S_{NO}	S_{SR}	S_{SO}	S_P	S_I	S_O
1	Aerobic growth of heterotrophs on S_{PH}				$-f_{ZBH,P}$		$\frac{-(1-Y_{hPH})}{Y_{hPH}}$
2	Anoxic growth of heterotrophs on S_{PH}	$\frac{-(1-Y_{hPH})}{2.86\ Y_{hPH}}$			$-f_{ZBH,P}$		
3	Aerobic growth of heterotrophs on S_M				$-f_{ZBH,P}$		$\frac{-(1-Y_{hM})}{Y_{hM}}$
4	Anoxic growth of heterotrophs on S_M	$\frac{-(1-Y_{hM})}{2.86\ Y_{hM}}$			$-f_{ZBH,P}$		
5	Aerobic growth of heterotrophs on S_V				$-f_{ZBH,P}$		$\frac{-(1-Y_{hV})}{Y_{hV}}$
6	Anoxic growth of heterotrophs on S_V	$\frac{-(1-Y_{hV})}{2.86\ Y_{hV}}$			$-f_{ZBH,P}$		
7	Aerobic growth of heterotrophs on X_{CH}				$-f_{ZBH,P}$		$\frac{-(1-Y_{hCH})}{Y_{hCH}}$
8	Anoxic growth of heterotrophs on X_{CH}	$\frac{-(1-Y_{hCH})}{2.86\ Y_{hCH}}$			$-f_{ZBH,P}$		
9	Decay of heterotrophs				$f_{ZBH,P}$ $-f_{Ep,H} \cdot f_{ZEH,P}$		
10	Hydrolysis of X_S						
11	Adsorption of S_{CH}						
12	Volatilization of S_V						
13	Ammonification						
14	Nitrifier growth	$\frac{1}{Y_N}$			$-f_{ZBN,P}$		$\frac{-(4.57 - Y_N)}{Y_N}$
15	Nitrifier decay				$f_{ZBN,P}$ $-f_{Ep,N} \cdot f_{ZEN,P}$		
16	S Oxidizer growth		$\frac{-1}{Y_S}$	$\frac{1}{Y_S}$	$-f_{ZBS,P}$		$\frac{-(2.00 - Y_S)}{Y_S}$
17	S Oxidizer decay				$f_{ZBS,P}$ $-f_{Ep,S} \cdot f_{ZES,P}$		

Table 3.3: Process Rate Equations for Petroleum Refinery Wastewater Treatment Model.

PROCESS	PROCESS RATE EQUATIONS, ρ_i
1 Aerobic growth of heterotrophs on S_{PH}	$\mu_{hPH} \cdot \frac{S_{PH}}{K_{sPH} + S_{PH} + S_{PH}^2/K_I} \cdot Z_{BH} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
2 Anoxic growth of heterotrophs on S_{PH}	$\eta_{grow} \cdot \mu_{hPH} \cdot \frac{S_{PH}}{K_{sPH} + S_{PH} + S_{PH}^2/K_I} \cdot Z_{BH} \cdot AirNo \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4Yes$
3 Aerobic growth of heterotrophs on S_M	$\mu_{hM} \cdot \frac{S_M}{K_{sM} + S_M} \cdot Z_{BH} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
4 Anoxic growth of heterotrophs on S_M	$\eta_{grow} \cdot \mu_{hM} \cdot \frac{S_M}{K_{sM} + S_M} \cdot Z_{BH} \cdot AirNo \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4Yes$
5 Aerobic growth of heterotrophs on S_V	$\mu_{hV} \cdot \frac{S_V}{K_{sV} + S_V} \cdot Z_{BH} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
6 Anoxic growth of heterotrophs on S_V	$\eta_{grow} \cdot \mu_{hV} \cdot \frac{S_V}{K_{sV} + S_V} \cdot Z_{BH} \cdot AirNo \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4Yes$
7 Aerobic growth of heterotrophs on X_{CH}	$\mu_{hCH} \cdot \frac{X_{CH}/Z_{BH}}{K_{sCH} + X_{CH}/Z_{BH}} \cdot Z_{BH} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
8 Anoxic growth of heterotrophs on X_{CH}	$\eta_{grow} \cdot \mu_{hCH} \cdot \frac{X_{CH}/Z_{BH}}{K_{sCH} + X_{CH}/Z_{BH}} \cdot Z_{BH} \cdot AirNo \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4Yes$
9 Decay of heterotrophs	$b_H \cdot Z_{BH}$
10 Hydrolysis of X_S	$K_H \cdot \frac{X_S/Z_{BH}}{K_X + X_S/Z_{BH}} \cdot Z_{BH} \cdot (AirYes + \eta_{sol} \cdot AirNo \cdot NO_3Yes)$
11 Adsorption of S_{CH}	$K_A \cdot (\Gamma_{maxCH} - \frac{X_{CH}}{Z_{BH}}) \cdot S_{CH} \cdot Z_{BH}$
12 Volatilization of S_V	$K_V \cdot S_V$
13 Ammonification	$K_R \cdot S_{ON} \cdot Z_{BH}$
14 Nitrifier growth	$\mu_N \cdot \frac{S_{NH}}{K_{sNH} + S_{NH}} \cdot Z_{BN} \cdot AirYes \cdot NH_3Yes$
15 Nitrifier decay	$b_N \cdot Z_{BN}$
16 S Oxidizer growth	$\mu_S \cdot \frac{S_{SR}}{K_{sS} + S_{SR}} \cdot Z_{BS} \cdot AirYes \cdot NH_3Yes$
17 S Oxidizer decay	$b_S \cdot Z_{BS}$

Table 3.4: List of Stoichiometric Parameters Used in the Petroleum Refinery Activated Sludge Model.

SYMBOL	DESCRIPTION	VALUE	UNITS
Heterotrophs			
Y_{hPH}	Yield on phenolic COD	0.600	gcell COD yield (g COD utilized)$^{-1}$
Y_{hM}	Yield on mixed COD	0.555	gcell COD yield (g COD utilized)$^{-1}$
Y_{hV}	Yield on volatile COD	0.600	gcell COD yield (g COD utilized)$^{-1}$
Y_{hCH}	Yield on enmeshed hydrocarbons	0.555	gcell COD yield (g COD utilized)$^{-1}$
$f_{ZBH,N}$	Nitrogen content of active mass	0.068	g N (g COD)$^{-1}$ in active organisms
$f_{ZEH,N}$	Nitrogen content of endogenous mass	0.068	g N (g COD)$^{-1}$ in endogenous residue
$f_{ZBH,P}$	Phosphorus content of active mass	0.021	g P (g COD)$^{-1}$ in active organisms
$f_{ZEH,P}$	Phosphorus content of endogenous mass	0.021	g P (g COD)$^{-1}$ in endogenous residue
$f_{Ep,H}$	Fraction of active mass remaining as endogenous residue	0.05	g COD endog. mass (g COD active mass)$^{-1}$
$f_{cv,H}$	Ratio COD/VSS	1.42	g COD (g VSS)$^{-1}$
$f_{cv,CH}$	Ratio COD/VSS of hydrocarbon	3.5	g COD (g VSS)$^{-1}$
$f_{max,CH}$	Maximum number of sites for adsorption of hydrocarbon	1.0	g COD (g VSS)$^{-1}$
Nitrifiers			
Y_N	Yield	0.15	g cell COD yield (g N utilized)$^{-1}$
$f_{ZBN,N}$	Nitrogen content of active mass	0.068	g N (g COD)$^{-1}$ in active organisms
$f_{ZEN,N}$	Nitrogen content of endogenous mass	0.068	g N (g COD)$^{-1}$ in endogenous residue
$f_{ZBN,P}$	Phosphorus content of active mass	0.021	g P (g COD)$^{-1}$ in active organisms
$f_{ZEN,P}$	Phosphorus content of endogenous mass	0.021	g P (g COD)$^{-1}$ in endogenous residue
$f_{Ep,N}$	Fraction of active mass remaining as endogenous residue	0.08	g COD endog. mass (g COD active mass)$^{-1}$
$f_{cv,N}$	Ratio COD/VSS	1.42	g COD (g VSS)$^{-1}$

Table 3.4: List of Stoichiometric Parameters Used in the Petroleum Refinery Activated Sludge Model (cont'd).

SYMBOL	DESCRIPTION	VALUE	UNITS
Reduced sulphur oxidizers			
Y_S	Yield	0.15	g cell COD yield (g S utilized)$^{-1}$
$f_{ZBS,N}$	Nitrogen content of active mass	0.068	g N (g COD)$^{-1}$ in active organisms
$f_{ZES,N}$	Nitrogen content of endogenous mass	0.068	g N (g COD)$^{-1}$ in endogenous residue
$f_{ZBS,P}$	Phosphorus content of active mass	0.021	g P (g COD)$^{-1}$ in active organisms
$f_{ZES,P}$	Phosphorus content of endogenous mass	0.021	g P (g COD)$^{-1}$ in endogenous residue
$f_{Ep,S}$	Fraction of active mass remaining as endogenous residue	0.05	g COD endog. mass (g COD active mass)$^{-1}$
$f_{cv,S}$	Ratio COD/VSS	1.42	g COD (g VSS)$^{-1}$

Table 3.5: List of the Kinetic parameters used in the Petroleum Refinery Activated Sludge Model.

SYMBOL	DESCRIPTION	VALUE	UNITS
Heterotrophs			
μ_{hM}	Maximum specific growth rate on mixed COD	3.2	d^{-1}
K_{sM}	Half saturation coefficient for mixed COD	5.0	$g\ COD\ m^{-3}$
μ_{hPH}	Maximum specific growth rate on phenolic COD	4.3	d^{-1}
K_{sPH}	Half saturation coefficient for phenolics	1.0	$g\ COD\ m^{-3}$
K_I	Inhibition coefficient for phenolics	60.0	$g\ COD\ m^{-3}$
μ_{hV}	Maximum specific growth rate on volatile COD	1.5	d^{-1}
K_{sV}	Half saturation coefficient for volatile COD	30.0	$g\ COD\ m^{-3}$
μ_{hCH}	Maximum specific growth rate on adsorbed X_{CH}	2.0	d^{-1}
K_{sCH}	Half saturation coefficient for X_{CH}	0.15	$g\ COD\ m^{-3}$
b_H	Organism decay rate	0.529	d^{-1}
K_H	Maximum specific hydrolysis rate	2.81	d^{-1}
K_X	Half saturation coefficient for hydrolysis	0.15	$g\ COD\ (g\ COD)^{-1}$
K_R	Ammonification rate	0.06	$m^3\ (g\ COD\ .\ d)^{-1}$
K_A	Adsorption rate for S_{CH}	0.10	$m^3\ (g\ COD\ .\ d)^{-1}$
K_V	Volatilization rate	60	$m^3\ (g\ COD\ .\ d)^{-1}$
Nitrifiers			
μ_N	Maximum specific growth rate	0.36	d^{-1}
K_{sNH}	Half saturation coefficient for growth	1.0	$g\ N\ m^{-3}$
b_N	Organism decay rate	0.04	d^{-1}
Sulphur species oxidizers			
μ_S	Maximum specific growth rate	0.75	d^{-1}
K_{sS}	Half saturation coefficient for growth	1.0	$g\ COD\ m^{-3}$
b_S	Organism decay rate	0.04	d^{-1}

Table 3.6: List of the Switching Function Parameters Used in the Petroleum Refinery Activated Sludge Model.

SYMBOL	DESCRIPTION	VALUE	UNITS
K_{OH}	Aerobic/anoxic growth	0.002	$g\ O\ m^{-3}$
K_{NA}	Ammonia limit	0.05	$g\ N\ m^{-3}$
K_{NO}	Nitrate limit	1.0	$g\ N\ m^{-3}$
K_{LP}	Soluble phosphorus limit	1.0	$g\ P\ m^{-3}$

Table 3.7: Definition of Switching Functions used in the Petroleum Refinery Activated Sludge Model.

SWITCHING FUNCTION	EQUIVALENT	DEFINITION
AirYes	1 - AirNo	$\frac{S_o}{K_{OH} + S_o}$
AirNo	1 - AirYes	$\frac{K_{OH}}{K_{OH} + S_o}$
NH_3Yes	1 - NH_3No	$\frac{S_{NH}}{K_{NA} + S_{NH}}$
NH_3No	1 - NH_3Yes	$\frac{K_{NA}}{K_{NA} + S_{NH}}$
NO_3Yes	1 - NO_3No	$\frac{S_{NO}}{K_{NO} + S_{NO}}$
NO_3No	1 - NO_3Yes	$\frac{K_{NO}}{K_{NO} + S_{NO}}$
PO_4Yes	1 - PO_4No	$\frac{S_P}{K_{LP} + S_P}$
PO_4No	1 - PO_4Yes	$\frac{K_{LP}}{K_{LP} + S_P}$

CHAPTER 4

CALIBRATION OF PETROLEUM REFINERY MODEL

4.1 INTRODUCTION

In Chapter 3 a structured mechanistic model was proposed to represent an activated sludge system treating petroleum refinery wastewaters. This Chapter explains how the model was calibrated. Calibration requires data which reflect the response of the activated sludge system for a known set of operating conditions. Characterization of the influent wastewater is also a necessary part of the experimental database required for model calibration; that is, the division of the total influent COD and TKN into model component concentrations.

The database for model calibration was provided by the results of the earlier study involving the operation of laboratory-scale activated sludge systems treating wastewater from the Imperial Oil Refinery at Nanticoke, Ontario (Baker, 1993). The experimental activated sludge system was monitored for a number of different operating conditions (different sludge ages) for both constant loading and dynamic loading scenarios.

The results of both the constant loading and dynamic loading experiments were used in the calibration process to quantify the values of the different model parameters. Calibrating the model involved determining *a single set of numerical values for the stoichiometric and kinetic model parameters* such that the model could predict system response for a range of operating conditions with reasonable accuracy. The calibration procedure based on the experimental data was an iterative one:

> One set of data was used to obtain estimates of the model parameters. The parameters were adjusted until the model predictions matched observed experimental behaviour. The next stage in the process was to apply the model

with these values for the model coefficients to data for other sets of conditions. If the selected values were not adequate the values were adjusted iteratively until the model predicted the response of all data sets with reasonable accuracy.

Part of the iterative calibration procedure involved evaluating the model structure. Initially the proposed model was somewhat different from that presented in Chapter 3. During the calibration process it was found necessary to modify the initial model structure in a number of respects before arriving at the "final" model. The point here is that model calibration and development of the model itself is also an iterative procedure.

4.2 SUMMARY OF EXPERIMENTAL PROGRAMME

Experiments were conducted on single-reactor laboratory activated sludge units to collect the information required for model development. The parameters measured on these units were designed to allow determination of the stoichiometry and kinetics of the system treating petroleum refinery wastewater. The experimental programme for this earlier study is described in detail by Baker (1993). In summary, information was needed on the removal of organic material in the wastewater and the associated growth characteristics of the microorganisms for a given organic load. Data on the use of nitrogen compounds for growth and nitrification in the reactor also were necessary. The removal of reduced sulphur species was important and also needed to be characterized.

During the experimental programme activated sludge units were operated under both constant and dynamic loading conditions. For the constant loading each unit received influent wastewater at a fixed flow rate (and concentration). Data from these systems facilitated determination of stoichiometric parameters, but did not provide information on kinetic response. For the dynamic loading experiments, each day influent wastewater was introduced at a constant rate (and concentration) over 12 hours, with no feed over the remaining 12 hours; this cycle was repeated each day. Monitoring the dynamic response of the system over a 24 hour cycle provided information on the kinetic response of the system.

To provide the necessary data on the behaviour of the laboratory-scale activated sludge system a number of parameters were monitored. During both the constant loading and dynamic loading experiments the following parameters were measured daily on the activated sludge unit:

Influent Chemical Oxygen Demand (Unfiltered)
Effluent Chemical Oxygen Demand (Unfiltered and Filtered)
Influent Total Kjeldahl Nitrogen (Unfiltered)
Effluent Total Kjeldahl Nitrogen (Filtered)
Effluent Nitrate (Filtered)
Total Suspended Solids
Volatile Suspended Solids
Oxygen Utilization Rate (mg/L/hr)

Each of these values were reported in terms of concentration with the exception of OUR.

These parameters were collected for the constant loading system operating at two different sludge ages and for the dynamic loading system, also at two different sludge ages. Furthermore, to supplement the daily measurements collected on the continuous flow unit, several analyses were conducted periodically. This information enabled the influent wastewater and the biomass to be characterized. These parameters were:

Influent Chemical Oxygen Demand (Filtered)
Influent Total Kjeldahl Nitrogen (Filtered)
Influent Sulphate
Effluent Sulphate
Influent Ammonia
Influent Phenolics
Influent Oils and Greases (hydrocarbons)
COD/VSS ratio of the sludge
TKN/VSS ratio of the sludge

The remaining information required for model calibration was determined in a series of different batch tests. Volatilization batch tests were performed on raw wastewater samples in order to estimate the rate at which volatile organic compounds were stripped from the system. Also, batch decay rate tests were performed on activated sludge in order to determine the decay rate of the organisms in this system. These tests helped to quantify certain model parameters which were difficult to determine from operation of continuous flow systems.

The observed behaviour in the constant loading and dynamic loading experiments are reported during the calibration procedure, along with the information provided by conducting the individual batch tests. The characteristics of the different batches of wastewater used to operate these systems also are tabulated.

4.3 MODEL CALIBRATION

Calibration of the petroleum refinery activated sludge model involved determination of two different types of model parameter. One set of model parameters describes the stoichiometry of the system by specifying the yields of the microorganisms and the composition of the biomass in terms of COD, nitrogen, and phosphorus. These values provide information on the amount of influent COD, TKN, and phosphorus required to produce a given mass of microorganisms. The yield of the biomass on an organic compound also impacts the oxygen requirements of the system. The second set of model parameters quantifies the kinetic parameters in the system and establish the rate at which different reactions occur within the reactor. These reaction rates determine the rate of growth of biological components in the reactor and the rate at which particular contaminants are removed from the activated sludge system. Quantifying both groups of model parameters is important for proper calibration of the refinery activated sludge model in order to obtain accurate predictions of system response. The determination of each of the parameters is now discussed in detail.

4.3.1 Stoichiometric Parameters

Yields of the Heterotrophs:

The yield of the heterotrophs specifies the mass of microorganisms which is generated when a unit mass of substrate COD is utilized. The value can vary with different sources of organic carbon. As an example, for heterotrophic growth in an activated sludge system treating municipal wastewaters, the yield of organisms has been observed to be near constant (0.666 g cell COD per g of COD utilized) even for different wastewater sources. In contrast, growth yield on hydrocarbons has been reported as 0.555 g cell COD per g COD (Payne, 1970). The substrate not converted to biomass is oxidized to generate the energy requirements for cell growth and maintenance. Therefore, the value of the yield in turn affects the oxygen utilization rate (OUR) in the system. If the yield of a particular organism on a given organic material is low then the corresponding OUR will be high since more energy is required to generate and maintain the microorganism from a given mass of influent organic material utilized. In summary, the relationship between yield and energy requirements impacts the mass of organisms present in the activated sludge system and the oxygen consumed in the process. These were identified in Chapter 3 as important aspects of system performance to quantify in these models.

For the specific case of petroleum refinery wastewater the influent was divided into 4 categories of biodegradable COD: (1) phenolics, (2) mixed organic compounds, (3) volatile organics, and (4) enmeshed hydrocarbons. Each of these groups has different chemical properties, and as a result, the yield of organisms on the various substrates may differ. Determination of the yield coefficients to be used in the mechanistic model was conducted using a number of approaches. The literature (Payne, 1970) reported values of heterotrophic yields for a range of organic compounds including a yield of 0.555 g cell COD per gram of hydrocarbon COD utilized. This was the value assigned to the yield of heterotrophs on adsorbed hydrocarbons (Y_{hCH}). Experience with the degradation of phenolic compounds and volatile organic compounds in the petrochemical wastewaters (see Chapter 6) suggested that organism yield on these compounds was of the order of 0.600 g cell COD per gram of phenolics or volatile organic COD (Y_{hPH}, Y_{hV}). Therefore, this value was assumed in the petroleum refinery application for these two model components, but was confirmed as appropriate in the calibration procedure.

Specific information was not available on the yield of the mixed organic compounds (Y_{hM}) because it was a composite of many individual compounds. Its value was determined by fitting the model predictions to the actual experimental results of both the volatile solids concentration and oxygen utilization rate. Both constant loading and dynamic loading results were used in this calibration.

The calibration of the yield coefficients involved consideration of several coefficients simultaneously since the VSS concentration and OUR of the system are affected by several parameters. These include $f_{Ep,H}$, the fraction of active mass remaining as endogenous residue, and f_{enm} and f_{up}, the division of the particulate fraction into enmeshed and unbiodegradable portions. Therefore, the process of determining the value of the yield coefficient was conducted iteratively in conjunction with these parameters.

A range of values for the yield between 0.666 and 0.555 g cell COD per gram of COD utilized was tested in the model for the mixed COD component (Y_{hM}). This range includes the two extreme values of yield coefficients generally associated with growth: (1) yields normally measured in municipal activated sludge systems (0.666 g/g), and (2) the lower yields associated with growth on hydrocarbon material (0.555 g/g). A yield of 0.666 g per g on mixed COD caused the model predictions to grossly overestimate the VSS in all the experimental runs so was not considered a reasonable estimate of the yield. The oxygen utilization rate was slightly overestimated except during the dynamic loading experiment operating at a 5 day sludge age where the OUR was significantly underestimated. A value of 0.600 g cell COD per gram of mixed COD utilized over-predicted the VSS concentration and the OUR by up to 13 percent of the observed values for the constant loading experiments. During the dynamic loading experiments, the VSS concentrations were overestimated by up to 25-30%, with the most marked discrepancy during system operation at a short sludge age. These observations indicate the importance of having both constant loading and dynamic loading experiments to correctly establish values for the model coefficients. Finally, when the yield associated with growth on hydrocarbons (0.555 g cell COD per g COD utilized) was assigned to the yields of organisms on mixed COD, the model produced very reasonable estimates of the VSS and OUR values (all within ± 9 percent with the exception of one value which will be discussed later) measured during both constant and dynamic loading experiments (Table

4.1). Since many of the mixed organic compounds are likely to have the characteristics of soluble hydrocarbon, this is not an unreasonable observation.

Table 4.1: Sensitivity of model predictions to different heterotrophic yields on mixed COD. Model predictions are compared to observed values of activated sludge systems operating under constant loading conditions and at nominal sludge ages of 10 and 20 days. The yield on hydrocarbon is assumed to be 0.555 mg cell COD per mg COD utilized and the yield on phenolics and volatile organic compounds is assumed to be 0.600 mg cell COD per mg COD utilized.

OBSERVED PARAMETERS	*MODEL PREDICTIONS*		
	$Y_{hM} = 0.666$ *g cell COD (g COD util.)*$^{-1}$	$Y_{hM} = 0.600$ *g cell COD (g COD util.)*$^{-1}$	$Y_{hM} = 0.555$ *g cell COD (g COD util.)*$^{-1}$
10 DAY SRT			
VSS = 849 mg L^{-1}	1046.1 (+23 %)	905.9 (+6.7%)	824.4 (-2.9%)
OUR= 20.3 mg L^{-1} hr^{-1}	21.8 (+7.4%)	23.0 (+13.3%)	23.7 (+16.7%)
20 DAY SRT - Batch 1			
VSS = 1120 mg L^{-1}	1519.6 (+39.8%)	1294.3 (+15.6%)	1167.7 (+4.3%)
OUR= 24.0 mg L^{-1} hr^{-1}	24.1 (+4.8%)	25.2 (+5.0%)	25.7 (+7.1%)
20 DAY SRT - Batch 2			
VSS = 1094 mg L^{-1}	1375.1 (+22.8%)	1173.9 (+8.0%)	1059.9 (-3.1%)
OUR= 23.0 mg L^{-1} hr^{-1}	23.3 (+2.9%)	24.4 (+6.1%)	25.1 (+9.1%)

NOTE : The fractional values for the endogenous residue, enmeshed particulate and unbiodegradable particulate in the influent were assumed to be the same in each of the above model simulations. The value for $f_{Ep,H}$ was equal to 0.05 g COD endog. mass per g COD active mass, X_S was 0.07 g COD m^{-3}, and X_I was 0.02 g COD m^{-3}.

These model predictions assumed that the yield of organisms on phenolics (Y_{hPH}) and volatile organics (Y_{hV}) is 0.600 g cell COD per g COD utilized. Assigning this value to these yield coefficients produced reasonable model predictions. In order to establish the sensitivity of the model to these particular coefficients, the system was modelled assigning a value of 0.555 g cell COD per g COD utilized to Y_{hV} and Y_{hPH}. The model predicted the observed response within 17 percent for all the VSS and OUR measurements. The model predictions were in a similar range for a yield coefficient of 0.666 g cell COD per g COD utilized for volatile organics and phenolics. Since the laboratory activated sludge system treating the refinery wastewaters does not actually treat large quantities of either of these compounds the model was not sensitive to these two parameters. Therefore, the value of 0.600 was selected for each of these growth yields since it predicted the appropriate behaviour for the petrochemical system (see Chapter 6).

A yield of 0.555 g cell COD per gram COD utilized was considered the optimum value for growth yields on hydrocarbon COD (Y_{hCH}) and mixed COD (Y_{hM}) for all the experimental runs. Using this value for the growth on hydrocarbon and mixed COD, the response of the system operating at the different conditions could be reasonably predicted as long as the $f_{Ep,H}$, f_{enm}, and f_{up} fractions were fitted appropriately. Table 4.1 tabulates the predicted and observed values for VSS and OUR using the three different values for organism yield on mixed COD in each of the three constant loading experimental runs. The data indicate the significant impact that the yield coefficient for this COD component has on the observed VSS and OUR in the activated sludge system. Since the mixed COD constitutes a significant fraction of the influent wastewater, the model predictions of the laboratory activated sludge system are sensitive to this parameter.

The results of the fitting procedure for the different yield coefficients including the mixed COD, indicated that the yields associated with petroleum refinery wastewater are lower than the microorganism yields on municipal wastewater. This observation is in agreement with the findings of researchers that hydrocarbons need to be converted to fatty acids before being utilized in the organism energy cycles. The transformation requires the additional input of oxygen and energy which results in a lowering of cell yield on these substrates (Ertola *et al.*, 1965).

Nitrogen and Phosphorus Content of the Heterotrophs:

Microorganisms primarily require organic material in order to grow, but they also require certain nutrients. Two of the most important nutrients required to sustain growth are nitrogen and phosphorus. Insufficient levels of these two nutrients can cause many problems in an activated sludge system such as settling problems due to filamentous organism growth and extracellular slime production. Microorganism growth also becomes limited. With sufficient nutrient levels growth should proceed normally with specific fractions of the active biomass consisting of nitrogen and phosphorus. The nutrient fractions of all the heterotrophs, despite the different sources of organic material, were assumed to be the same in this model.

The nitrogen component of the active organism mass, $f_{ZBH,N}$, was determined in the petroleum refinery activated sludge system by measuring the TKN/VSS ratio of the suspended solids (Baker, 1993). A TKN/VSS ratio of 0.1 g N per g of volatile suspended solids was indicated. To maintain consistent units, the value used in the model needed to be in the units of g N per g of organism COD. To convert the TKN/VSS ratio into these units the observed value of 0.1 g N per g of VSS was divided by the COD/VSS ratio of 1.42 (also determined experimentally) to obtain a value of 0.068 g-N per gram of COD in the active organisms. The nitrogen fraction in the biomass is included in the nitrogen balance calculation on the system.

The phosphorus component, $f_{ZBH,P}$, was not measured experimentally, but rather assumed to be the same as the fraction of phosphorus in heterotrophs growing in municipal wastewater. Since phosphorus removal was not specifically being considered in this initial modelling effort, the actual phosphorus component of the VSS was not critical as long as sufficient levels were available for growth. No phosphorus balance was performed on the system. The value assumed for the P content of the active organism mass was 0.02 g P per gram of organism COD.

The endogenous mass residue in the system also contains fractions of nitrogen and phosphorus. For purposes of this initial modelling study, the nitrogen and phosphorus components of the endogenous mass were assumed to be identical to the fractions present in the active mass. The nitrogen fraction in the endogenous residue, $f_{ZEH,N}$, was assigned the value of 0.068 g-N per g of COD and the phosphorus fraction, $f_{ZEH,P}$, was assigned 0.02 g-P per g of COD.

Endogenous residue fraction for the Heterotrophs ($f_{Ep,H}$):

The fraction of active mass remaining as endogenous residue after decay, $f_{Ep,H}$, was determined by fitting the model predictions to the observed experimental results. As indicated earlier, its value must be calibrated in conjunction with the values for the yield coefficients since the endogenous residue fraction also impacts both the VSS and OUR of the system. As the organisms decay some of the organic material is recycled back into new organism growth requiring oxygen, while the remaining fraction is unbiodegradable residue. This unbiodegradable component contributes to the suspended solids concentration in the reactor. The higher the endogenous residue the higher the solids concentration, but the lower the OUR. By changing the endogenous fraction, $f_{Ep,H}$, for a specific heterotrophic yield the model predictions were matched to the observed VSS and OUR.

To complicate matters, however, the division of particulate COD (approximately 9% of the total influent COD) into enmeshed and unbiodegradable fractions also impacts the VSS and OUR predictions so these fractions also needed to be considered during the fitting procedure. For each fraction of endogenous residue tested in the model, the fractions of enmeshed and unbiodegradable particulate COD were adjusted until the model predictions best matched the experimental observations. This process was iterative in nature since predictions of all the constant loading and dynamic loading experimental results had to be optimized with these wastewater fractions and system characteristics. With the endogenous fraction, $f_{Ep,H}$, equal to 0.05 (g COD endogenous mass per g of COD active mass) an enmeshed COD fraction, f_{enm}, of 0.07 and a unbiodegradable particulate fraction, f_{up}, of 0.02 in the influent COD, the model predicted values within 9 percent of the observed results with exception of the OUR measured on the 10 day system. Reasons why this value is overestimated are discussed in Section 4.4. Therefore, the values indicated above were assigned to the coefficients in the petroleum refinery activated sludge model. The comparison of model and observed results is discussed later.

To estimate the sensitivity of the model a range of plausible values for the endogenous fraction ($f_{Ep,H}$) was established. Values of 0.040 to 0.120 g COD endogenous mass per g of active mass were tested in the model. For example, an $f_{Ep,H}$ of 0.06 produces model predictions within approximately 10 percent of actual values. Similarly, a value of 0.04 or

0.07 for $f_{Ep,H}$ produced reasonable predictions of the observed system response (within 20 percent). Therefore, the model predictions are not extremely sensitive to the choice of the fraction of biomass which remains as endogenous residue. Increasing the unbiodegradable particulate fraction and decreasing the enmeshed fraction in the influent tended to have a more marked impact on the system although predictions remained within 20 percent of observed values. The most obvious change was an increase in reactor VSS concentrations predicted by the model. By establishing these ranges for the parameters, it was clear that there was some flexibility in the selection of both $f_{Ep,H}$ and the particulate influent COD fractions used in the model.

COD/VSS Ratio for the Heterotrophs ($f_{cv,H}$):

In the experimental study measurements were made of the COD of the volatile suspended solids (VSS) in the reactor. Initially it was anticipated that the observed COD/VSS ratio would be close to 1.42 g COD/g VSS; this value is typical for organisms grown on a range of substrate types. For the system operated at a 20 day sludge age the observed value was 1.44 (±0.09). However, for the 10 day sludge age the value was significantly higher at 1.55 (± 0.06). The increased value at the shorter sludge age appeared to be due to less complete degradation of adsorbed hydrocarbon. A typical hydrocarbon will have a COD to mass ratio of approximately 3 g COD/g. Therefore, assuming that the organisms themselves have a COD/VSS ratio of 1.42, the observed COD/VSS ratio will increase as the amount of adsorbed hydrocarbon increases.

From the experimental measurements it was not possible to quantify the division between organism mass and adsorbed hydrocarbon mass within the VSS. However, the model provided predictions of biomass and hydrocarbon content for different operating sludge ages. These predictions depend on a range of model parameters such as yield coefficients, growth rate on adsorbed hydrocarbon, etc., as well as the influent hydrocarbon content. Despite these complex interactions, when a value of 1.42 was assumed for the COD/VSS ratio of the biomass, model predictions of the composite COD/VSS ratio (including COD of biomass and hydrocarbon) were close to the observed values. This value was assumed for all the microorganisms in the petroleum refinery activated sludge system: the heterotrophs, nitrifiers, and reduced sulphur oxidizers.

Stoichiometric Parameters for the Nitrifiers:

The same parameters established for the heterotrophs also had to be determined for the nitrifiers. These were values for the (1) nitrifier yield, Y_N, (2) the nitrogen and phosphorus components of the nitrifier active and endogenous mass, $f_{ZBN,N}$, $f_{ZBN,P}$, $f_{ZEN,N}$ and $f_{ZEN,P}$, (3) the fraction of nitrifier active mass remaining as endogenous mass, $f_{Ep,N}$, and the COD/VSS ratio, $f_{cv,N}$. No attempt was made to determine these parameters from the experimental data. Values for these parameters used in modelling nitrifier behaviour in municipal activated sludge systems were accepted. It should be noted that any discrepancy in these values from their true values has minimal impact on the overall system parameters since the concentration of nitrifiers in the system is negligible compared to the concentration of heterotrophs. The values for these parameters used in the petroleum refinery model are listed in Table 3.5.

Stoichiometric Parameters for the Reduced Sulphur Oxidizers:

The stoichiometric parameters associated with the reduced sulphur oxidizers also needed to be quantified. These were (1) the reduced sulphur oxidizer yield, Y_S, (2) the nitrogen and phosphorus components of active and endogenous mass, $f_{ZBS,N}$, $f_{ZBS,P}$, $f_{ZES,N}$ and $f_{ZES,P}$, the fraction of active mass remaining as endogenous mass, $f_{Ep,S}$, and (3) the COD/VSS ratio, $f_{cv,S}$. Similar to the situation with the nitrifier population, individual analysis of each of these parameters was impractical and no attempt was made to determine values from the experimental data. Therefore, the values assumed were the same as those used to describe nitrifier growth. The concentration of reduced sulphur oxidizers is usually less than the nitrifier concentration so any error in these values from their true values has even less of an impact on the overall system parameters. The values for these parameters used in the petroleum refinery model are listed in Table 3.5.

4.3.2 Kinetic Parameters

Parameters for Phenol Utilization:

The kinetic parameters quantifying the utilization of phenolics for organism growth are the maximum growth rate , μ_{hPH}, the half-saturation coefficient for phenolics, K_{sPH}, and the inhibition coefficient, K_I. Many previous studies on phenol degradation in biological systems indicated that it is easily biodegradable and can be used readily for organism growth. One problem which does arise with phenolic compounds is that they are inhibitory to growth processes at high concentrations. Therefore, to account for the possibility of organism growth under inhibitory conditions, the Haldane equation was used to model growth on phenolics. In general, the concentrations found in a petroleum refinery wastewater are sufficiently low to avoid inhibitory growth, but spike loadings of phenolics are not unusual. If the concentrations of phenolics are low, the Haldane equation reduces to Monod growth kinetics. This was the case in the laboratory scale system where the influent phenolics concentration was approximately 10 mg/L. Because the concentration of the compounds in the system was so low, the inhibitory growth kinetics did not significantly impact model predictions. As a result the kinetic coefficients determined during the calibration of the petrochemical model (Chapter 6) were utilized in this system and provided adequate predictions when applied to the petroleum refinery application. A value of 4.3 d^{-1} was assigned to the μ_{hPH} parameter in the petroleum refinery model; a value of 1.0 g COD m^{-3} was assigned to the half-saturation coefficient, K_{sPH}; and the inhibition constant, K_I, was set at 60 gCOD m^{-3}.

Parameters for Mixed Soluble Substrate Utilization:

The maximum growth rate, μ_{hM}, and the half-saturation coefficient for organism growth on mixed COD also had to be determined for the petroleum refinery activated sludge model. This COD component contains a variety of compounds. The dynamic experiments, however, indicated that these compounds were readily biodegradable. As a result the values for these two kinetic parameters were assumed to be the same as those used for the utilization of soluble substrate for growth in a municipal wastewater. Values of μ_{hM} equal to 3.2 d^{-1} and K_{sM} equal to 5.0 g COD m^{-3} were used in the refinery activated sludge model.

Parameters for Volatile Organic Substrate Utilization:

The removal of volatile organic COD in these activated sludge systems can follow two potential pathways: (1) utilization of VOC's by organisms for growth processes, and (2) stripping from the surface of the aeration basins. Each of these mechanisms competes to control the behaviour of these volatile organic compounds which in turn influences the overall response of the activated sludge system. For example, if the stripping rate is high then a significant portion of the VOC's are stripped from the system leaving less organic substrate available for growth processes. However, if the stripping rate is lower and growth on VOC's dominates the stripping process, then more oxygen is utilized in the system (OUR increases) to oxidize the material and more biological solids (X_V) are produced. The relative rates of both organism growth and volatilization of volatile organic compounds, therefore are very important in controlling the behaviour of these systems. For these two removal processes, three model parameters must be quantified: (1) the maximum growth rate, μ_{hV}, (2) the half-saturation coefficient, K_{sV}, and (3) the volatilization rate, K_V.

One of the problems with determining values for these model coefficients is the competitive nature of the two removal mechanisms i.e. it is difficult to isolate each removal process occurring in the activate sludge system. Therefore, an approach needed to be implemented to approximate the rates for each process.

To approximate the rate of stripping of volatile organic compounds from the system a series of batch tests were performed. These tests involved aerating a batch of influent wastewater at a rate which approximated the rate used in the laboratory-scale activated sludge system. No sludge was added to the influent in an attempt to isolate the stripping mechanism. Over a period of several hours samples were drawn from the system and the COD and TKN were measured. The test was continued until no more COD appeared to be removed from the system (at this point the remaining COD is considered non-volatile). This provided a means to estimate the rate at which COD and TKN was lost from the system, although experiments indicated that negligible TKN was volatilized from these systems. An example of the COD loss in one of these batch tests is illustrated in Figure 4.1(a). By plotting the drop in COD concentration in the test versus time in semi-log form a straight line plot was generated. The slope of this line represents the stripping rate of the volatile COD from the system. Figure 4.1 (b) illustrates this procedure. This procedure was repeated for a number of influent batch tests and a value of 60 day^{-1} was determined as a reasonable approximation for K_V.

One other concern should be mentioned with respect to determining the model parameters for the removal of volatile organic compounds - the possible loss of VOC's from the feed tank. Samples for COD measurements on feed were taken when the daily influent was prepared and placed in the feed container. The feed was pumped into the activated sludge system during the next 24 hours. During this period there was possible loss of VOC from the tank. Two affects resulted from this situation:

(1) difficulty in measuring the kinetics for VOC compounds, and
(2) uncertainty in the VSS concentrations and mass balance calculations.

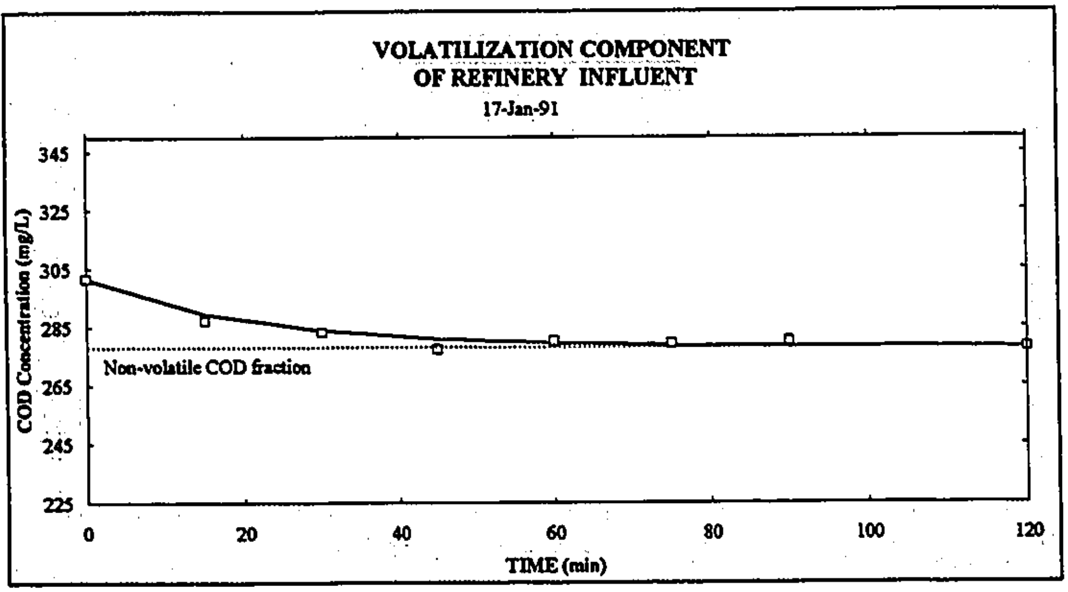

Figure 4.1(a): The results of a volatilization batch test (January 17, 1991) are illustrated to show the drop in COD with time due to the stripping of volatile organic compounds.

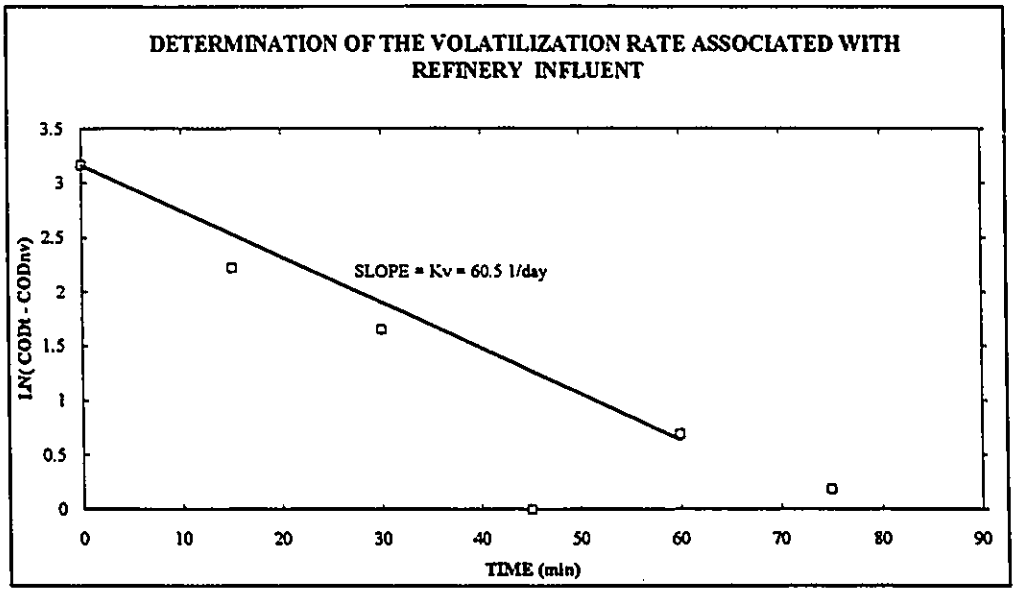

Figure 4.1(b): This semi-log plot illustrates the method used to estimate the stripping rate of volatile organic compounds from the activated sludge system. The K_V calculated from the slope of the line is the stripping rate for the compounds in the absence of activated sludge.

The uncertainty associated with the concentration of VOC's which reached the activated sludge system, made it difficult to determine the values to use for the growth parameters on volatile organic compounds. The values assigned for μ_{hV} and K_{sV} were those determined during calibration of the petrochemical activated sludge system (see Chapter 6). The values were:

$\mu_{hV} = 1.5\ d^{-1}$,
$K_{sV} = 30.0\ g\ COD\ m^{-3}$

Using these values for generating model predictions produced reasonable results despite the uncertainty in the measurements (Table 4.2). Loss of VOC's from the feed tank would contribute to the slight overestimation of volatile suspended solids concentration in the reactor. Table 4.2 also illustrates the influence of increasing the half-saturation constant to 200 g COD m^{-3} which would significantly reduce growth rates on VOC's and therefore, reduce the volatile suspended solids produced.

Table 4.2: Comparison of model predictions for the constant loading systems for the volatile organic COD half-saturation coefficient K_{SV}, equal to 30 and 200 g COD m^{-3}.

OBSERVED PARAMETERS	*MODEL PREDICTIONS*	
	K_{sV} = 200.0 g COD m^{-3}	*K_{sV} = 30.0 g COD m^{-3}*
10 DAY SRT		
VSS = 849 mg L^{-1}	824.2 (-2.9 %)	911.9 (+7.4%)
OUR= 20.3 mg L^{-1} hr^{-1}	23.8 (+17.0%)	25.6 (+25.6%)
20 DAY SRT - Batch 1		
VSS = 1120 mg L^{-1}	1167.5 (+4.2%)	1242.0 (+10.9%)
OUR= 24.0 mg L^{-1} hr^{-1}	25.8 (+7.5%)	27.0 (+12.5%)
20 DAY SRT - Batch 2		
VSS = 1094 mg L^{-1}	1059.8 (+2.5%)	1093.0 (+1.0%)
OUR= 23.0 mg L^{-1} hr^{-1}	25.1 (+9.1%)	25.6 (+11.3%)

This stage in the calibration procedure illustrated the critical nature of determining the volatile organics in the wastewater and the rate at which these compounds are stripped from the system. The VOC's have a significant impact on the VSS of the reactor and the oxygen consumed. Further studies of the volatilization processes in these systems would assist in determining more accurate model coefficients.

Parameters for Adsorbed Hydrocarbon Utilization:

The use of adsorbed hydrocarbon for microorganism growth proceeds via a different mechanism than the utilization of other carbon sources. In the model, it is proposed that influent hydrocarbon is adsorbed onto the organism mass, and the adsorbed material is utilized for biological growth. As a result, the growth on hydrocarbons is a slower process and the maximum growth rate is considerably lower. A value of 2.0 d^{-1} was assigned to μ_{hCH} in the petroleum refinery model. The half-saturation coefficient (K_{sCH}) was set equal to 0.15 g hydrocarbon COD (g cell COD)$^{-1}$. These values are similar to values for growth of particulate COD in municipal systems (Dold & Marais, 1984). More specific research into this removal mechanism would increase knowledge on the kinetics of the reaction, but for the current work these values appear reasonable.

Organism Decay Rate, b':

To determine the organism decay rate of the sludge treating the petroleum refinery wastewaters, a batch aerobic digestor was operated over a period of several days. Each day the OUR of the mixture was measured in order to monitor the decrease in oxygen consumption as the organisms decay. With fewer organisms requiring oxygen for growth and maintenance processes the overall oxygen demand declined. Test results for sludge removed from the laboratory activated sludge system operating at a 20 day SRT are illustrated in Figure 4.2.

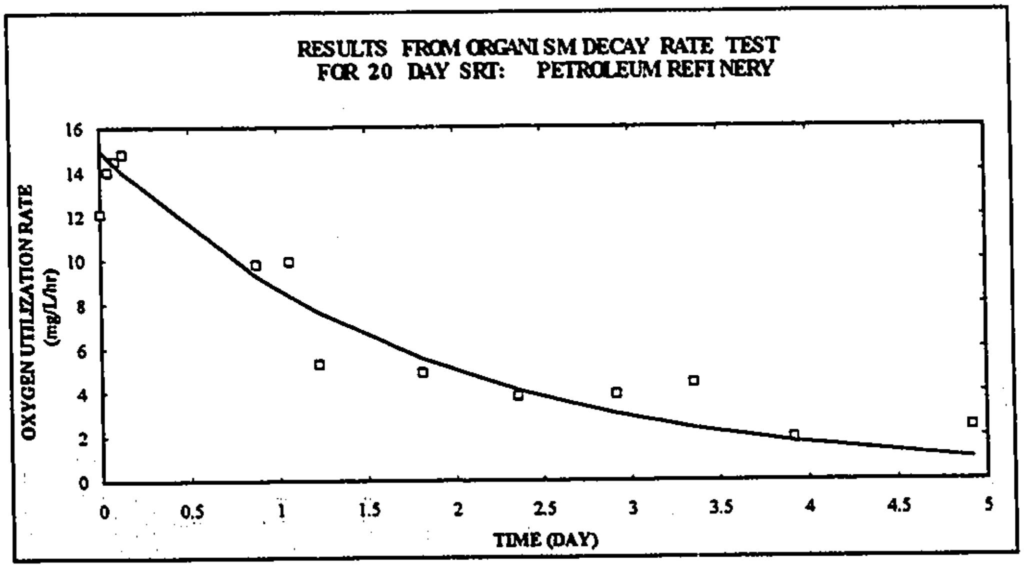

Figure 4.2: The results of an organism decay rate test on a sludge treating petroleum refinery wastewaters in an activated sludge system operating at 20 days. The decrease in OUR is monitored over a period of 5 days.

The decay process was assumed to be first order with respect to the concentration of active organisms in the system. With this assumption, the information presented in Figure 4.2 was used to calculate the net organism decay rate, b. A semi-log plot of the OUR measured in the aerobic digestor with respect to time was plotted. By determining the slope of the linear portion of the response, the net organism decay rate, b, was calculated. This procedure is illustrated in Figure 4.3.

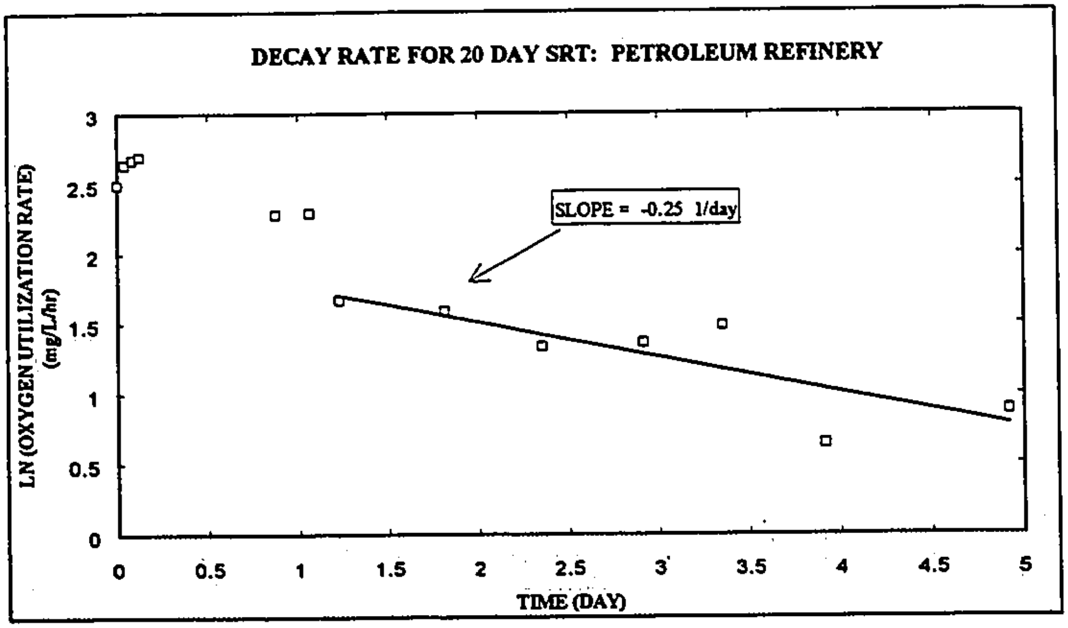

Figure 4.3: The relationship between the Ln of the oxygen utilization rate *versus* time in an aerobic digestor handling sludge which treated petroleum refinery wastewaters is illustrated. By calculating the slope of the linear portion of the response the organism decay rate of the sludge was determined. The net decay rate was calculated as 0.25 day^{-1}.

In the aerobic digestor it was noted that the initial readings of OUR were higher than expected. It was hypothesized that this response was due to the presence of adsorbed hydrocarbon on the sludge that had not been utilized. The initial OUR readings were, therefore, a combination of endogenous respiration and degradation of the adsorbed hydrocarbons. Once the hydrocarbon COD was consumed, the organism decay rate could be determined. Therefore, to determine the decay rate the straight line plot of Ln(OUR) *versus* time was fit to the later portion of the curve in Figure 4.3. This resulted in a net decay rate of 0.25 day^{-1}. A similar test was performed on sludge removed from the system operating at a 10 day SRT and a net decay rate of 0.25 day^{-1} was determined. For municipal systems a value of 0.24 day^{-1} usually is associated with the net decay of organisms so these values appear reasonable.

For the model, the death-regeneration concept was used to quantify the organism decay rate. This approach requires the determination of the overall decay rate (b') rather than the net decay rate (b) determined from the experimental procedure, and the endogenous residue ($f_{Ep,H}$). Therefore, for modelling purposes the value of b calculated above needed to be transformed to the overall decay rate, b'. The equations required to transform this value are described in Appendix 3. Using these relationships for model calibration, the following values were determined for b' and $f_{Ep,H}$:

b' = 0.529 day^{-1},
$f_{Ep,H}$ = 0.05 g COD endogenous mass per g COD active mass

Anoxic Growth Factors:

Growth under anoxic conditions was not considered in this study, but the equations which govern this growth behaviour were included in the model so they could be considered at a later date. Since no experiments were conducted to establish the anoxic growth factors and the equations themselves were not utilized in model predictions, the anoxic growth coefficients for a municipal activated sludge system were assumed.

Hydrolysis of Slowly Biodegradable Substrate (X_S):

The model assumes that the small amount of slowly biodegradable influent COD (±2% of the total) is adsorbed onto the sludge mass and hydrolysed before being used for growth. Three coefficients must be specified in the model; these are the hydrolysis rate coefficient, K_H, the half-saturation constant, K_X, and the anoxic hydrolysis factor, η_{sol}.

Again, values used in the activated sludge treatment of municipal wastewater were assumed. The following values were assigned: $K_H = 2.81\ d^{-1}$, $K_X = 0.15$ g COD (g COD)$^{-1}$, and $\eta_{sol} = 0.37$. Since the experimental programme determined that the majority of the influent COD was soluble substrate, these parameters were assumed to have a minimal impact on the model predictions. As a result, this behaviour was not studied specifically in this initial modelling project.

Ammonification Rate (K_R):

The ammonification rate (K_R) impacts the rate at which organic nitrogen is converted to ammonia in order to be utilized by the microorganisms either as a nitrogen source for growth or as an ammonia source for nitrification. The rate of ammonification was determined by adjusting the ammonification rate parameter, K_R, until the predicted TKN and nitrate concentrations in the constant loading and dynamic loading experiments matched observed values. This was done in conjunction with determining the nitrifier constants. As an example, if the model was predicting concentrations of nitrate which were higher than observed in the experimental runs then the ammonification rate was lowered. Decreasing the rate of conversion of organic nitrogen to ammonia assisted in decreasing the nitrate concentration, while maintaining the TKN concentration. The ammonification rate was adjusted iteratively with the nitrifier coefficients until the model predicted values of nitrate production and TKN consumption similar to the values found experimentally in each of the constant and dynamic loading experiments. A rate of 0.06 m^3 $gCOD^{-1}d^{-1}$ was found to satisfy the observations.

Growth and decay of Nitrifiers:

The parameters required to specify the nitrification kinetics of the petroleum refinery activated sludge system were the maximum specific growth rate, μ_N, the half-saturation coefficient for growth, K_{sNH}, and the organism decay rate, b_N. The values for the latter two parameters were taken from experience with municipal nitrification systems. The half-saturation constant (K_{sNH}) was assigned a value of 1.0 g N m^{-3} and the decay rate of the nitrifiers (b_N) was assigned 0.04 d^{-1}.

The maximum nitrifier growth rate (μ_N), was determined by fitting the model predictions of the TKN and nitrate concentrations with those observed in the dynamic loading experiments. Changing the nitrifier growth rate to best match the TKN and nitrate concentrations of the different operating systems enabled its value to be estimated. A growth rate of 0.36 d^{-1} predicted the best results for all the dynamic loading experiments.

Figure 4.4a and 4.4b provide an example of the influence on model predictions of nitrate and TKN when a growth rate of 0.2 d^{-1} or 0.75 d^{-1} are used in the model *versus* the value of 0.36d^{-1} actually selected. These graphs are for the system operating at a 5 day SRT under dynamic loading conditions. This illustrates the sensitivity of the nitrification response in the system and the need to accurately determine the growth rate of the nitrifiers in order to predict system response.

Sulphur Oxidizers:

The importance of biological sulphur oxidation only became apparent in the latter stages of the experimental project when the refinery changed to processing a sour crude oil and the concentration of reduced sulphur compounds in the wastewater increased significantly. The only data available for quantifying the sulphur oxidizer behaviour were grab samples of influent and effluent sulphate; the change in sulphate (SO_4) was used as an indication of the extent of sulphur oxidation. There was not experimental data available to evaluate

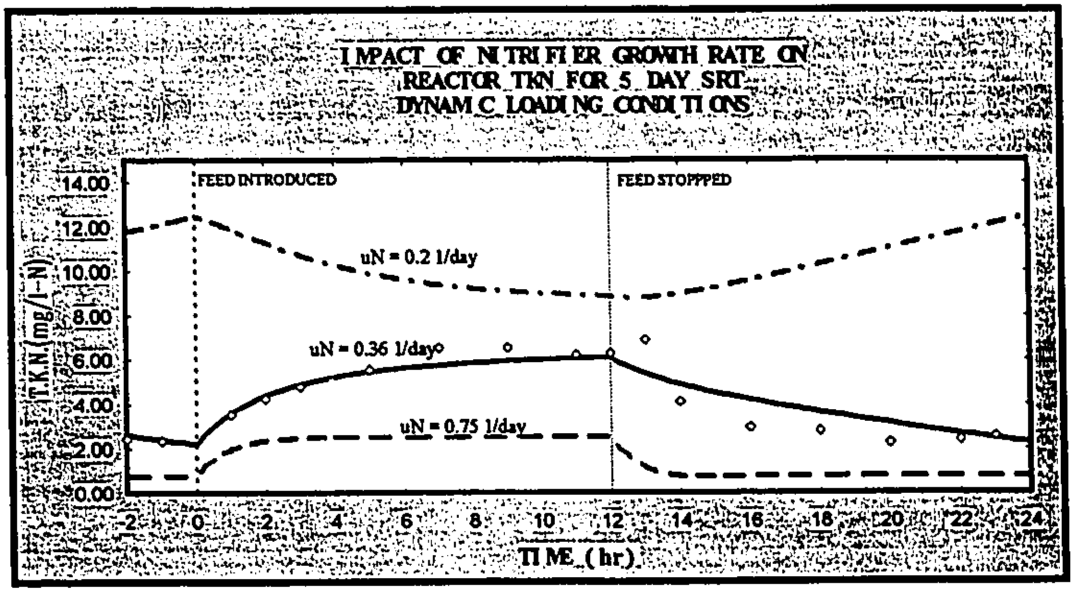

Figure 4.4a: The influence of the nitrifier growth rate on the TKN concentration in the laboratory activated sludge unit under dynamic loading conditions and operating at a 5 day SRT.

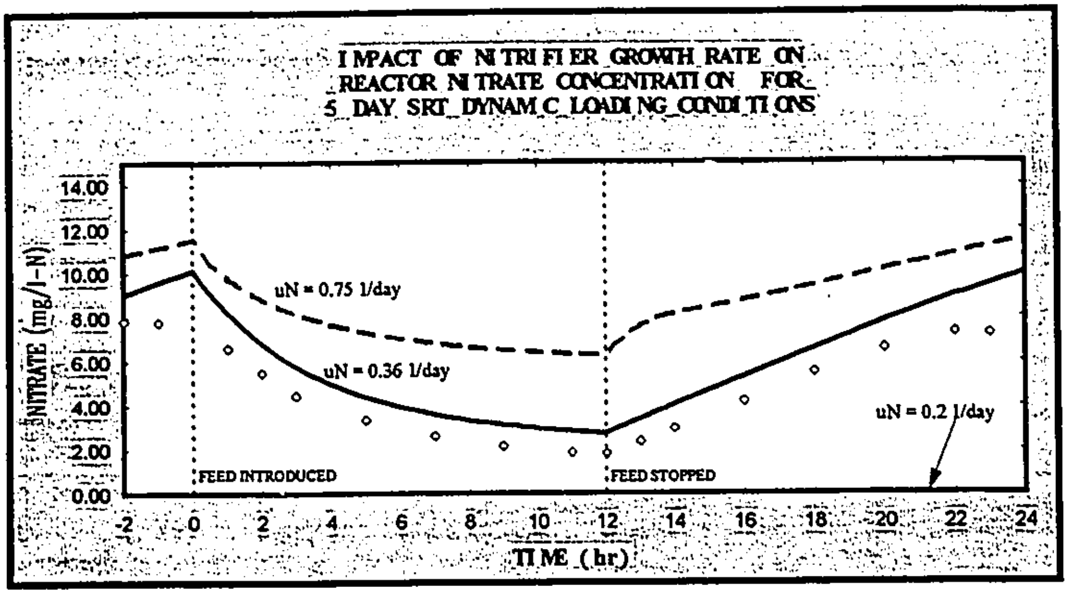

Figure 4.4b: The influence of the nitrifier growth rate on the nitrate concentration in the laboratory activated sludge unit under dynamic loading conditions and operating at a 5 day SRT.

kinetic response of sulphur oxidizers. However, from the limited experimental data and from the response of the OUR in dynamic experiments, it was evident that the sulphur oxidation process is a rapid one.

The model parameters which had to be quantified to describe the behaviour of the sulphur oxidizers were the maximum specific growth rate, μ_S, the half-saturation coefficient for growth, K_{sS}, and the organism decay rate for reduced sulphur oxidizers, b_S. In the model the following values were assigned:

μ_S = 0.75 day-1
K_{sS} = 1.0 g COD m^{-3}
b_S = 0.04 day^{-1}

These values were used in the model simulations and the results appeared reasonable.

4.3.3 Summary of Model Calibration

The model parameters which were determined using the methods outlined above resulted in a calibrated model for the petroleum refinery activated sludge system. As indicated above, many of the model parameters were measured directly during the experimental programme while others were assumed to be similar to the values associated with municipal wastewater treatment. The remaining values were determined by fitting the model prediction to the results observed in the laboratory activated sludge systems.

The following two sections demonstrate the calibrated model predictions for the constant and dynamic loading cases, respectively.

4.4 APPLICATION TO CONSTANT LOADING RESULTS

The experimental study on the petroleum refinery wastewaters (Baker, 1993) provided data on the steady state operation of single-reactor aerobic activated sludge systems operated at sludge ages of 10 and 20 days. Comparison between observed values and model predictions for each of these sludge ages are discussed in the following sections.

4.4.1 10 Day Sludge Retention Time

The nature of the influent wastewater treated in the system operating at steady state at a 10 day SRT is listed in Table 4.3 (Baker, 1993). The total influent COD, TKN, sulphur compounds, and phosphorus concentrations are presented in this table along with the fractions of the different wastewater components.

The system operating at a 10 day SRT took considerable time to reach steady state because the biomass had to acclimate to the bench scale system, and there were some operational difficulties. As a result, the data collected on this operating system had the most uncertainty associated with it. Despite the problems, the model was able to predict the behaviour of the system fairly accurately. The comparison of the model predictions to the actual observed values in the system operating at a 10 day sludge age are illustrated in Table 4.4.

Table 4.3: Characteristics of the petroleum refinery influent wastewater for the 10 day SRT. The total loadings of COD, TKN, phosphorus, and sulphur compounds are listed along with the fractions of the different model components. The true sludge age of the system was 7.7 days.

PARAMETER	*SYMBOL*	*VALUE*	*UNITS*
TOTAL INFLUENT LOADINGS			
(Unfiltered)			
COD		258	mg COD L-1
TKN		14.0	mg N L-1
P		11.0	mg P L-1
S		2.3	mg S L-1
WASTEWATER FRACTIONS			
Phenolics	fph	0.11	g COD g^{-1} COD
Volatile organics	fv	0.20	g COD g^{-1} COD
Hydrocarbons	fch	0.14	g COD g^{-1} COD
Mixed organics	fm	difference	g COD g^{-1} COD
Enmeshed organics	fenm	0.07	g COD g^{-1} COD
Unbiodegradable soluble COD	fus	0.147	g COD g^{-1} COD
Unbiodegradable particulate COD	fup	0.02	g COD g^{-1} COD
Ammonia fraction of TKN	fnh	0.85	g N g^{-1} N
Reduced sulphur of influent S	fsr	1.0	g S g^{-1} S

Table 4.4: Comparison of Observed Values and Model Predictions of Steady State Operation at Sludge Age of 10 Days.

PARAMETER	*SLUDGE AGE 10 DAYS*		*UNITS*
	OBSERVED	*PREDICTED*	
Volatile SS	849	824.4 (2.9%)	mg VSS L^{-1}
Effluent COD (unfiltered)	56	-	mg COD L^{-1}
Effluent COD (filtered)	41	42.8 (4.4%)	mg COD L^{-1}
Effluent TKN (filtered)	2.3	1.7	mg N L^{-1}
Effluent NO_3-N	8.6	9.6	mg NO_3-N L^{-1}
OUR	20.3	23.8 (17%)	mg O_2 L^{-1} h^{-1}

The COD balance and the nitrogen balance calculated on this system closed at 79 and 85 percent respectively. A significant impact on the COD balance is the loss of VOC's from the system, both due to stripping in the aeration tank and losses from the feed tank, as mentioned earlier. Due to the uncertainty associated with these particular mass balances, the calibration procedure emphasized model parameters which most closely matched the other data sets as long as the predictions for the 10 day SRT were reasonable. The above model predictions were within approximately 17 percent of the experimental observations. Considering the uncertainty in this particular experimental data set and the success of the model in predicting system behaviour of the remaining operating conditions, these predictions are very reasonable.

Other factors also contributed to the uncertainty in the data at the 10 day SRT. The measurements of the effluent COD showed more variability than for other operating conditions suggesting one of two problems. Either the clarifier was not operating in a consistent manner and allowed solids to outflow from the system on some days and not others, or there were some inconsistencies with the sampling of the effluent COD. In either case, the possibility of error in the measured values of filtered and unfiltered effluent COD created uncertainty in the calculation of actual sludge age of the system. An accurate value of sludge age is very important for obtaining accurate model predictions.

Analytical problems with the TKN measurements for the batch of wastewater on which the steady state parameters of the 10 day SRT system were determined caused some uncertainty in the TKN measurements. Therefore, only a limited number of measurements for TKN concentration were available for calibrating the model to a 10 day SRT operation. Using these measurements in the model resulted in slightly higher predictions of nitrate concentrations than measured experimentally, while the effluent TKN predictions and measurements were reasonably close. Due to the overestimation of nitrate production, the model prediction of oxygen utilization rate also was slightly elevated. The model predictions of TKN and nitrate concentrations in the system were reasonable despite uncertainty in the experimental values.

Finally, the volatile solids concentration was increasing slightly towards the end of the 10 day SRT operating conditions suggesting that system operation was changing slightly and therefore, was not quite at steady state. This introduced error in the value of VSS chosen for use in the model. Each of these analytical problems and observations created uncertainty in the experimental data for the 10 day SRT system. Despite these complications, reasonable model predictions (within ±17%) were obtained by considering all the data sets during the calibration procedure.

4.4.2 20 Day Sludge Retention Time

The laboratory activated sludge system also was operated at a 20 day SRT under constant loading conditions for two different batches of influent wastewater. The influent characteristics of each of these batches are listed in Table 4.5. Comparison of model predictions to observed values is discussed below and presented in Table 4.6 (a) and (b).

The comparison of experimental results and model predictions indicated excellent results for the activated sludge system operating at the 20 day SRT. All system parameters were estimated within 5 percent of actual values with the exception of effluent TKN. The low numerical values for effluent TKN concentrations distorted the percentage difference between the model and actual measured values. For this reason, it was better to compare the actual TKN measurements rather than percent differences. The ability of the model to predict both the OUR and VSS in the system supported the selection of 0.555 g cell COD per g COD utilized for the growth yield on mixed COD.

Model estimates of effluent TKN and nitrate on treatment of Batch #1 influent were similar to the measured values. The results with Batch #2 were not quite as successful, but very reasonable. In the second batch of wastewater the hypothesis is that the wastewater contained a slightly higher fraction of unbiodegradable organic nitrogen. Since this nitrogen fraction was not quantified in the model influent wastewater characteristics, the ammonification process in the model was able to convert unbiodegradable organic nitrogen into ammonia. Therefore, nitrogen was being ammonified which was not available in the actual system. Subsequently, the excess ammonia was converted to nitrate using more oxygen. This situation explains some of the discrepancy in the second set of data, but in general the model predictions compare very well to observed values.

Table 4.5: Characteristics of the petroleum refinery influent wastewater for the system at a 20 day SRT. The total loadings of COD, TKN, phosphorus, and sulphur compounds are listed along with the fractions of the different model components. The actual sludge age of the system operating with Batch 1 was 14.9 days while the Batch 2 was processed at 13.0 days.

PARAMETER	*SYMBOL*	*VALUE*		*UNITS*
TOTAL INFLUENT LOADINGS		Batch 1	Batch 2	
(Unfiltered)				
COD		237	229	mg COD L-1
TKN		14.0	14.0	mg N L-1
P		11.0	11.0	mg P L-1
S		2.3	2.3	mg S L-1
WASTEWATER FRACTIONS				
Phenolics	fph	0.11	0.11	g COD g^{-1} COD
Volatile organics	fv	0.13	0.066	g COD g^{-1} COD
Hydrocarbons	fch	0.14	0.14	g COD g^{-1} COD
Mixed organics	fm	difference	difference	g COD g^{-1} COD
Enmeshed organics	fenm	0.07	0.07	g COD g^{-1} COD
Unbiodegradable soluble COD	fus	0.168	0.21	g COD g^{-1} COD
Unbiodegradable particulate COD	fup	0.02	0.02	g COD g^{-1} COD
Ammonia fraction of TKN	fnh	0.85	0.85	g N g^{-1} N
Reduced sulphur of influent S	fsr	1.0	1.0	g S g^{-1} S

Table 4.6(a): Comparison of Observed Values and Model Predictions of Steady State Operation for Batch 1 at a Nominal Sludge Age of 20 Days.

PARAMETER	*SLUDGE AGE 20 DAYS*		*UNITS*
	BATCH 1		
	OBSERVED	*PREDICTED*	
MODEL OUTPUT			
Volatile SS	1120	1167.5 (+4.1%)	mg VSS L^{-1}
Effluent COD (unfilt.	51	-	mg COD L^{-1}
Effluent COD (filtered)	43	43.4 (+0.9%)	mg COD L^{-1}
Effluent TKN (filtered)	1.2	1.1	mg N L^{-1}
Effluent NO_3-N	10.0	10.9	mg NO_3-N L^{-1}
OUR	24.0	25.8 (7.0%)	mg O_2 L^{-1} h^{-1}

Table 4.6(b): Comparison of Observed Values and Model Predictions of Steady State Operation for Batch 2 at a Nominal Sludge Age of 20 Days.

PARAMETER	*SLUDGE AGE 20 DAYS*		*UNITS*
	BATCH 2		
	OBSERVED	*PREDICTED*	
MODEL OUTPUT			
Volatile SS	1087.0	1059.8 (-2.6%)	mg VSS L^{-1}
Effluent COD (unfilt.	64.2	-	mg COD L^{-1}
Effluent COD (filtered)	52.2	51.0 (-2.4%)	mg COD L^{-1}
Effluent TKN (filtered)	1.9	1.2	mg N L^{-1}
Effluent NO_3-N	9.4	10.7	mg NO_3-N L^{-1}
OUR	23.0	25.1 (+8.4%)	mg O_2 L^{-1} h^{-1}

4.4.3 Summary of Modelling Constant Loading Systems

In summary, the calibrated model was able to predict reasonably the behaviour of the activated sludge system under steady state conditions operating at both 10 day and 20 day sludge ages. The problems with the model predictions and observed values have been identified, yet despite these problems the values agreed within 11%. This indicated that this initial modelling effort adequately described the stoichiometry of the reactions occurring within the system.

4.5 APPLICATION TO DYNAMIC LOADING RESULTS

Operation of the steady state or constant loading systems did not provide information on the kinetic component of system behaviour. For the steady state system the ability of the model to predict the response of the system depended largely on the appropriate stoichiometric coefficients e.g. the yield coefficients, Y. In a full-scale setting, however, an activated sludge system rarely receives a constant flow and constant load influent stream. Dynamic situations are much more difficult to predict, but necessary if a model is to be applied successfully to a full-scale plant. Comparison of the model predictions for the dynamic loading experiments are described below for two different sludge ages.

4.5.1 5 Day Sludge Retention Time

The influent characteristics of the wastewater used for the 5 day SRT dynamic loading experiment are tabulated in Table 4.7. Model predictions of the response of this system were compared with the actual values measured in the laboratory and are illustrated graphically in Figs. 4.5(a)-(e). In each of these plots, the start and finish of the feed period are indicated.

Table 4.7: Characteristics of the petroleum refinery influent wastewater for the 5 day SRT with dynamic loading. The total loadings of COD, TKN, phosphorus, and sulphur compounds are listed along with the fractions of the different model components. The actual sludge age of the system was 4.1 days.

PARAMETER	*SYMBOL*	*VALUE*	*UNITS*
TOTAL INFLUENT LOADINGS (Unfiltered)			
COD		255	mg COD L-1
TKN		13.3	mg N L-1
P		11.0	mg P L-1
S		2.3	mg S L-1
WASTEWATER FRACTIONS			
Phenolics	fph	0.11	g COD g^{-1} COD
Volatile organics	fv	0.22	g COD g^{-1} COD
Hydrocarbons	fch	0.14	g COD g^{-1} COD
Mixed organics	fm	difference	g COD g^{-1} COD
Enmeshed organics	fenm	0.07	g COD g^{-1} COD
Unbiodegradable soluble COD	fus	0.13	g COD g^{-1} COD
Unbiodegradable particulate COD	fup	0.02	g COD g^{-1} COD
Ammonia fraction of TKN	fnh	0.85	g N g^{-1} N
Reduced sulphur of influent S	fsr	1.0	g S g^{-1} S

Figure 4.5(a) illustrates the comparison of the observed effluent COD and the model predictions at the 5 day SRT operating condition. The model provided excellent predictions of the level of the COD measured in the effluent, although the shape of the response in the model system was slightly more dramatic than in the actual system. The

model predicted a slight increase in effluent COD during the feed period due to a minor accumulation of soluble phenolics and mixed COD which were not degraded during the short residence time in the system. This was not observed in the actual system. The laboratory system showed no increase in effluent COD indicating that the model provided conservative estimates of these values. The difference between the model and the observed results was minimal, but it is advantageous to have any discrepancy on the conservative side.

The oxygen utilization rate response of the system during a 24 hour feed period is illustrated in Fig. 4.5(b). In general terms, model predictions accurately followed the actual OUR response of the system and predicted the total oxygen utilized in the degradation process. However, the OUR was slightly underestimated during the feed period and overestimated upon termination of the feed wastewater. The model predicted the sharp increase in oxygen consumption in the reactor immediately upon receiving wastewater, where it remained at a peak utilization rate until the feed was terminated. At this time, there was a sharp decrease in both the model predictions and observed values of OUR. Both the model and the actual system produced the "shoulder" effect which corresponded to the completion of the nitrification process to a pre-feed concentration. This "shoulder" phenomena was described in Baker (1993) as the utilization of ammonia accumulated in the reactor during the high feed rate period. Therefore, the nitrifiers continued to oxidize the remaining ammonia after the feed stopped. Once the accumulated ammonia was utilized, the OUR dropped to endogenous levels.

The nitrogen components of the modelled system are illustrated in Figs. 4.5(c) and 4.5(d) and were consistent with this "shoulder" response in the OUR curve. The TKN increased over the feed period and then dropped off, while the nitrate concentration essentially was the mirror image. From this response, it is evident that during the 12 hour feed period, ammonia (NH_3) entered faster than it could be utilized. This resulted in an accumulation of TKN and indicated that the nitrification rate was insufficient to handle the ammonia loading. From the start of the feed period to the finish there must be an increase in Z_{BN} concentration because the rate of accumulation decreased. When the feed stopped, the ammonia was converted to nitrate, and the soluble organic nitrogen was converted to ammonia and then to nitrate. The apparent decrease in nitrate concentration during feed period was a result of dilution of the nitrate compounds present in the reactor due to incoming flow.

The actual concentration of nitrate predicted by the model was slightly higher (1.0 mg N/L) than observed results. This may partially be a result of neglecting to specify the unbiodegradable fraction of organic nitrogen in the influent wastewater. If the unbiodegradable fraction is not quantified in the model then the ammonification reaction proceeds at its assigned rate and will convert organic nitrogen into ammonia which cannot actually be ammonified in the experimental system. The result is more ammonia being nitrified than is present in the laboratory system. This would account for the overestimate of the nitrate concentration observed from the model. In summary, however, the model was successful at predicting the nitrification kinetics of the 5 day SRT system operating under dynamic conditions.

Finally, the volatile suspended solids of the experimental system were accurately predicted by the model and are illustrated in Fig. 4.5 (e). The model estimates are slightly higher than the measured VSS concentrations, but are within 13 percent. The high volatile COD fraction in the influent suggests that this data set was sensitive to the volatilization process. The problems discussed earlier with quantifying this fraction and its behaviour may contribute to this error. For example, unaccounted VOC loss from the experimental system would result in model predictions which overestimated actual measurements.

There was an apparent decrease in VSS in the laboratory reactor during the feed period. This was due to a limitation in the hydraulics of the laboratory setup. Taking this phenomena into account the model provided reasonable estimates of the measured VSS in the reactor during dynamic flow conditions in a 5 day SRT system.

In summary, the model was successful at predicting the response of the activated sludge system while operating under a short sludge age (5 day SRT) and dynamic loading conditions.

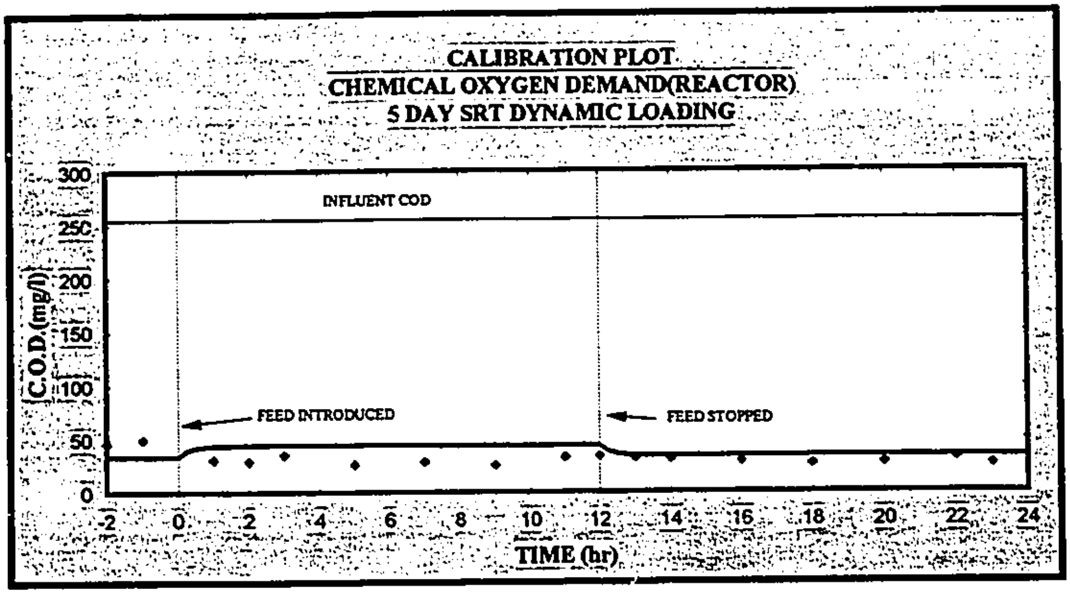

Figure 4.5(a) Comparison of Model Predictions of Reactor Chemical Oxygen Demand with Observed Experimental Values for 5 Day SRT Dynamic Loading System.

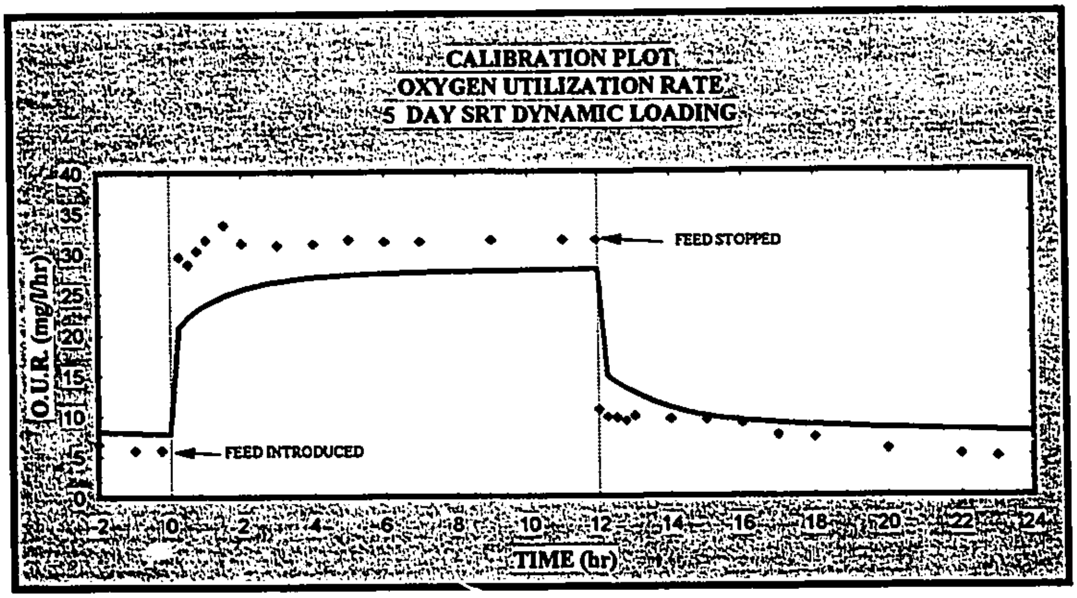

Figure 4.5(b) Comparison of Model Predictions of Oxygen Utilization Rate with Observed Experimental Values for 5 Day SRT Dynamic Loading System.

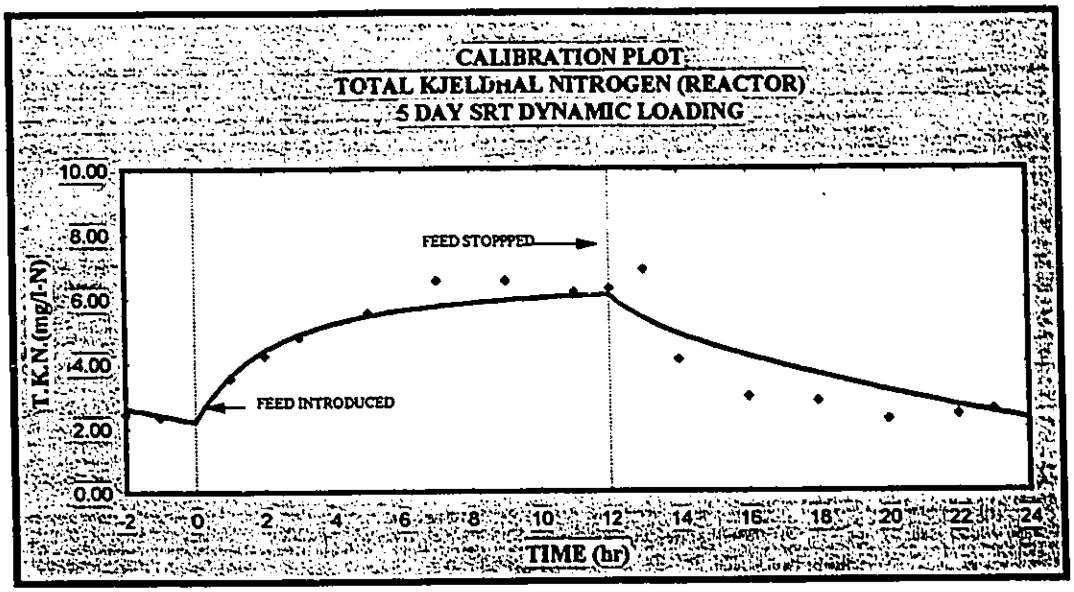

Figure 4.5(c) Comparison of Model Predictions of Reactor Total Kjeldahl Nitrogen Concentration with Observed Experimental Values for 5 Day SRT Dynamic Loading System.

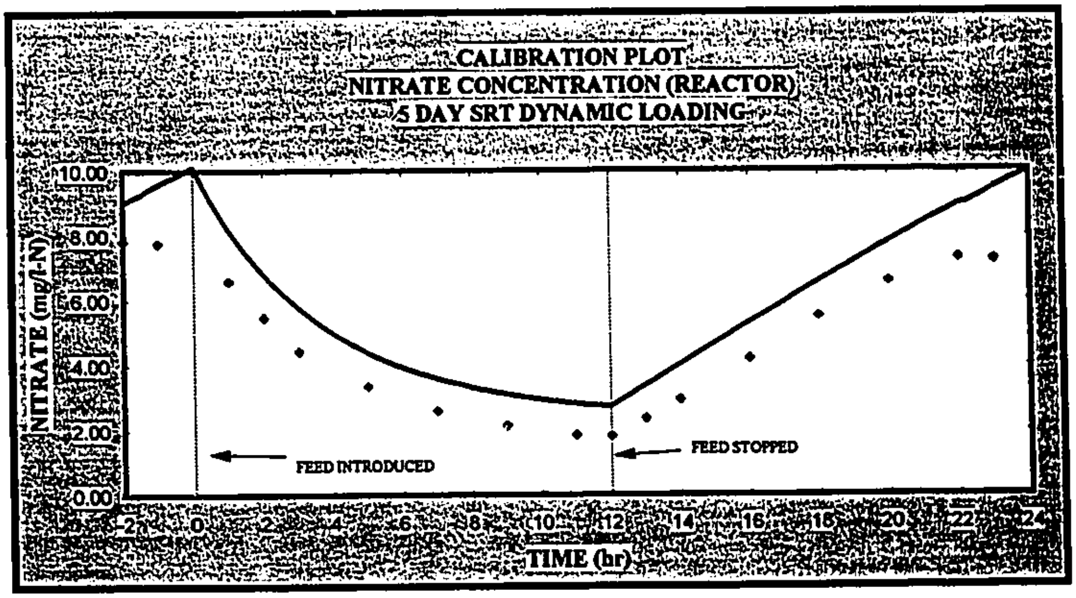

Figure 4.5(d) Comparison of Model Predictions of Reactor Nitrate Concentration with Observed Experimental Values for 5 Day SRT Dynamic Loading System.

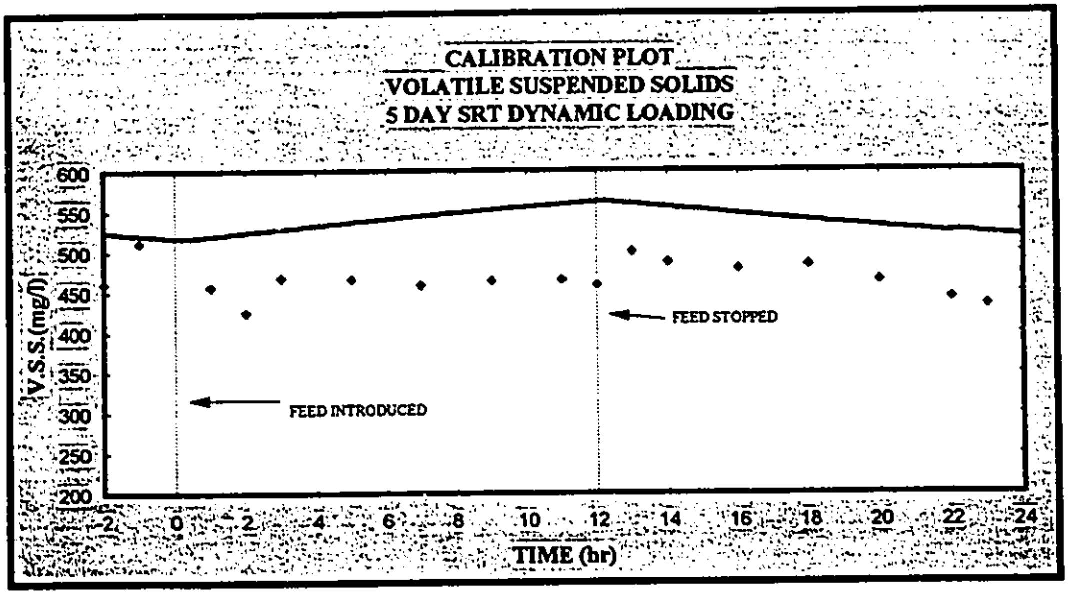

Figure 4.5(e) Comparison of Model Predictions of Volatile Suspended Solids Concentration with Observed Experimental Values for 5 Day SRT Dynamic Loading System.

4.5.2 20 Day Sludge Retention Time

The influent characteristics of the wastewater used for the 20 day SRT dynamic loading experiment are tabulated in Table 4.8. Using these influent characteristics, model predictions were generated and compared with the actual values observed in the laboratory. The comparisons are illustrated graphically in Figs. 4.6 (a)-(e). Again, the start and finish of the feed period is indicated on each graph.

The model provided excellent predictions of the effluent COD measured in the activated sludge system operating at a nominal sludge age of 20 days under dynamic flow conditions as illustrated in Fig. 4.6 (a). There was a very slight increase in effluent COD predicted in the response of the model which was not apparent in the actual system, but the difference was insignificant. Figure 4.6 (a) also illustrates the success of the system in removing the majority of the COD in the influent wastewater.

Table 4.8: Characteristics of the petroleum refinery influent wastewater for the 20 day SRT system operating under dynamic loading conditions. The total loadings of COD, TKN, phosphorus, and sulphur compounds are listed along with the fractions of the different model components. The actual sludge age of the system was 13.3 days.

PARAMETER	*SYMBOL*	*VALUE*	*UNITS*
TOTAL INFLUENT LOADINGS (Unfiltered)			
COD		260	mg COD L-1
TKN		14.0	mg N L-1
P		11.0	mg P L-1
S		2.3	mg S L-1
WASTEWATER FRACTIONS			
Phenolics	fph	0.11	g COD g^{-1} COD
Volatile organics	fv	0.15	g COD g^{-1} COD
Hydrocarbons	fch	0.14	g COD g^{-1} COD
Mixed organics	fm	difference	g COD g^{-1} COD
Enmeshed organics	fenm	0.07	g COD g^{-1} COD
Unbiodegradable soluble COD	fus	0.14	g COD g^{-1} COD
Unbiodegradable particulate COD	fup	0.02	g COD g^{-1} COD
Ammonia fraction of TKN	fnh	0.85	g N g^{-1} N
Reduced sulphur of influent S	fsr	1.0	g S g^{-1} S

Figure 4.6(b) illustrates the accuracy of the model in predicting the oxygen utilization rate of this system during dynamic inflow conditions. When the system began to receive feed, the OUR measured in the laboratory system and the model predictions of OUR increased immediately to a maximum level. At the termination of feed, both model and observed values dropped precipitously to about 50 percent of the maximum OUR. This was followed by a short "shoulder" effect to account for the completion of the nitrification kinetics, and finally the small slow drop in the OUR to endogenous levels. The model predicted the experimental system very accurately although the final endogenous OUR was a couple of milligrams per litre higher than the observed value. The shape and maximum OUR levels were extremely well estimated by the model.

The nitrogen components of the 20 day SRT system operating under dynamic flow conditions were predicted reasonably well by the model. The shape of the dynamic response curve produced by the model for both the reactor TKN and nitrate concentrations followed the actual system response very closely. The reactor TKN concentration only rose a couple of milligrams per litre in both the model and laboratory systems indicating the ability of the 20 day system to assimilate large changes in influent conditions without hindering system performance. Alternatively, the reactor nitrate concentration decreased during the feed period due to: (1) the hydraulic impacts mentioned during analysis of the system operating at a 5 day SRT, and (2) the inability of the nitrification system to utilize the excess ammonia levels in the system. As soon as the feed was terminated, however, the nitrate concentration gradually increased back to original pre-feed levels.

Despite the shape of the model TKN and nitrate concentration response curves matching the experimental results, the actual predicted values were off by 1 mg/L-N. As mentioned briefly during the analysis of the 5 day SRT dynamic loading system, this may be due to the fact that the fraction of unbiodegradable organic nitrogen in the influent was not specified. The model structure does not consider the unbiodegradable portion of organic nitrogen in the influent since it was assumed that the soluble unbiodegradable fraction would pass directly through the system and be measured in the influent and effluent as TKN, and the particulate unbiodegradable fraction would become enmeshed in the biomass and exit from the system in the waste sludge. In either case the unbiodegradable TKN would appear to have negligible impact on the nitrogen kinetics of the system. When this fraction is not quantified, however, there is the potential that the ammonification process in the model will convert organic nitrogen to ammonia which is not actually available in the experimental system. The excess ammonia subsequently is nitrified to nitrate. If this occurs, the nitrate concentration in the reactor would be overestimated and the TKN concentrations would be underestimated in the model predictions. This seemed to be the case with the 20 day SRT operating system and supports the inclusion of this fraction in the influent wastewater characteristics. The discrepancies between the model and observed values of TKN and nitrate which resulted from this model inadequacy were relatively small, however.

The final parameter, which was compared to establish the success of the model, was the volatile suspended solids in the reactor. The results are illustrated in Fig. 4.6(e). The model accurately predicted the VSS concentration measured in the reactor if the affects of the hydraulics in the clarifier were taken into account. This indicated that the model accurately predicted the sludge production in this system and when combined with the excellent results for the oxygen utilization rate supported the selection for the cell yield on mixed COD of 0.555 g cell COD per g COD utilized.

In summary, the calibrated model compared well to the observed response of a system operating at a sludge age of 20 days and under dynamic influent flow conditions. The shape of the response curves generated by the model accurately reproduced the measured results, and the actual concentrations of the parameters agreed well with observed values.

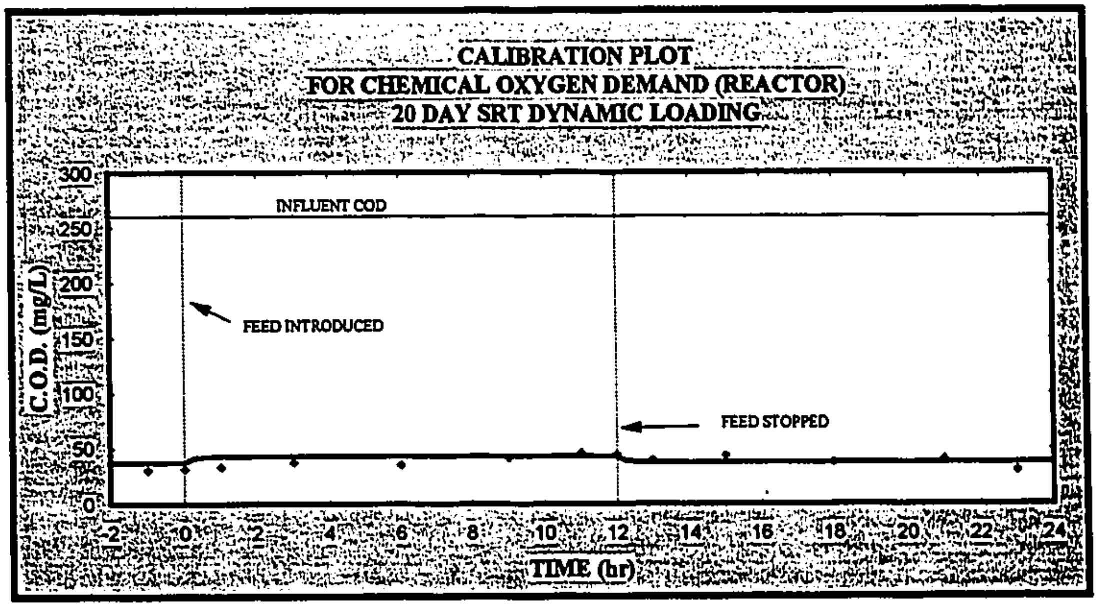

Figure 4.6(a) Comparison of Model Predictions of Reactor Chemical Oxygen Demand with Observed Experimental Values for 20 Day SRT Dynamic Loading System.

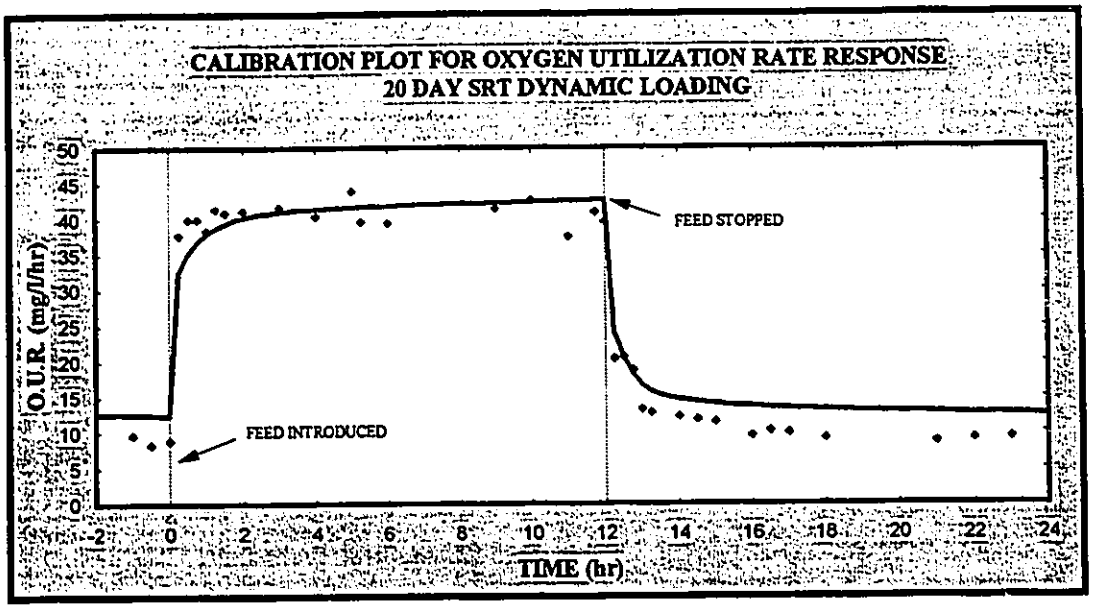

Figure 4.6(b) Comparison of Model Predictions of Oxygen Utilization Rate with Observed Experimental Values for 20 Day SRT Dynamic Loading System.

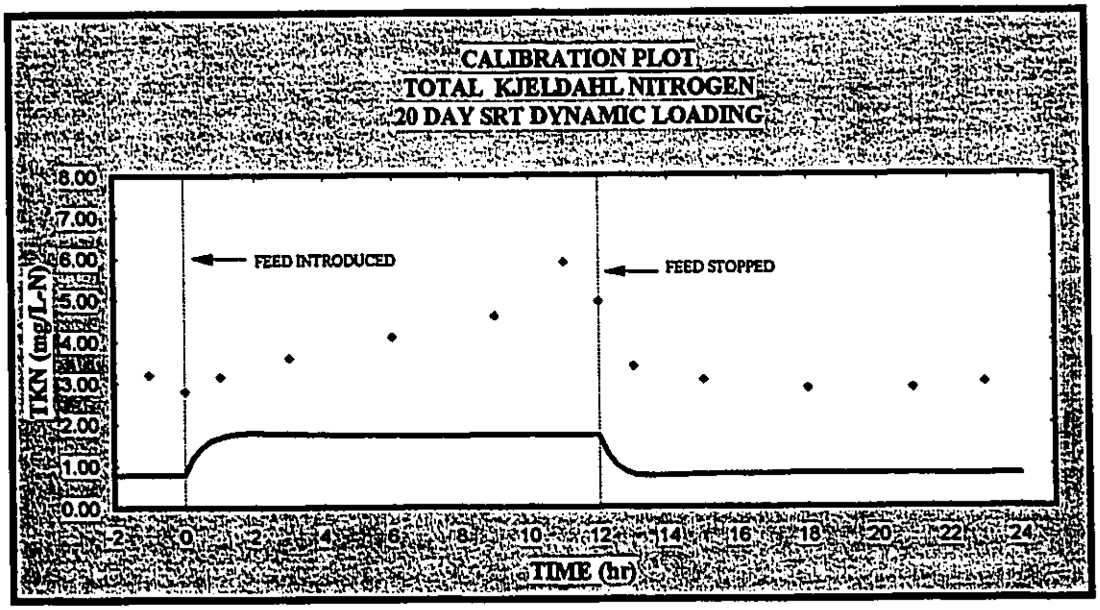

Figure 4.6(c) Comparison of Model Predictions of Reactor Total Kjeldahl Nitrogen Concentration with Observed Experimental Values for 20 Day SRT Dynamic Loading System.

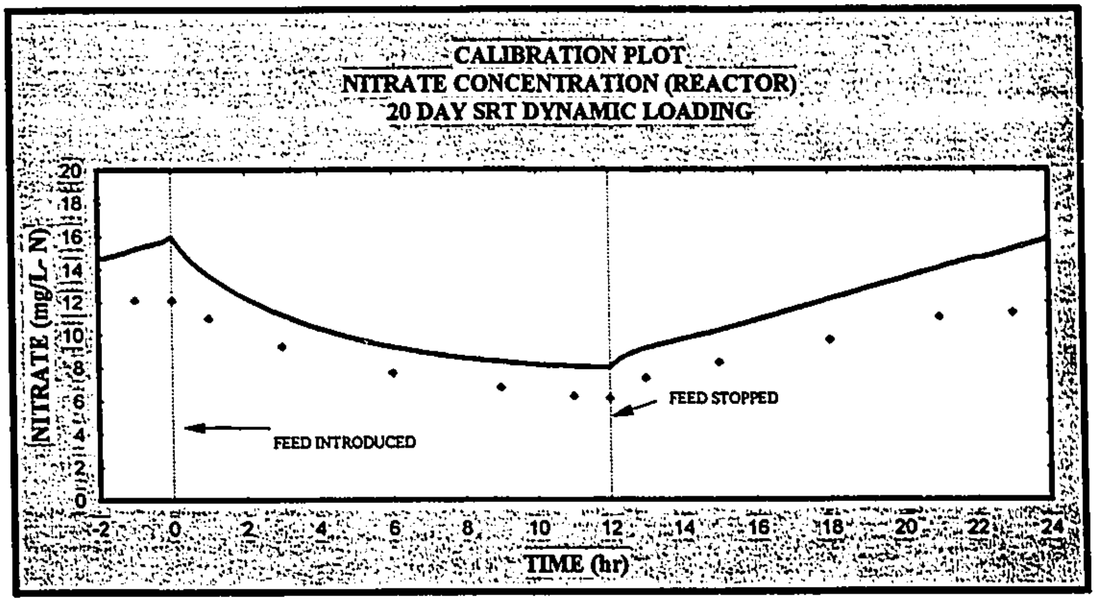

Figure 4.6(d) Comparison of Model Predictions of Reactor Nitrate Concentration with Observed Experimental Values for 20 Day SRT Dynamic Loading System.

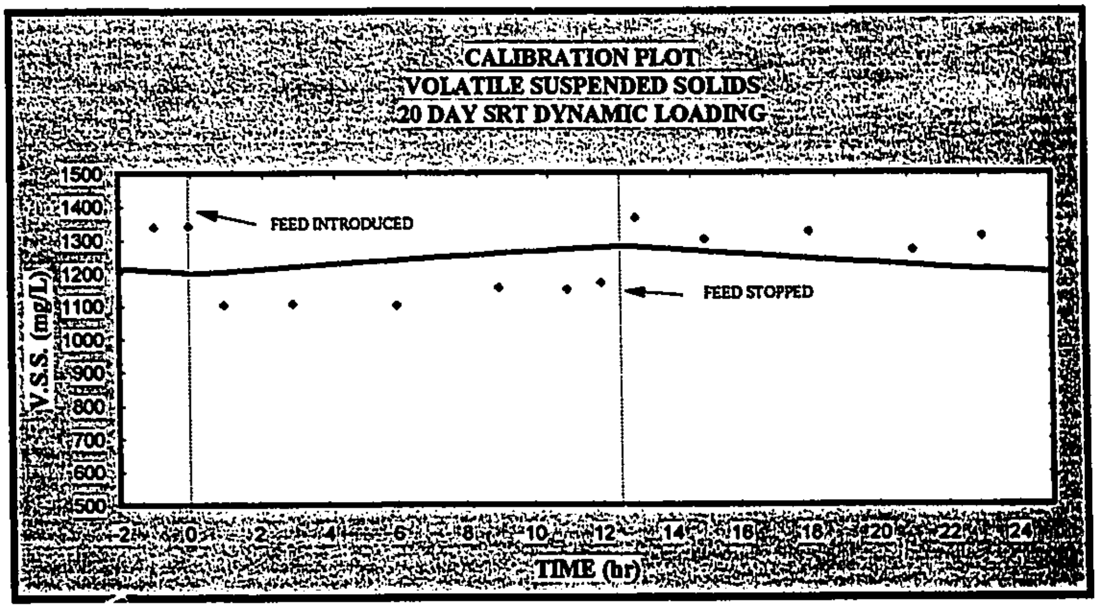

Figure 4.6(e): Comparison of Model Predictions of Volatile Suspended Solids Concentration with Observed Experimental Values for 20 Day SRT Dynamic Loading System.

4.6 SUMMARY OF MODEL CALIBRATION

In the above discussion the behaviour of a laboratory-scale activated sludge system treating petroleum refinery wastewater was used to calibrate the model coefficients in the mechanistic model described in Chapter 3. The operation of the laboratory scale activated sludge system provided the data necessary to complete the calibration. The results of the calibration procedure were used to simulate the model in order to compare model predictions to observed behaviour of the petroleum refinery activated sludge systems operated under constant and dynamic flow conditions and at different sludge ages (5, 10, and 20 day SRT). The model predictions agreed well with the observed behaviour. As a result, a model is available that can be used as a tool to understand better the behaviour of an actual petroleum refinery activated sludge plant and assist operations staff in optimizing the operation of their system.

This chapter has shown model fits for various systems operating at different sludge ages, and under constant and dynamic loading conditions. For any one system adjustments to the model parameters could be made to force a very close fit. However, the objective has been to determine a single set of stoichiometric and kinetic parameters which would provide at least a reasonable fit for all experimental systems.

CHAPTER 5

MODEL DEVELOPMENT FOR AN ACTIVATED SLUDGE SYSTEM TREATING PETROCHEMICAL WASTEWATERS

5.1 INTRODUCTION

The objective of this portion of the study was to develop a dynamic mechanistic model for predicting the behaviour of an activated sludge system operating at a petrochemical facility. Using the model framework developed in Chapter 3 for treatment of petroleum refinery wastewaters, a model which describes an activated sludge system treating petrochemical wastewaters was developed. The aim of this approach was to illustrate that the model developed for petroleum refinery wastewaters can be adapted to a petrochemical system with relatively minor modifications. As described earlier, the rationale was as follows. Since petroleum and petrochemical refineries are involved in the production of a variety of products from the same original feedstock, it was expected that the wastewaters from these systems would comprise a similar spectrum of chemical compounds. The similarities in chemical properties of these various compounds suggested that the removal mechanisms which control system behaviour should be similar for each system. As a result, the model structure developed using a petroleum refinery system should be applicable provided the characteristics of the new wastewater are quantified. Therefore, only limited experimentation should be required to obtain the data necessary to calibrate the model for the particular system of concern rather than the extensive experimentation needed for initial model development. This approach was applied using wastewater generated at the petrochemical facility at Sarnia, Ontario and is described in the following two chapters.

This chapter presents the modifications required to adapt the activated sludge model treating petroleum refinery wastewaters to a form which describes the behaviour of the petrochemical system. The components which must be included in the model and the removal mechanisms which apply to these compounds are identified. The resulting mechanistic model is presented in the matrix format described during development of the petroleum refinery activated sludge model in Chapter 3. In order to simulate the overall behaviour of the wastewater treatment scheme, the mechanistic model of the activated sludge system treating the petrochemical wastewater then was incorporated in a computer simulation package called the General Purpose Simulator (GPS-X^{TM}). This element of model development enabled the model to be calibrated using the behaviour of the full-scale system, supplemented with the results of limited experimentation. The experimental program and the calibration procedure of the model is discussed in Chapter 6.

5.2 IDENTIFICATION OF MODEL COMPONENTS AND PROCESSES FOR AN ACTIVATED SLUDGE SYSTEM TREATING PETROCHEMICAL WASTEWATERS

The same steps were required to develop the model of the activated sludge system treating petrochemical wastewaters as required to develop the model of the petroleum refinery application i.e. a series of compounds had to be identified as key to the particular activated sludge system, and a set of rate equations representing the transformations of these compounds within the system needed to be identified. However, the development of the petroleum refinery model simplified the procedure significantly for the petrochemical case since the removal mechanisms in petroleum refinery systems are similar. This simplified the mathematical formulation of the model. The key modifications involved the identification of the components which are important in the petrochemical system and identification of the mechanisms associated with the particular compound or group of compounds. Using the model developed for the petroleum refinery system as a basis, development of the model for the activated sludge system treating the petrochemical wastewaters is described below.

5.2.1 Components Incorporated in the Petrochemical Model

The first stage in developing the model of the petrochemical system was to identify the components present in the petrochemical wastewater and the organisms involved in the biological treatment process. Characterization of the petroleum refinery wastewater provided insight into the types of compounds to expect. For example, phenolics, volatile organic compounds, hydrocarbons, and reduced sulphur compounds tend to be characteristic of most petroleum related wastewaters. These were included in development of the activated sludge model treating petrochemical wastewaters. Certain specific compounds which dominated the behaviour of this petrochemical system also needed to be included in the model and now are identified. The nature of the influent compounds is reflected in the types of organisms growing in the system.

In order to determine the components to include in the model, a thorough analysis of the full-scale wastewater treatment system at the petrochemical site was conducted. This involved consideration of the six different streams entering the plant, each differing in composition and strength. Monitoring programs performed by the plant personnel provided extensive data on the operation of this facility and the types of compounds treated. In general, wastewater input streams to the petrochemical activated sludge plant consist largely of organic carbon in the form of a particular alcohol compound, phenolics, volatile organics, a particular aliphatic amine, and various other hydrocarbons and mixed organic compounds.* Nitrogen input to the system is principally that associated with the amine and low concentrations of free ammonia. Biomass in the system is composed of heterotrophs growing on the organic inputs, and nitrifiers which convert influent ammonia to nitrate.

Before identifying the specific compounds and groups of compounds included in the model, the model notation is briefly restated. As established during development of the petroleum refinery model, biomass components are represented by the symbol Z_i, soluble components in the model are identified by the symbol S_i and the particulate components

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* Due to proprietory information the identification of the alcohol compound and the aliphatic amine must remain confidential. The compounds referred to in developing the model refer to two specific forms of these compounds. Therefore, one must not assume automatically that the kinetics associated with these two compounds refer to the general groups of compounds. For purposes of discussion the compounds will be referred to as alcohol P and aliphatic amine P to denote that the compounds refer to the two forms specifically found in this petrochemical treatment system.

by the symbol X_i. Subscripts are utilized to identify different components. The concentrations of the model components are expressed in units of "mg/L". For the different components the following mass basis was used:

Soluble organic components	COD
Particulate organic/biomass components	COD
Nitrogen-containing components	Elemental N
Sulphur-containing components	Elemental S

Conversion factors (COD/VSS ratio) are used to convert measurements of volatile solids in terms of "mg VSS/L" to equivalent units of "mgCOD/L." The ratios were measured experimentally.

5.2.1.1 Biomass Components

The types of reaction occurring in the petrochemical system indicated that two major types of organism needed to be included in the model. Heterotrophic organisms (Z_{BH}) are the main component of the biomass since they result from growth on the COD in the influent. The system also has the potential to nitrify, so nitrifiers (Z_{BN}) were included in the model. Unlike the petroleum refinery application, sulphur oxidizers were not found to be significant in treatment of this particular petrochemical wastewater.

Along with these active biomass components, a component associated with the decay processes also was included in the model. As described in the petroleum refinery model decay of organisms results in an endogenous mass which cannot be degraded further, but contributes to the volatile solids concentration in the reactor. This endogenous mass is represented by the symbol Z_E. These three classifications constitute the biomass components of the model.

5.2.1.2 Organic Components

The organic component of the petrochemical wastewater consists of a composite mixture of many different carbon compounds. Due to the large number of compounds present, a bulk parameter such as COD was essential for quantifying the organic components. Within the total influent COD, however, a number of different components needed to be monitored in order to determine the overall response of this particular system. As shown in Fig. 5.1, the first classification involved dividing the COD into biodegradable and unbiodegradable portions. Within each division further fractionation into various soluble and particulate components was necessary. This characterization of the total influent COD was based on five factors: (1) experience gained during development of the petroleum refinery activated sludge model, (2) measurements on the influent wastewater on-site at the petrochemical treatment facility; (3) experience gained during plant operation; (4) experience gained during environmental monitoring programs; and (5) an interest or need to track the fate of specific compounds (or related groups of compounds) in the system e.g. phenolics.

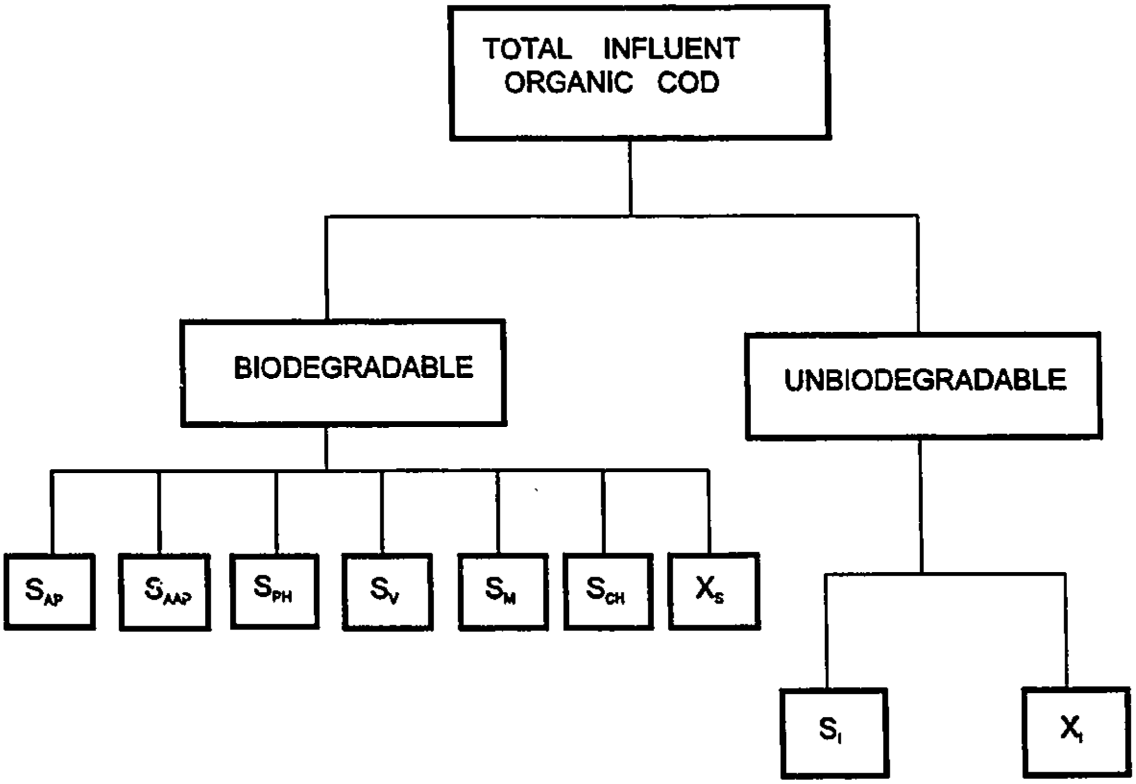

Figure 5.1: Petrochemical Refinery Wastewater Characterization of the Total Influent Organic Chemical Oxygen Demand (COD).

Six groups of biodegradable soluble organic COD were incorporated into the petrochemical activated sludge model.

Alcohol P COD (S_{AP}): One of the processing trains at the petrochemical refinery generates a waste stream which contains high concentrations of an alcohol compound. This stream consists almost solely of this particular contaminant. In order to ensure that the activated sludge system removes this compound, it was important that a model of the system incorporated the alcohol as a model component in order to track its fate. Due to proprietary information the exact alcohol compound cannot be identified so it will be referred to as "alcohol P" to indicate that it is specific to this petrochemical system.

Aliphatic amine P COD (S_{AAP}): This contaminant also was identified by plant personnel as an important indicator of system performance. During one of the refining processes, there is the potential for discharge of significant concentrations of this contaminant to the wastewater treatment plant. With the possibility of increased effluent COD concentration during these spills, it was important to track changes in concentration in the system. Since there is nitrogen associated with the amine which hydrolyses to ammonia, there also was the potential for increased ammonia levels in the effluent during these spills. Due to these concerns, this compound was included in the model as a component to be monitored. Again, due to proprietary information the exact amine compound cannot be identified so it will be referred to as "aliphatic amine P" to indicate that it is specific to this petrochemical system.

Phenolic COD (S_{PH}): This particular petrochemical treatment facility treats an off-site source of phenolics which is extremely concentrated (>150 000 mg/L), although the flowrate is very low. Such a concentrated stream of phenolics may have inhibitory impacts on the activated sludge system if dilution with other influent streams is not sufficient to reduce the concentration to below the inhibitory levels. As a result, phenolics potentially can influence system behaviour significantly and needed to be included in the model.

Volatile organic COD (S_V): As indicated in the development of the petroleum refinery model, volatile organic compounds have significant influences on the behaviour of the activated sludge plant if present in sufficient quantities. VOC's contribute to the air emissions from a treatment plant, and in so doing reduce the organic material which is available for degradation. Therefore, the rate at which these compounds volatilize from the system influences the oxygen consumption and the mass of organisms generated. In the petrochemical facility, the concentration of volatile organic compounds was significant and warranted inclusion as a model component.

Soluble hydrocarbon COD (S_{CH}): Since the petrochemical facility processes derivatives of crude oil, it was expected that hydrocarbon COD is present in these wastewaters. Development of the petroleum refinery model identified the significance of these compounds on system behaviour. To review briefly, these compounds tend to be large molecules which must be hydrolysed prior to use by the microorganism. Therefore, it was hypothesized that the hydrocarbon COD in the soluble form (S_{CH}) was adsorbed onto the sludge to generate a particulate form of hydrocarbon COD (X_{CH}). This adsorbed material is hydrolysed and used for growth processes. As a result of these removal processes the hydrocarbon COD behaves like slowly biodegradable COD which influences the oxygen consumption pattern in the system. Furthermore, like the petroleum refinery case, influent oils and greases have a significant impact on the settleability of the sludge. Monitoring the changes in concentration of these compounds, therefore, is important for predicting a number of system characteristics and was included in the petrochemical refinery model.

Mixed substrate soluble COD (S_M): The mixed COD component was included to account for all the compounds present in the wastewater in small concentrations. It provides a bulk model component where compounds which do not require individual attention can be included in order to determine their overall influence on system behaviour.

These six categories of biodegradable soluble COD constitute the majority of the influent COD. However, to completely specify the influent COD a slowly biodegradable particulate COD (X_S) component must also be included, as well as two unbiodegradable COD components (S_I and X_I). These components serve the same purpose identified in the petroleum refinery model.

These influent components selected for modelling the petrochemical activated sludge system vary only slightly from the petroleum refinery influent characterization. The addition of two specific components groups was necessary, however, to complete the characterization for this system. By including these subgroups the behaviour of the system was described more accurately. This illustrates that development of the petroleum refinery model (Chapter 3) assisted in successfully identifying the main sub-groups in this system.

Figure 5.1 illustrates the breakdown of the influent into these fractions. The actual values of these various components were determined for the influent wastewater streams during the experimental stage of the project.

5.2.1.3 Nitrogen Components

Five different nitrogen components needed to be considered in the petrochemical activated sludge system. The total influent TKN was divided into two main groups : (1) ammonia nitrogen (S_{NH}), and (2) organic nitrogen (TKN). The organic nitrogen fraction was broken down further into three other forms of nitrogen. These were soluble organic nitrogen (S_{ON}), the nitrogen associated with the aliphatic amine (S_{AAP}), and particulate organic nitrogen (X_{ON}) as shown in Fig. 5.2. Nitrate nitrogen (S_{NO}) also needed to be included in the model to track any nitrification occurring in the system.

The incorporation of both the particulate organic nitrogen and the aliphatic amine as nitrogen sources was identified by analysis of the influent characteristics. These two components were neglected in the development of the petroleum refinery model as they were assumed to be negligible in that situation. For the petrochemical refinery situation this was not the case.

The ammonia nitrogen serves as a source of nitrogen for the growth of biomass, and as substrate for the autotrophic organisms (nitrification by nitrifiers). Any organic nitrogen in the wastewater was assumed to be hydrolysed to ammonia nitrogen before being utilized. For the case of particulate organic nitrogen (X_{ON}), it was assumed that the particulate form of the nitrogen was converted to the soluble form (S_{ON}) before being ammonified.

The remaining classification of nitrogen, nitrate, was incorporated as a model component to account for nitrate production during nitrification within the reactor. As discussed in the petroleum refinery model development, the nitrate concentration was assumed to consist of both nitrite and nitrate. Since the conversion of ammonia to nitrite is normally considered to be the rate limiting step in nitrification, a single reaction to the nitrate form was assumed with negligible impact on the accuracy of the model.

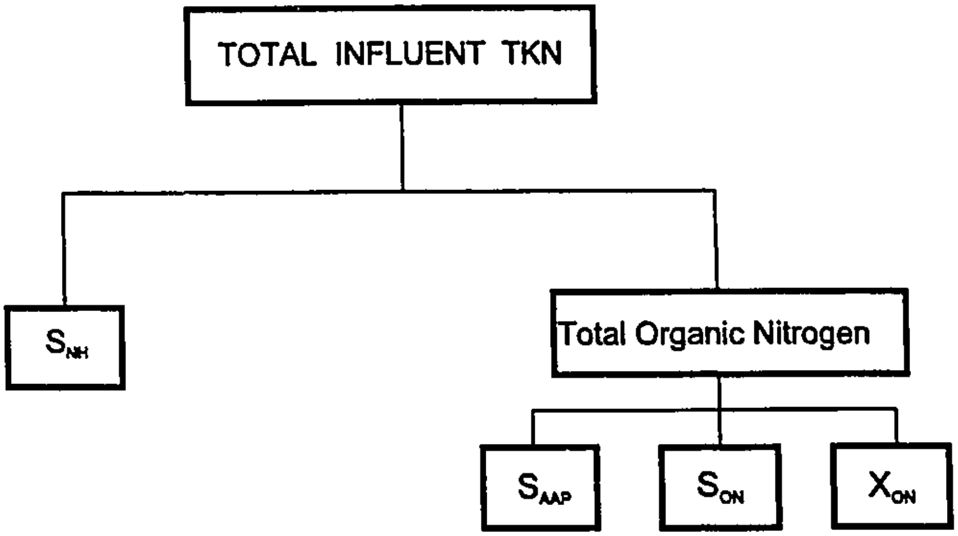

Figure 5.2: Petrochemical Refinery Wastewater Characterization of the Influent Total Kjeldahl Nitrogen (TKN).

5.2.1.4 Sulphur Components

Sulphur compounds were identified by the personnel at the petrochemical facility as important compounds in determining system behaviour. Again, this was a result of the potential impact on the oxygen utilization rate in the activated sludge system. In this situation, sodium meta-bisulphite is added during the refining process as an oxygen scavenger. Any residual compound was removed in the activated sludge system. However, unlike the petroleum refinery application where reduced sulphur compounds were biologically oxidized, it was assumed that any reduced sulphur in this petrochemical influent was chemically oxidized to sulphate in the activated sludge process. This involved a minor modification to the mathematical equations in the activated sludge model, but confirmed the importance of sulphur oxidization as a removal process.

Two types of sulphur species were considered; these were reduced sulphur species (S_{SR}) and sulphate sulphur (S_{SO}) as shown in Fig. 5.3. Any sulphate in the influent was assumed to pass through the system unchanged.

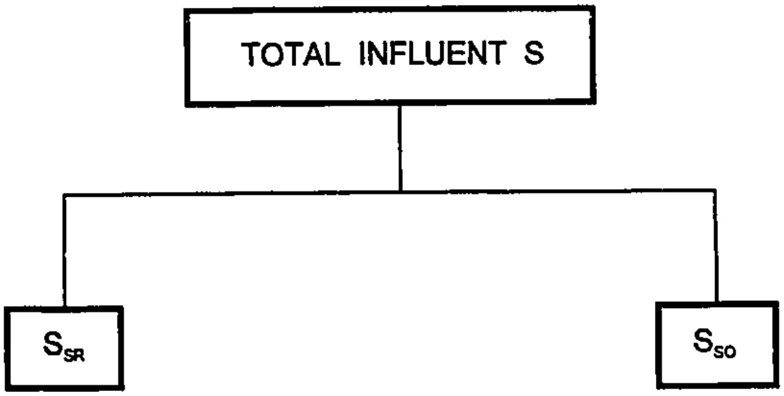

Figure 5.3: Petrochemical Refinery Wastewater Characterization of the Total Influent Sulphur Compounds.

5.2.1.5 Miscellaneous

As described in the development of the petroleum refinery model, phosphorus is required for the synthesis of organism mass in the growth process. However, some form of phosphorus must often be added to these systems due to a deficiency of this nutrient for growth processes. On the other hand, the system is required to meet certain regulatory standards of this compound so it is important not to add excess phosphorus. Monitoring the levels of phosphorus in these systems, therefore, is important. As a result, soluble phosphate (S_P) was included in the petrochemical model.

One other important component specified in the model was the dissolved oxygen concentration, S_O. As indicated earlier it represents the concentration of oxygen in the reactor which is often controlled by the operator rather than being internally regulated by the activated sludge process itself. The main advantage of including the oxygen term in the model is that it allows the oxygen utilization rate (OUR) to be determined.

Table 5.1 lists the 21 components incorporated in the model, together with symbols and units.

Table 5.1: Definition of Component Symbols in the Petrochemical Model

COMP.	SYMBOL	DEFINITION	UNITS
1	Z_{BH}	Active heterotrophic biomass	g cell COD m^{-3}
2	Z_{BN}	Active nitrifier biomass	g cell COD m^{-3}
3	Z_E	Endogenous mass	g COD m^{-3}
4	X_S	Slowly biodegradable substrate	g COD m^{-3}
5	X_{CH}	Adsorbed hydrocarbon substrate	g COD m^{-3}
6	X_I	Particulate unbiodegradable matter	g COD m^{-3}
7	X_{ON}	Particulate organic nitrogen	g N m^{-3}
8	S_{AP}	Alcohol from Petrochemical facility	g COD m^{-3}
9	S_{AAP}	Aliphatic amine (P)	g COD m^{-3}
10	S_{PH}	Phenolic biodegradable soluble COD	g COD m^{-3}
11	S_V	Volatile organic COD	g COD m^{-3}
12	S_M	Mixed substrate soluble COD	g COD m^{-3}
13	S_{CH}	Soluble hydrocarbon COD	g COD m^{-3}
14	S_{NH}	Ammonia nitrogen	g N m^{-3}
15	S_{ON}	Soluble organic nitrogen	g N m^{-3}
16	S_{NO}	Nitrate nitrogen	g N m^{-3}
17	S_{SR}	Reduced sulphur	g S m^{-3}
18	S_{SO}	Sulphate	g S m^{-3}
19	S_P	Soluble phosphate	g P m^{-3}
20	S_I	Unbiodegradable soluble substrate	g COD m^{-3}
21	S_O	Oxygen	g (-COD) m^{-3}

5.2.2 Processes Incorporated in the Petrochemical Model

There are a number of different processes occurring within the activated sludge system treating petrochemical wastewaters. As identified during development of the model for petroleum refinery wastewaters, many of the processes are biological in nature while others are classified as physicochemical processes. This section identifies the processes included in the activated sludge model treating wastewaters from the petrochemical refinery and associates the mechanism with a particular compound of interest. The form of the equations used in the model to represent each of the processes is described. Generally, these equations are the same as those outlined in the petroleum refinery model although some adaptation was required to formulate equations for the additional groups of compounds. This procedure confirmed the ability of the petroleum refinery model to be adapted to a different type of petroleum based system once the model components were modified. The mechanistic model is presented in Table 5.2 (three parts). The method of presentation used in Table 5.2 is discussed in Section 5.3.

Aerobic Growth of Heterotrophs: As indicated in Chapter 3, heterotrophic organisms tend to utilize soluble substrate for growth in a similar manner for different types of organic compounds. Differences arise in the rate of growth so the kinetic behaviour which applies to each group of compounds must be determined separately. However, the form of the growth mechanism on alcohol P (S_{AP}), aliphatic amine P (S_{AAP}), volatile organic compounds (S_V), and mixed COD (S_M) was assumed to be the same for each of these forms of COD. The Monod expression was used to model the biological growth on each component. In these equations growth was based on the bulk concentration of COD i.e. mass per unit of system volume of the organic compound of concern. Growth of organisms on mixed COD is given as an example:

$$\rho_7 = \mu_{hM} * \frac{S_M}{K_{sM} + S_M} * Z_{BH} * \text{AirYes} * \text{NH}_3\text{Yes} * \text{PO}_4\text{Yes} \qquad (5.1).$$

Switching functions were attached to the rate equations to reduce the process rate to zero when there is no oxygen present or when the biological growth processes are nutrient (nitrogen and/or phosphorus) limited.

Aerobic Growth of Heterotrophs Treating Phenolic COD (S_{PH}): Growth of heterotrophic organisms under the inhibitory conditions associated with high concentrations of phenolic compounds were identified during the development of the petroleum refinery model. As discussed, the presence of high concentrations of phenolics slows the ability of the organism to degrade the organic. As the concentration of phenolics decreases, the organism growth rate begins to increase again, and at sufficiently low levels growth returns to normal rates. A modified version of the Monod equation called the Haldane equation has been shown to describe this inhibition phenomena effectively (Rozich, 1983, 1985). The Haldane equation was used in the petroleum refinery model structure, and also was used in the petrochemical model to describe the behaviour of heterotrophs treating phenolic compounds (Equation 5.2).

$$\rho_3 = \mu_{hPH} * \frac{S_{PH}}{K_{sPH} + S_{PH} + \frac{S_{PH}^2}{K_I}} * Z_{BH} * \text{AirYes} * \text{NH}_3\text{Yes} * \text{PO}_4\text{Yes} \qquad (5.2).$$

Switching functions were added to the growth expression to force the growth rate to zero in the absence of oxygen or limiting quantities of nitrogen and phosphorus.

Aerobic Growth of Heterotrophs on Hydrocarbon COD (S_{CH}): The fate of the hydrocarbon COD component (S_{CH}) also was handled somewhat differently than growth on soluble COD. Utilization of hydrocarbon COD was represented using the Monod equation, but with growth expressed as a function of the concentration of the hydrocarbon COD adsorbed on the heterotrophic biomass. The surface concentration was estimated as X_{CH}/Z_{BH}. Equation 5.3 represents this growth mechanism:

$$\rho_9 = \mu_{hCH} * \frac{\frac{X_{CH}}{Z_{BH}}}{K_{sCH} + \frac{X_{CH}}{Z_{BH}}} * Z_{BH} * \text{AirYes} * \text{NH}_3\text{Yes} * \text{PO}_4\text{Yes} \qquad (5.3).$$

Switching functions were added to the growth expression to force the growth rate to zero in the absence of oxygen or limiting quantities of nitrogen and phosphorus.

Anoxic Growth of Heterotrophs: Anoxic growth of heterotrophs was not considered in this study, but the anoxic growth equations were included in the model for completeness. The expressions used in the petroleum refinery model were based on expressions developed for the municipal activated sludge systems (Billing and Dold, 1988). Similar equations were applied in the modelling of the petrochemical system and are not repeated here.

Decay of Heterotrophs: Decay of microorganisms in the petrochemical refinery activated sludge model was assumed to be the same as decay in the petroleum refinery model and was modelled using the "death-regeneration" hypothesis (Ekama & Marais, 1980). This assumes a constant decay rate in the reactor with the generation of a fraction ($f_{Ep,H}$) of material which is non-biodegradable and contributes to the endogenous residue (Z_E). The remaining fraction ($1-f_{Ep,H}$) is added to the mass of slowly biodegradable substrate (X_S) already present in the reactor for biological growth. A first order process with respect to the concentration of heterotrophs was assumed in the model for the decay of biomass, where b_H is the overall decay rate:

$$\rho_{11} = b_H * Z_{BH} \qquad (5.4).$$

Hydrolysis of Particulate COD: As described in the development of the petroleum refinery activated sludge model, the small amount of biodegradable particulate COD (X_S) in the petrochemical influent was assumed to be enmeshed in the sludge mass upon entering the reactor. The enmeshed substrate is broken down extracellularly into readily biodegradable mixed soluble substrate (S_M) by enzymes produced by the microorganisms and then utilized for growth. The hydrolysis/solubilization process again was modelled using Levenspiel's surface reaction kinetics theory (Levenspiel, 1972) in a Monod type growth equation represented by the following expression:

$$\rho_{12} = K_H * \frac{\frac{X_S}{Z_{BH}}}{K_X + \frac{X_S}{Z_{BH}}} * Z_{BH} * (\text{AirYes} + \eta_{sol} * \text{AirNo} * \text{NO}_3\text{Yes}) \qquad (5.5).$$

The rate of hydrolysis is based on the surface concentration of particulate COD and is approximated by dividing the concentration of particulate COD (X_S) by the concentration of biomass (Z_B) in the reactor.

Included with the rate equation were switching functions which decrease the hydrolysis rate to zero if there is no oxygen or nitrate in the system, or decrease the rate if only nitrate is available. The assumption here is that not all heterotrophs are capable of hydrolysis under anoxic conditions.

Adsorption of Hydrocarbon COD: Adsorption of hydrocarbon COD (S_{CH}) was included in the model as a separate equation to the hydrolysis and growth equation since the hydrocarbon COD in the influent is effectively soluble. Therefore, it is not enmeshed in the sludge mass directly upon entering the reactor. Rather, it was hypothesized that the hydrocarbon COD is adsorbed on to the biomass which causes it to take on characteristics of particulate matter (X_{CH}). Once adsorbed to the biomass, it is hydrolysed by the enzymes before being utilized for growth.

The adsorption of hydrocarbon onto the biomass was modelled in the same way that was used in the petroleum refinery model format. It was assumed to follow first order kinetics with respect to the bulk concentration of hydrocarbon COD (S_{CH}) in the system and the concentration of heterotrophs (Z_{BH}). The model equation includes a driving force term to account for the decrease in the rate of adsorption as the number of available sites diminishes. This term is expressed as $\{f_{maxCH} - X_{CH}/Z_{BH}\}$. Equation 5.6 represents this mechanism:

$$\rho_{13} = K_A * \left\{ f_{maxCH} - \frac{X_{CH}}{Z_{BH}} \right\} * S_{CH} * Z_{BH} \qquad (5.6).$$

Volatilization of Volatile Organic COD: The volatilization of volatile organics (S_V) from the wastewater was modelled using a first order equation (Equation 5.7) with respect to the concentration of soluble volatile organic COD:

$$\rho_{14} = K_V * S_V \qquad (5.7).$$

This is the same form utilized in the petroleum refinery model. Volatilization of these compounds has been identified in plant operation and was confirmed experimentally to assist in determining rates of volatilization.

Hydrolysis of particulate organic nitrogen: Particulate organic nitrogen (X_{ON}) was assumed to be hydrolysed to soluble organic nitrogen (S_{ON}) in conjunction with the particulate organic compounds (X_S). This was due to the assumption that the particulate organic nitrogen is associated with particulate COD. Therefore, hydrolysis of this particulate matter generates soluble COD and soluble organic nitrogen. To model the rate of soluble organic nitrogen generation, the rate equation for hydrolysis of the particulate COD was multiplied by the ratio of X_{ON} to X_S:

$$\rho_{15} = \rho_{12} * \frac{X_{ON}}{X_S} \qquad (5.8),$$

where ρ_{12} is the expression for hydrolysis of particulate COD (X_S) given in Equation 5.5. Once hydrolysed, the nitrogen contributes to the pool of soluble organic nitrogen to be converted to ammonia.

Ammonification: The conversion of organic nitrogen (S_{ON}) to ammonia (S_{NH}) is referred to as ammonification. Organic nitrogen in the wastewater is converted to ammonia in order to be utilized by the organisms for growth or to undergo nitrification. This reaction is often the limiting step in having sufficient available nitrogen for growth. As indicated in Chapter 3, a first order reaction was used to represent this conversion process:

$$\rho_{16} = K_N * S_{ON} * Z_{BH} \qquad (5.9).$$

Hydrolysis of Aliphatic Amine P: The hydrolysis of aliphatic amine P (S_{AAP}) was assumed to follow a first order reaction with respect to its concentration in the system, and the concentration of heterotrophs. The nitrogen from hydrolysis was added to the total pool of ammonia in the system, and the organic component was added to the pool of mixed COD. Equation 5.10 was used to represent this process:

$$\rho_{17} = K_R * S_{AAP} * Z_{BH} \tag{5.10}$$

Nitrifier Growth: Growth of nitrifiers (Z_{BN}) was represented by Monod kinetics in the manner used for the petroleum refinery model:

$$\rho_{18} = \mu_N * \frac{S_{NH}}{K_{sNH} + S_{NH}} * Z_{BN} * \text{AirYes} * \text{NH}_3\text{Yes} * \text{PO}_4\text{Yes} \tag{5.11}$$

The equation was expressed in terms of the bulk concentration of ammonia in the reactor, and included two switching functions which decrease the organism growth rate to zero if insufficient levels of oxygen and ammonia are present in the system.

Nitrifier Decay: The decay of nitrifiers (Z_{BN}) was assumed to proceed similarly to the decay of heterotrophs. The expression for decay of the nitrifier organisms (Equation 5.12) was represented as a first order rate equation with respect to the concentration of nitrifiers in the system:

$$\rho_{19} = b_N * Z_{BN} \tag{5.12}$$

Sulphur Oxidization: The conversion of reduced sulphur compounds (S_{SR}) in the petrochemical facility was represented as a chemical oxidation process. The process was modelled as a first order reaction with respect to the concentration of reduced sulphur compounds in the influent streams. Equation 5.13 represents this process:

$$\rho_{20} = K_{sR} * S_{SR} * \text{AirYes} \tag{5.13}$$

Each of the processes described above is one of the many reactions occurring within the activated sludge system to remove compounds from the petrochemical wastewater and support growth of the microorganisms. Their kinetic expressions are tabulated on the right hand side of Table 5.2 (ie.Part 3).

Table 5.2: Model Matrix for the Petrochemical Model (Part1).

COMPONENT	1	2	3	4	5	6	7	8	9	10	11	12
PROCESS	Z_{BH}	Z_{BN}	Z_E	X_S	X_{CH}	X_I	X_{ON}	S_{AP}	S_{AN}	S_{PH}	S_V	S_M
1 Aerobic growth of heterotrophs on S_{AP}	1							$\frac{-1}{Y_{hAP}}$				
2 Anoxic growth of heterotrophs on S_{AP}	1							$\frac{-1}{Y_{hAP}}$				
3 Aerobic growth of heterotrophs on S_{PH}	1									$\frac{-1}{Y_{hPH}}$		
4 Anoxic growth of heterotrophs on S_{PH}	1									$\frac{-1}{Y_{hPH}}$		
5 Aerobic growth of heterotrophs on S_V	1										$\frac{-1}{Y_{hV}}$	
6 Anoxic growth of heterotrophs on S_V	1										$\frac{-1}{Y_{hV}}$	
7 Aerobic growth of heterotrophs on S_M	1											$\frac{-1}{Y_{hM}}$
8 Anoxic growth of heterotrophs on S_M	1											$\frac{-1}{Y_{hM}}$
9 Aerobic growth of heterotrophs on X_{CH}	1				$\frac{-1}{Y_{hCH}}$							
10 Anoxic growth of heterotrophs on X_{CH}	1				$\frac{-1}{Y_{hCH}}$							
11 Decay of heterotrophs	- 1		$f_{Ep,H}$	$1 - f_{Ep,H}$								
12 Hydrolysis of X_S				- 1								1
13 Adsorption of S_{CH}					1							
14 Volatilization of S_V											- 1	
15 Hydrolysis of X_{ON}							-1					
16 Ammonification												
17 Hydrolysis of S_{AAP}									- 1			1
18 Nitrifier growth		1										
19 Nitrifier decay		- 1	$f_{Ep,N}$	$1 - f_{Ep,N}$								
20 Chemical SO_3 oxidation												

Table 5.2: Model Matrix for the Petrochemical Model (Part 2).

COMPONENT	13	14	15	16	17	18	19	20	21
PROCESS	S_{CH}	S_{NH}	S_{ON}	S_{NO}	S_{SR}	S_{SO}	S_P	S_I	S_O
1 Aerobic growth of heterotrophs on S_{AP}		$-f_{ZBH,N}$					$-f_{ZBH,P}$		$\frac{-(1-Y_{hAP})}{Y_{hAP}}$
2 Anoxic growth of heterotrophs on S_{AP}		$-f_{ZBH,N}$		$\frac{-(1-Y_{hAP})}{2.86\ Y_{hAP}}$			$-f_{ZBH,P}$		
3 Aerobic growth of heterotrophs on S_{PH}		$-f_{ZBH,N}$					$-f_{ZBH,P}$		$\frac{-(1-Y_{hPH})}{Y_{hPH}}$
4 Anoxic growth of heterotrophs on S_{PH}		$-f_{ZBH,N}$		$\frac{-(1-Y_{hPH})}{2.86\ Y_{hPH}}$			$-f_{ZBH,P}$		
5 Aerobic growth of heterotrophs on S_V		$-f_{ZBH,N}$					$-f_{ZBH,P}$		$\frac{-(1-Y_{hV})}{Y_{hV}}$
6 Anoxic growth of heterotrophs on S_V		$-f_{ZBH,N}$		$\frac{-(1-Y_{hV})}{2.86\ Y_{hV}}$			$-f_{ZBH,P}$		
7 Aerobic growth of heterotrophs on S_M		$-f_{ZBH,N}$					$-f_{ZBH,P}$		$\frac{-(1-Y_{hM})}{Y_{hM}}$
8 Anoxic growth of heterotrophs on S_M		$-f_{ZBH,N}$		$\frac{-(1-Y_{hM})}{2.86\ Y_{hM}}$			$-f_{ZBH,P}$		
9 Aerobic growth of heterotrophs on X_{CH}		$-f_{ZBH,N}$					$-f_{ZBH,P}$		$\frac{-(1-Y_{hCH})}{Y_{hCH}}$
10 Anoxic growth of heterotrophs on X_{CH}		$-f_{ZBH,N}$		$\frac{-(1-Y_{hCH})}{2.86\ Y_{hCH}}$			$-f_{ZBH,P}$		
11 Decay of heterotrophs		$f_{ZBH,N}$ $-f_{Ep,H} \cdot f_{ZEH,N}$					$f_{ZBH,P}$ $-f_{Ep,H}$ $\cdot f_{ZEH,P}$		
12 Hydrolysis of X_S									
13 Adsorption of S_{CH}	-1								
14 Volatilization of S_V									
15 Hydrolysis of X_{ON}			1						
16 Ammonification		1	-1						
17 Hydrolysis of S_{AAP}		0.219							
18 Nitrifier growth		$-1/Y_N$ $-f_{ZBN,N}$		$\frac{1}{Y_N}$			$-f_{ZBN,P}$		$\frac{-(4.57-Y_N)}{Y_N}$
19 Nitrifier decay		$f_{ZBN,N}$ $-f_{Ep,N} \cdot f_{ZEN,N}$					$f_{ZBN,P}$ $-f_{Ep,N}$ $\cdot f_{ZEN,P}$		
20 Chemical SO_3 oxidation		$-f_{ZBS,N}$			-1	1			-0.5

Table 5.2: Process Rate Equations for Petrochemical Model (Part 3).

	PROCESS	PROCESS RATE EQUATIONS, ρ_i
1	Aerobic growth of heterotrophs on S_{AP}	$\mu_{hAP} \cdot \frac{S_{AP}}{K_{sAP}+S_{AP}} \cdot Z_{BH} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
2	Anoxic growth of heterotrophs on S_{AP}	$\eta_{grow} \cdot \mu_{hAP} \cdot \frac{S_{AP}}{K_{sAP}+S_{AP}} \cdot Z_{BH} \cdot AirNo \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4Yes$
3	Aerobic growth of heterotrophs on S_{PH}	$\mu_{hPH} \cdot \frac{S_{PH}}{K_{sPH}+S_{PH}+S_{PH}^2/K_I} \cdot Z_{BH} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
4	Anoxic growth of heterotrophs on S_{PH}	$\eta_{grow} \cdot \mu_{hPH} \cdot \frac{S_{PH}}{K_{sPH}+S_{PH}+S_{PH}^2/K_I} \cdot Z_{BH} \cdot AirNo \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4Yes$
5	Aerobic growth of heterotrophs on S_V	$\mu_{hV} \cdot \frac{S_V}{K_{sV}+S_V} \cdot Z_{BH} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
6	Anoxic growth of heterotrophs on S_V	$\eta_{grow} \cdot \mu_{hV} \cdot \frac{S_V}{K_{sV}+S_V} \cdot Z_{BH} \cdot AirNo \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4Yes$
7	Aerobic growth of heterotrophs on S_M	$\mu_{hM} \cdot \frac{S_M}{K_{sM}+S_M} \cdot Z_{BH} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
8	Anoxic growth of heterotrophs on S_M	$\eta_{grow} \cdot \mu_{hM} \cdot \frac{S_M}{K_{sM}+S_M} \cdot Z_{BH} \cdot AirNo \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4Yes$
9	Aerobic growth of heterotrophs on X_{CH}	$\mu_{hCH} \cdot \frac{X_{CH}/Z_{BH}}{K_{sCH}+X_{CH}/Z_{BH}} \cdot Z_{BH} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
10	Anoxic growth of heterotrophs on X_{CH}	$\eta_{grow} \cdot \mu_{hCH} \cdot \frac{X_{CH}/Z_{BH}}{K_{sCH}+X_{CH}/Z_{BH}} \cdot Z_{BH} \cdot AirNo \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4Yes$
11	Decay of heterotrophs	$b_H \cdot Z_{BH}$
12	Hydrolysis of X_S	$K_H \cdot \frac{X_S/Z_{BH}}{K_X+X_S/Z_{BH}} \cdot Z_{BH} \cdot (AirYes + \eta_{sol} \cdot AirNo \cdot NO_3Yes)$
13	Adsorption of S_{CH}	$K_A \cdot \{f_{maxCH} - \frac{X_{CH}}{X_{BH}}\} \cdot S_{CH} \cdot Z_{BH}$
14	Volatilization of S_V	$K_V \cdot S_V$
15	Hydrolysis of X_{ON}	$\rho_{12} \{\frac{X_{ON}}{X_S}\}$
16	Ammonification	$K_N \cdot S_{ON} \cdot Z_{BH}$
17	Hydrolysis of S_{AAP}	$K_R \cdot S_{AAP} \cdot Z_{BH}$
18	Nitrifier growth	$\mu_N \cdot \frac{S_{NH}}{K_{sNH}+S_{NH}} \cdot Z_{BN} \cdot AirYes \cdot NH_3Yes \cdot PO_4Yes$
19	Nitrifier decay	$b_N \cdot Z_{BN}$
20	Chemical SO_3 oxidation	$K_{sR} \cdot S_{SR} \cdot AirYes$

5.3 THE PETROCHEMICAL MODEL REPRESENTATION

5.3.1 The Matrix Representation

The matrix format again was utilized to present the compounds, processes, and reaction terms in the model of the activated sludge model treating the petrochemical wastewaters (Table 5.2). Since the matrix method has been thoroughly described previously, only a brief summary will be provided here to outline the model of the activated sludge system treating wastewaters from the petrochemical refinery. Across the top of the matrix the 21 components of interest in the model, which were discussed above, are listed in symbol form. The j processes occurring within the reactor are tabulated down the left hand side of the table. For the petrochemical system this included 20 different biological and physicochemical reactions. The rate equations (ρ_j) which govern the reactions are tabulated down the right hand side of the table. The kinetic parameters used in the rate equations are listed in Table 5.4. Determination of these values is discussed in Chapter 6. Finally, the body of the matrix (Table 5.2, Parts 1 & 2) contains the stoichiometric coefficients (ν_{ij}) defining the mass action relationship between the components in the individual processes. The stoichiometric parameters are listed in Table 5.3. Again, the numerical values listed in this table are discussed in Chapter 6.

As discussed before, multiplication of the rate equation by the stoichiometric coefficient determines the impact of the given process on the particular model component. Using these reaction equations in conjunction with the reactor configuration and flow patterns of the activated sludge system to form mass balance equations on the system for each compound, a complete mathematical representation of the system is formulated. Solving the system of equations quantifies the actual values of the system components. For the petrochemical case, the GPS-X^{TM} simulator was utilized to generate this system of equations. The details of this simulation package are described in Section 5.4.

The sign convention used for the stoichiometric coefficients was the same as that used to develop the petroleum refinery model. Any reaction term consuming the component is negative, while any reaction term producing the component is positive. Similarly, the growth process coefficients were normalized with respect to biomass concentration rather than substrate concentration.

The use of switching functions also was implemented in the model to switch on or off the reaction equations which apply to the conditions operating in the activated sludge system. Switching functions for oxygen, nitrogen and phosphorus were included in the model. The switching functions maintain the flexibility of the model to predict system response under different operating conditions i.e. aerobic, anoxic, or anaerobic. Table 5.5 lists the switching function parameters and specifies the corresponding symbol and value used in the reaction equations. The form of the switching functions used in the petrochemical facility model are defined in Table 5.6

5.4 INCORPORATING THE ACTIVATED SLUDGE SYSTEM MODEL IN THE GPS (GENERAL PURPOSE SIMULATOR)

In order to simulate the overall behaviour of the petrochemical wastewater treatment system the GPS-X^{TM} (General Purpose Simulator) software package was utilized. The reason that such a simulation program was required was due to the complexity of the activated sludge system operating at the petrochemical site. The system is composed of four aeration basins operated in series followed by three clarifiers. The system receives six different influent streams at different points in the process. Four high strength streams enter the first aeration basin, while two lower strength streams enter the second aeration basin. This operating mode provides a longer hydraulic residence time in the system for those streams which require an extended contact time for complete treatment. The GPS-X^{TM} simulation software provided the structure to model the configuration of this complex petrochemical activated sludge system.

In the GPS-X^{TM}, various process icons were available for building an appropriate plant flow sheet. These included alternatives such as an aeration basin, a mixing tank, or a clarifier. A flow sheet of the system is constructed by selecting the icons which represent the unit operations in the system. The flowsheet for this petrochemical treatment system is shown in Figure 5.4. Having established the configuration of the system, the GPS-X^{TM} then assigns a model, such as the mechanistic model developed above, to each activated sludge tank in the flowsheet. Furthermore, it attaches a model of the settling behaviour to each clarifier in the system. For this application, the mechanistic model of the petrochemical system was incorporated in the simulation model so that the mathematical equations which describe the overall system were generated.

Table 5.3: List of Stoichiometric Parameters Used in the Petrochemical Activated Sludge Model.

SYMBOL	DESCRIPTION	VALUE	UNITS
Heterotrophs			
Y_{hM}	Yield on mixed COD	0.666	gcell COD yield (g COD utilized)$^{-1}$
Y_{hAP}	Yield on AP	0.600	gcell COD yield (g COD utilized)$^{-1}$
Y_{hPH}	Yield on phenolics	0.600	gcell COD yield (g COD utilized)$^{-1}$
Y_{hV}	Yield on volatile organics	0.600	gcell COD yield (g COD utilized)$^{-1}$
Y_{hCH}	Yield on enmeshed hydrocarbons	0.555	gcell COD yield (g COD utilized)$^{-1}$
$f_{ZBH,N}$	Nitrogen content of active mass	0.068	g N (g COD)$^{-1}$ in active organisms
$f_{ZEH,N}$	Nitrogen content of endogenous mass	0.068	g N (g COD)$^{-1}$ in endogenous residue
$f_{ZBH,P}$	Phosphorus content of active mass	0.021	g P (g COD)$^{-1}$ in active organisms
$f_{ZEH,P}$	Phosphorus content of endogenous mass	0.021	g P (g COD)$^{-1}$ in endogenous residue
$f_{Ep,H}$	Fraction of active mass remaining as endogenous residue	0.10	g COD endog. mass (g COD active mass)$^{-1}$
$f_{cv,H}$	Ratio COD/VSS of biomass	1.42	g COD (g VSS)$^{-1}$
$f_{cv,CH}$	Ratio COD/VSS of hydrocarbon	3.50	g COD (g VSS)$^{-1}$
$f_{cv,X}$	Ratio COD/VSS of particulate material	2.30	g COD (g VSS)$^{-1}$
Nitrifiers			
Y_N	Yield	0.15	g cell COD yield (g N utilized)$^{-1}$
$f_{ZBN,N}$	Nitrogen content of active mass	0.068	g N (g COD)$^{-1}$ in active organisms
$f_{ZEN,N}$	Nitrogen content of endogenous mass	0.068	g N (g COD)$^{-1}$ in endogenous residue
$f_{ZBN,P}$	Phosphorus content of active mass	0.02	g P (g COD)$^{-1}$ in active organisms
$f_{ZEN,P}$	Phosphorus content of endogenous mass	0.02	g P (g COD)$^{-1}$ in endogenous residue
$f_{Ep,N}$	Fraction of active mass remaining as endogenous residue	0.08	g COD endog. mass (g COD active mass)$^{-1}$
$f_{cv,N}$	Ratio COD/VSS	1.42	g COD (g VSS)$^{-1}$

Table 5.4 : List of the Kinetic Parameters used in the Petrochemical Activated Sludge Model.

SYMBOL	DESCRIPTION	VALUE	UNITS
Heterotrophs			
μ_{hM}	Maximum specific growth rate on mixed COD	4.0	d^{-1}
K_{sM}	Half saturation coefficient for mixed COD	1.0	g COD m^{-3}
μ_{hAP}	Maximum specific growth rate on AP	1.1	d^{-1}
K_{sAP}	Half-saturation coefficient for AP	5.0	g COD m^{-3}
μ_{hPH}	Maximum specific growth rate on phenolics	4.3	d^{-1}
K_{sPH}	Half-saturation coefficient for phenolics	1.0	g COD m^{-3}
K_I	Inhibition coefficient for phenolics	60	g COD m^{-3}
μ_{hV}	Maximum specific growth rate on volatile organics	1.5	d^{-1}
K_{sV}	Half-saturation coefficient for volatile organics	30	g COD m^{-3}
μ_{hCH}	Maximum specific growth rate on adsorbed X_{CH}	2.0	d^{-1}
K_{sCH}	Half-saturation coefficient for X_{CH}	0.15	g COD(gCOD$^{-1)}$
b_H	Organism decay rate	0.62	d^{-1}
η_{sol}	Anoxic solubilization factor	0.37	-
η_{grow}	Anoxic growth factor	1.00	-
K_H	Maximum specific hydrolysis rate for X_S	2.81	d^{-1}
K_X	Half-saturation coefficient for hydrolysis	0.15	g COD(gCOD)$^{-1}$
K_N	Ammonification rate	0.06	m^3 (g COD. d)$^{-1}$
K_R	Aliphatic amine P hydrolysis rate	0.10	m^3 (g COD. d)$^{-1}$
K_A	Adsorption rate for S_{CH}	0.10	m^3 (g COD. d)$^{-1}$
K_V	Volatilization rate for volatile organics	0.40	m^3 (g COD. d)$^{-1}$
Nitrifiers			
μ_N	Maximum specific growth rate	N/A	d^{-1}
K_{sNH}	Half-saturation coefficient for growth	1.0	g N m^{-3}
b_N	Organism decay rate	0.04	d^{-1}
Sulphite Oxidation			
K_{SR}	Sulphite oxidation rate	200	d^{-1}

Table 5.5: List of the Switching Function Parameters Used in the Petrochemical Activated Sludge Model.

SYMBOL	DESCRIPTION	VALUE	UNITS
K_{OH}	Aerobic/anoxic growth	0.002	$g\ O\ m^{-3}$
K_{NA}	Ammonia limit	0.05	$g\ N\ m^{-3}$
K_{NO}	Nitrate limit	1.0	$g\ N\ m^{-3}$
K_{LP}	Soluble phosphorus limit	1.0	$g\ P\ m^{-3}$

Table 5.6: Definition of Switching Functions used in the Petrochemical Activated Sludge Model.

SWITCHING FUNCTION	EQUIVALENT	DEFINITION
AirYes	1 - AirNo	$\frac{S_O}{K_{OH} + S_O}$
AirNo	1 - AirYes	$\frac{K_{OH}}{K_{OH} + S_O}$
NH3Yes	1 - NH3No	$\frac{S_{NH}}{K_{NA} + S_{NH}}$
NH3No	1 - NH3Yes	$\frac{K_{NA}}{K_{NA} + S_{NH}}$
NO3Yes	1 - NO3No	$\frac{S_{NO}}{K_{NO} + S_{NO}}$
NO3No	1 - NO3Yes	$\frac{K_{NO}}{K_{NO} + S_{NO}}$
PO4Yes	1 - PO4No	$\frac{S_P}{K_{LP} + S_P}$
PO4No	1 - PO4Yes	$\frac{K_{LP}}{K_{LP} + S_P}$

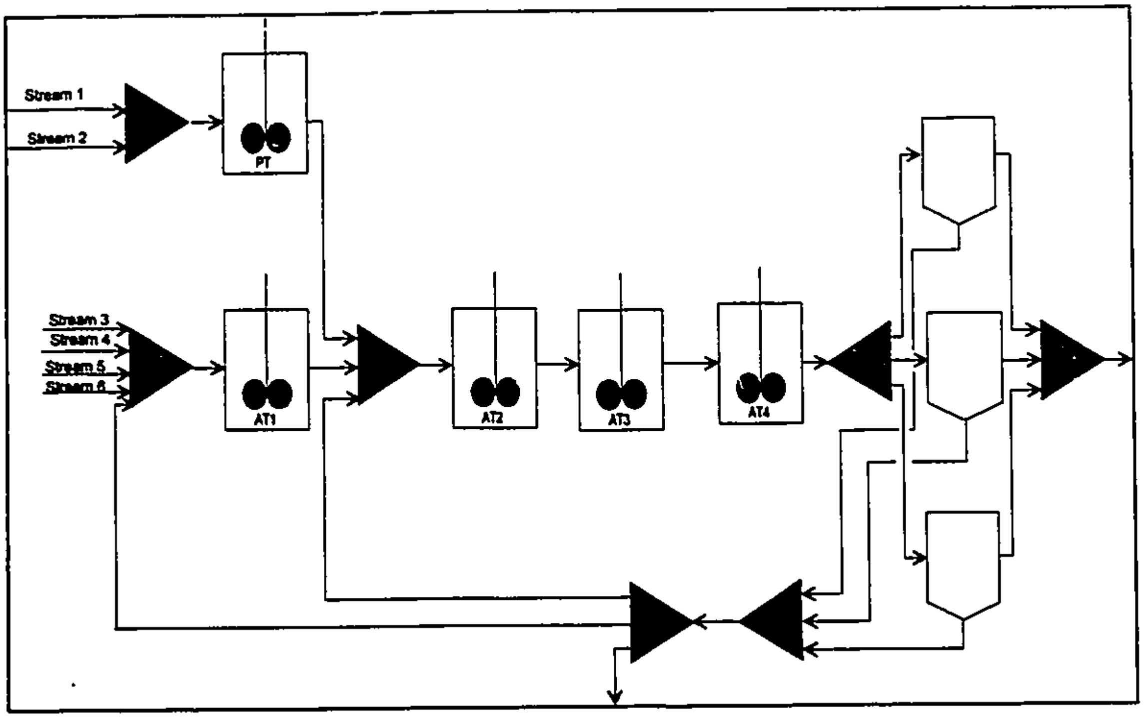

Figure 5.4: The schematic representation used to represent the petrochemical activated sludge system in the GPS-X. This diagram represents the current mode of operation at the facility.

The governing system equations were generated by combining the reaction equations in the mechanistic model with the reactor configuration, flow patterns, and wastewater quality specified in the GPS-X^{TM}. This resulted in a set of mass balance equations for each reactor for each compound of concern. The general form of the mass balance equation is the fundamental expression presented earlier:

$$\begin{array}{c}\text{Rate}\\ \text{of}\\ \text{Accumulation}\end{array} = \begin{array}{c}\text{Rate}\\ \text{of}\\ \text{input}\end{array} - \begin{array}{c}\text{Rate}\\ \text{of}\\ \text{output}\end{array} + \begin{array}{l}\text{Rate of}\\ \text{production}\\ \text{by reaction}\end{array} \quad (5.14)$$

The GPS-X^{TM} generated and solved this set of simultaneous non-linear differential equations to characterize the behaviour of the petrochemical activated sludge system.

This allowed model predictions to be compared with the actual system response. This was an important element for calibration of the petrochemical activated sludge model which is discussed in the following chapter.

In summary, the GPS-X^{TM} system enabled a complex activated sludge plant to be modelled and simulated with relative ease.

5.5 SUMMARY

The activated sludge model treating petrochemical wastewaters has been described above. The components characteristic of the petrochemical facility were identified and a model for the processes involved in removing these particular contaminants was proposed. Using the petroleum refinery model as a basis facilitated development because many of the processes occurring in the petroleum refinery model were applicable to the petrochemical system. The main exception was the use of chemical oxidation for the removal of reduced sulphur compounds in the petrochemical application, whereas biological oxidation occurred in the petroleum refinery case study. Other modifications included an equation to model the hydrolysis of the aliphatic amine P and the inclusion of an equation for the hydrolysis of particulate organic nitrogen. Otherwise, by determining the components of interest in the petrochemical system, the removal processes identified in the petroleum refinery system could be applied directly.

The next stage in the model development process was to illustrate the ability of the activated sludge model to predict the response of the system. In order to predict accurately system behaviour, the model must be calibrated using operational data from the treatment operation, supplemented with data from specifically designed experiments. Calibration involves the determination of a single set of stoichiometric and kinetic rates for the processes incorporated in the model. Determination of these values makes the model unique to the petrochemical facility. Chapter 6 describes the calibration/verification procedure.

CHAPTER 6

CALIBRATION AND VERIFICATION OF THE PETROCHEMICAL MODEL

6.1 INTRODUCTION

The key to a model effectively predicting the response of a system is the calibration of the model to known responses. In this case study, model calibration involved determining the stoichiometric and kinetic coefficients of each of the biological and physicochemical removal mechanisms occurring in the activated sludge system treating the petrochemical wastewater. With appropriate values for these coefficients, model predictions should correspond closely to the observed behaviour.

A different approach was used to formulate and calibrate the petrochemical model than that used to develop the petroleum refinery model. In the first case study, experimentation was needed to provide sufficient data to develop a model structure. As a result, an extensive experimental programme based on a continuous flow laboratory scale activated sludge system was conducted to identify the different relationships occurring in the system. With the basic structure in place, a more limited database is adequate for model calibration. Therefore, use of an alternative source of data which is easier to collect is advantageous. The use of batch tests has been used successfully in other situations (Ekama, 1986) to provide information on system behaviour, and batch tests are much easier to carry out than the operation of continuous flow systems. As a result, for the petrochemical activated sludge model considered in this study, data obtained from a range of batch tests and information on full-scale operation of the facility was thought to be sufficient for calibrating the model. The aim of applying this procedure to the development and calibration of the petrochemical activated sludge model was to confirm that this approach would generate a calibrated model of the system effectively.

Once calibrated, the final stage in model development was to verify the ability of the model to predict system response with an independent set of data. Testing a calibrated model with an independent set of data verifies that the model is applicable to different operating conditions, and not only the specific mode used to determine the model parameters. This procedure was necessary in the development of this model to confirm the ability of the calibrated model to describe the behaviour of the activated sludge system operating at the petrochemical facility.

The activated sludge system treating the wastewaters generated at the petrochemical facility consists of four aeration tanks and three clarifiers. It receives multiple influent streams which enter the facility at different feed points. Return activated sludge (RAS) recycle from the secondary clarifiers can be introduced or split between two aeration zones. The flowsheet of this more complex activated sludge system is illustrated in Figure 6.1. In order to model this system, the mechanistic activated sludge model formulated in Chapter 5 for petrochemical wastewater treatment was used in the GPS-X^{TM} computer simulation system. This program provided the structure for representing the multiple unit operations, input flows, and internal flow patterns characteristic of this treatment plant. It assigned the petrochemical activated sludge model to each aeration tank in the treatment system, and a 10-layer clarifier model to each clarifier. With the system configuration and model structure established, the GPS-X^{TM} generated the mass balance equations which represented the petrochemical activated sludge system. Solving this set of equations provided estimates of the response of each parameter in the treatment system to determine the overall system behaviour.

The following chapter discusses the calibration/verification stages which apply to the petrochemical activated sludge system and describes the experimental programme required to collect the necessary data for these procedures.

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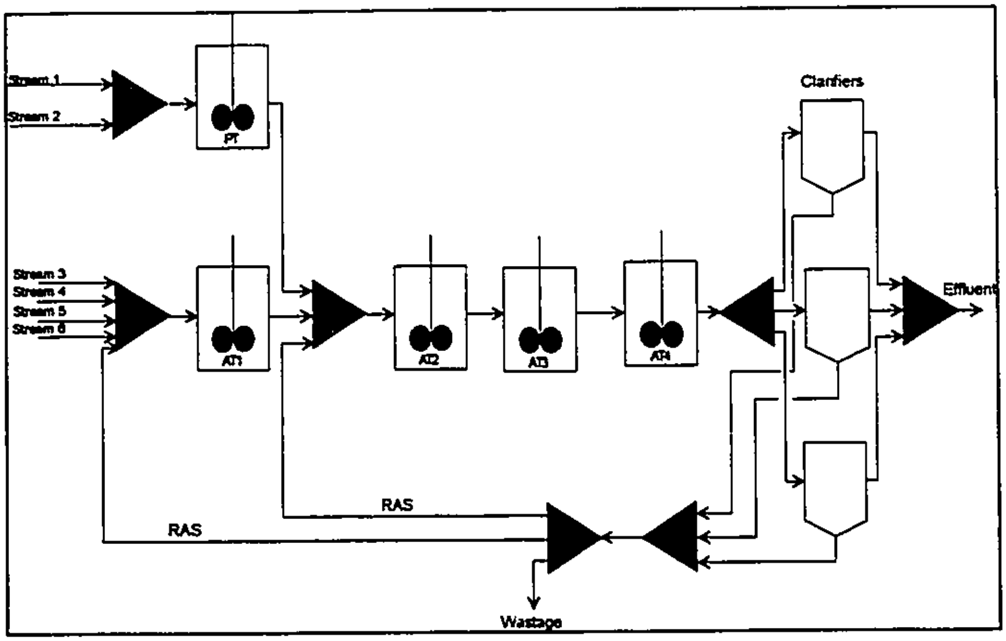

Figure 6.1: Schematic of the Petrochemical Activated Sludge System

6.2 CALIBRATION PROCEDURE

Calibration of the activated sludge model treating the wastewater generated at the petrochemical facility involved a number of sequential steps:

- Conducting an experimental programme to gather data required for the calibration process;
- Determination of the characteristics of each wastewater stream;
- Obtaining preliminary model predictions which approximate the actual system response;
- Determination of organism decay rate;
- Calibration of the model with the results of a series of batch experiments. This step also involved performing a sensitivity analysis;
- Verification of the calibrated model with an alternate set of data.

In this section, the rationale for each step in the process is discussed to provide an overview of the calibration procedure. Having established the general methodology, a detailed explanation of the different stages is presented in the following sections.

- ***Experimental Programme:*** In order to calibrate a model it is necessary to have information on the response of the system. Monitoring the behaviour of the actual system means that the model predictions can be compared and adjusted until the model is capable of predicting the actual response.

  An experimental programme was required to provide data on the relationships occurring within the system and relate system response to operating conditions such as sludge age, influent loadings, and flowrates. Some of this information was available from records on the full-scale operation of the petrochemical facility, but this data was incomplete and had to be supplemented with experimental data. Therefore, one of the first stages of model calibration was to collect the required data.

  The experimental programme involved conducting a series of batch tests in which sludge from the full-scale plant was mixed with samples of the individual influent streams. Over the duration of each batch test (approximately 3 to 5 hours) the responses of the oxygen utilization rate (OUR), filtered COD, and filtered TKN were monitored semi-continuously. These three parameters were identified as providing sufficient information for model calibration. The purpose of conducting separate batch tests on each of the influent streams was to enable the impact of individual influent components to be identified. Typically each stream contains only one or perhaps two of the model components at significant concentrations.

- ***Determination of the characteristics of each wastewater stream:*** Characterization of the influent is very important to both model formulation and calibration. Firstly, to decide what to model in any given system, the compounds present in the wastewater must be identified. Secondly, since the contaminants control the nature of the removal mechanisms, the behaviour of the activated sludge system depends on the compounds being treated. These points were highlighted in Chapter 5.

For purposes of model calibration specific information was required on the composition of the different influent streams. Actual concentrations of the various components were estimated for each influent stream using a number of sources: long term averages of plant data, daily measurements monitored by the plant, grab samples, and from batch tests run on the different influent streams.

- ***Initial model predictions which approximate the observed full-scale system response:*** The initial stage of model calibration involved simulating system response using the GPS-X^{TM} model with preliminary estimates of model parameters and influent conditions to generate predictions which approximated the response of the full-scale system. The quality of the influent wastewater was estimated using long term data. The preliminary kinetic and stoichiometric coefficients for the reactions in the model were estimated using the values determined for the petroleum refinery activated sludge model.

  At this stage of the calibration process a number of model parameters were adjusted to improve predictions. This procedure is described in Section 6.5. As a result of these preliminary simulations, baseline coefficients for the model and initial estimates of system behaviour were determined. Having model predictions in the "ball park" of actual system behaviour meant that the main calibration exercise could proceed more rapidly. For example, an important result of this stage was to obtain an estimate of the composition of mixed liquor in the system (i.e. concentrations of active organisms, endogenous residue, etc.). This information was necessary to define the initial conditions for modelling the batch experiments in the main part of the model calibration procedure.

- ***Determination of organism decay rate:*** An important factor in obtaining accurate predictions of the volatile suspended solids concentration in the system was having an accurate estimate of the decay rate of the organisms.

- ***Calibration of the model with the results of a series of batch experiments:*** Calibration of the petrochemical wastewater treatment plant model involved adjusting the stoichiometric and kinetic coefficients in the model equations until the model simulated the response of known system parameters. The main task in the procedure involved matching model predictions with observed results from one set of batch experiments treating individual influent streams to determine the model coefficients. The GPS-X^{TM} was configured to model the batch tests so that the model coefficients could be adjusted until model predictions compared to observed behaviour. Since simulation of the batch reactor tests was the crux of the calibration procedure, it is important that the approach used to determine the model parameters from these tests be described adequately .

In a number of cases the influent stream contained only one organic component. For example, Stream 4 essentially contains only phenolics (S_{PH}). Therefore, the batch test response was dominated by the removal behaviour for this compound. To calibrate the model to this particular batch test, adjustments were made to the parameters influencing removal of phenolics (e.g. μ_{hPH}, K_{sPH}, and K_I) until the predicted and observed responses for the monitored parameters matched with reasonable accuracy. For such a case, adjusting model parameters affecting other components (such as the amine S_{AAP}) had no influence on model predictions.

In other cases a particular model component was present at significant concentrations in more that one stream. For this situation, an iterative calibration procedure was used. The model parameters for the component were adjusted to provide a reasonable fit to data on one batch test. These parameters were applied to model a different batch test influenced by the same component. If necessary, the parameters were adjusted to provide an improved fit to the response in the second batch test. These adjusted parameters were re-applied to the first test, and perhaps refined further. The iterative calibration would be continued until a reasonable fit to observed data in both tests was obtained using a single set of model parameters.

The calibration procedure using the batch test data was very laborious as a result of the different combinations of components in the six influent streams. For example, Components 1 and 2 could be present in Streams 1 and 3, and Streams 2 and 3, respectively, while Component 3 was present in Streams 1 and 3. This situation would necessitate many iterations in the calibration procedure.

A further complication in the calibration procedure was estimating the active biomass concentration in the sludge at the start of each batch test. In the batch tests the individual influent streams were mixed with biomass taken directly from the return activated sludge stream in the treatment plant. A portion of this is active biomass, while the remaining sludge mass is not microbially active. The active biomass concentration is included in many of the kinetic model equations. Therefore, correct evaluation of the stoichiometric and kinetic coefficients also is dependent on an accurate estimate of the active biomass concentration in the sludge. Hence, a key parameter in the entire calibration procedure was determining the active biomass concentration in the batch tests. Determining the active biomass concentration in the sludge withdrawn from the full-scale plant for use in the batch tests also necessitated an iterative approach .

As indicated above, an initial estimate of the active biomass concentration in the full-scale treatment plant was determined by simulating the system using long term average concentrations of compounds treated by the petrochemical facility and default stoichiometric and kinetic coefficients from the petroleum refinery model (Baker & Dold, 1994). The value estimated from these preliminary model simulations was used to obtain estimates of the active biomass concentration used in the batch tests. With this active biomass concentration, the batch tests were simulated in the GPS-X^{TM} by adjusting the influent wastewater fractions and reaction coefficients until the experimental values of OUR, COD, and TKN were predicted. These adjusted values then were used in the GPS-X^{TM} simulation model of the full-scale petrochemical treatment plant to determine a new estimate of the active biomass concentration. If the new estimate was significantly different than the one used in the batch tests, the batch test simulations were recalibrated with the new estimate. The adjustment of coefficients and influent fractions was repeated until the active biomass concentration predicted by steady state simulation of the petrochemical treatment system converged to the value used in the batch test simulations.

Final adjustments to improve model predictions of the batch tests were conducted by slight modifications to the kinetic and stoichiometric coefficients, and the wastewater fractions. The various sources of data on influent characterization, such as the grab samples, batch test responses, and the calibration procedure itself, were utilized to fine tune the different wastewater fractions used in the batch test simulations. By simulating batch tests of all the influent streams, reasonable estimates of the different coefficients were determined. The model predictions are compared to the experimental batch tests in Figures 6.4 to 6.9. These plots are discussed in Section 6.6.

- ***Verification of model calibration with an alternate set of data :*** The final stage of model development was to verify that a model which had been calibrated against one set of experimental data (i.e. one series of batch tests) was able to predict effectively the response of the activated sludge system under a different set of conditions. Data from a second series of batch test were used for the verification process. Using the coefficients determined from the first data set, the second set of batch tests were simulated. With coefficients that have been determined correctly, simulations should predict the observed response of the second series of batch tests. The model verification predictions and experimental data observed in the batch tests are compared in Figures 6.10 to 6.12.

This completes the general discussion on the rationale involved in calibrating the activated sludge model of the petrochemical activated sludge system. Each of these steps is now presented in more detail. The experimental programme is discussed in Section 6.3 and the characterization of the influent wastewater streams is presented in Section 6.4. The information required to conduct the preliminary model simulations is discussed in Section 6.5. The results of calibrating the batch tests are presented and analysed in Section 6.6 and the verification procedure is discussed in Section 6.7. The specific values determined for the stoichiometric and kinetic coefficients are presented in Section 6.8 and 6.9. The influence of model coefficients on model predictions was determined through a sensitivity analysis discussed in Section 6.10.

6.3 EXPERIMENTAL PROGRAMME

The experimental programme was conducted to supplement data already available on full-scale operation of the petrochemical wastewater treatment system. A minimum of two data sets are needed to calibrate and verify any model. In this study, data collected during an intensive experimental program in February 1993 provided one set of data for model development, while data collected during June 1993 provided another set. The influent concentrations were different for the February and June time periods providing two substantially different sets of response data. The model coefficients were determined using data collected in six of the batch tests in conjunction with full-scale response data. Using these coefficients, model predictions were generated for three remaining batch tests to ensure that observed results were estimated appropriately by the model, thereby verifying the stoichiometric and kinetic coefficients determined through simulation of the first set of batch tests.

The experimental programme involved two main components:

(1) Collecting and analysing grab samples of the six influent streams and mixed liquor sludge samples from the full-scale plant; and

(2) Conducting aerobic batch tests in which activated sludge from the full-scale plant was mixed with each of the influent streams.

Grab samples: To characterize the influent wastewater streams and the activated sludge, grab samples were taken from the petrochemical system during the experimental periods. The following concentration analyses were performed on the wastewater samples:

Unfiltered COD
Filtered COD
Total Organic Carbon
Unfiltered TKN
Filtered TKN
Ammonia Nitrogen
Nitrate Nitrogen
Sulphate

The concentration analyses conducted on the sludge samples were:

Total Suspended Solids

Volatile Suspended Solids
Unfiltered COD
Filtered COD
Unfiltered TKN
Filtered TKN

The analyses performed on all the samples followed the methods outlined in Standard Methods (1992). The results of these tests are listed in Appendix 5. Some preliminary sampling performed during August 1992 is also included in these tables.

The measurements determined on these different samples not only assisted in characterizing the influent wastewaters, but also assisted in quantifying certain of the stoichiometric coefficients in the model.

Batch tests: To monitor the response of the activated sludge when treating different influent streams, the series of aerobic batch tests were performed on a mixture of each influent wastewater stream and activated sludge. The response of the mixture with time was monitored for a change in OUR, filtered COD, and filtered TKN.

The equipment required to conduct these tests was:

- 1200 mL flask,
- Constant temperature water bath equipped with a magnetic stirrer,
- Air supply and aerator,
- Portable dissolved oxygen (DO) meter and probe, and
- Chart recorder.

To conduct a test, a measured volume of one of the influent wastewater streams was mixed with a measured volume of activated sludge from the RAS recycle stream. The sample volumes of influent and sludge were determined by trial so that the organic material would be consumed by the activated sludge over a 2 to 4 hour period. Prior to mixing, the unfiltered and filtered COD and TKN concentrations were measured on the wastewater sample, and on the sludge samples the total and volatile suspended solids concentrations were determined in addition to filtered COD and TKN. These measurements assisted in determining the initial conditions in the batch test.

During each test, the mixture was kept at a constant temperature of 25°C, and was well mixed. Air was bubbled to the system to provide the oxygen requirements for organism growth. The contents of the reactor were sampled for filtered COD and TKN over the duration of the test. The change in OUR also was monitored at intervals.

To determine the oxygen utilization rate (OUR) in the sample, the mixture was aerated rapidly until a D.O. reading of 6 to 8 mg /L was reached. At this point the air supply was shut off (but the sample continued to be mixed) and the D.O. allowed to drop to 2 to 3 mg/L. This decrease was monitored on the chart recorder. By measuring the slope of the linear portion of the response, the OUR in the system at the time was determined. This procedure was repeated at intervals of a few minutes throughout the test until the OUR reached endogenous levels indicating that most of the biodegradable COD in the mixture had been utilized. The OUR associated with endogenous respiration was determined at the outset of each batch test on a sample of RAS.

The data collected during these batch tests on the influent streams were key to quantifying the kinetics of the different reactions occurring in the system. Results from these batch tests are reported in Appendix 6.

Another type of batch test was performed on the return activated sludge (RAS) to determine the decay rate of the organisms in the activated sludge. This involved aerating a sample of return activated sludge for several days without the addition of organic material from influent streams. The OUR was measured a couple of times daily to monitor the decrease in oxygen consumption with organism decay. A semi-log plot of the OUR with respect to time produced a straight line representing the decay rate of the organisms. The average decay rate calculated from the test was 0.24 day^{-1}.

This decay rate was used in the GPS-X^{TM} to simulate the actual decay rate test (Figure 6.2). Simulation of the test required an initial estimate of the biomass concentration in the activated sludge sample which the preliminary model simulations provided (Section 6.5). Modelling the decay rate test confirmed that the measured decay rate adequately predicted the observed test. This value was utilized in further simulations of the petrochemical activated sludge system, although model predictions had to be reconfirmed as the estimates of biomass changed throughout the calibration process.

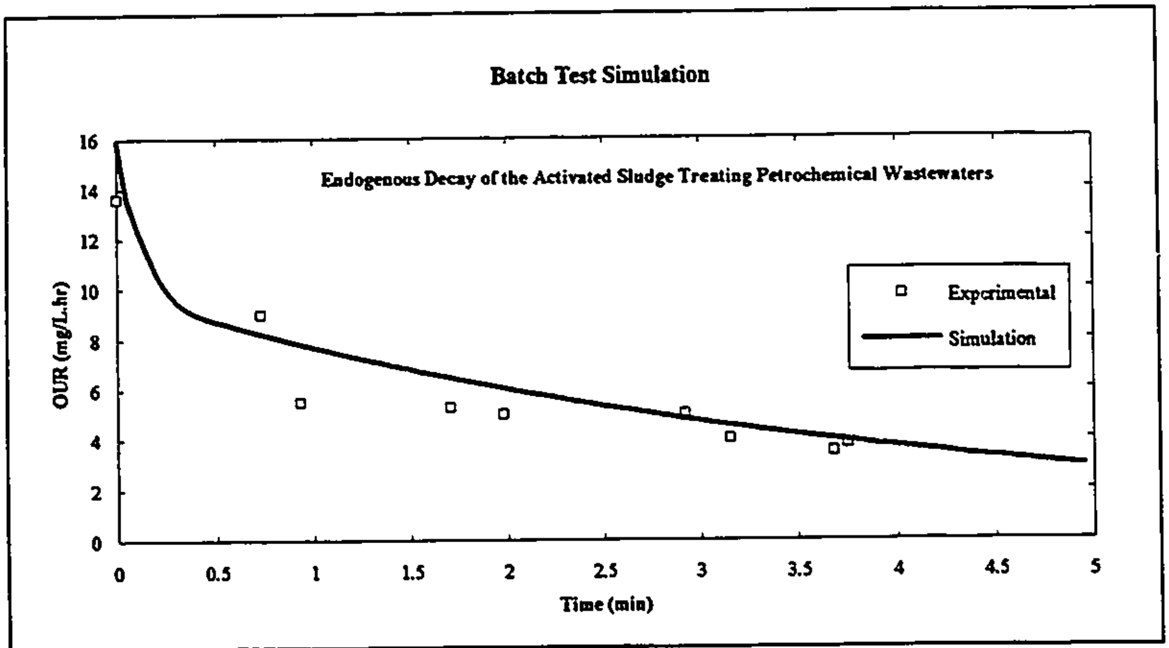

Figure 6.2 : The experimental results of an endogenous decay rate test are presented along with the simulated results of the test conducted using the GPS-X^{TM}. The model was able to predict the observed values of OUR measured in the experiment with reasonable accuracy.

The experimental data collected during the different tests described above were used in conjunction with information on full-scale operation of the plant to calibrate the petrochemical activated sludge system.

6.4 DETERMINATION OF WASTEWATER CHARACTERISTICS

An integral part of model development and calibration was identification of the concentrations of different components in the wastewater. This information was critical in deciding what components needed to be included in the model and the types of removal mechanisms to expect in the system. More pertinent to this section of the discussion, however, was the need to have influent stream characterization in order to identify correctly the values of the stoichiometric and kinetic coefficients in the model equations. The importance of this stage was described in Section 6.2, but the process of determining the wastewater characteristics is presented here.

The components incorporated in the petrochemical activated sludge model were identified in Chapter 5 as:

- *Soluble Mixed Organics* (S_M)
- *Alcohol P* (S_{AP})
- *Aliphatic amine P* (S_{AAP})
- *Phenolics* (S_{PH})
- *Volatile Organic Compounds* (S_V)
- *Soluble Hydrocarbons* (S_{CH})
- *Soluble inert organics* (S_I)
- *Inert Particulate Organics* (X_I)
- *Slowly Biodegradable Organic Particulate* (X_S)
- *Ammonia* (S_{NH})
- *Organic nitrogen* (S_{ON})
- *Particulate organic nitrogen* (X_{ON})
- *Nitrate* (S_{NO})
- *Reduced Sulphur (Sulphite)* (S_{SR})
- *Sulphate* (S_{SO})
- *Soluble Phosphate* (S_P)

Each of the six influent streams treated in the petrochemical treatment system had to be characterized in terms of the concentrations of these model components. Some of these components were measured directly during the experimental programme and could be determined readily. These were:

Ammonia nitrogen (S_{NH})
Nitrate nitrogen (S_{NO})
Sulphate (S_{SO})

Other direct measurements made on the influent wastewaters represented composite readings of different model components. When dealing with these measurements, the individual model components had to be estimated using a number of data sources. The following bulk measurements represent the following model compounds:

(1) *Filtered COD:* This measurement represents the summation of soluble COD components in the model. These are alcohol P (S_{AP}), aliphatic amine P (S_{AAP}), phenolics (S_{PH}), volatile organic COD (S_V), mixed COD (S_M), soluble hydrocarbons (S_{CH}), and unbiodegradable soluble COD (S_I).

(2) *Unfiltered COD:* This reading represents the sum of the particulate COD in the wastewater, as well as the soluble COD components. The particulate components associated with the influent are the slowly biodegradable particulate COD (X_S), and the particulate inert COD (X_I).

(3) *Filtered TKN:* This measurement represents the sum of ammonia nitrogen (S_{NH}), soluble organic nitrogen (S_{ON}), and the nitrogen component of the aliphatic amine (S_{AAP}).

(4) *Unfiltered TKN:* Experimental values of this compound include the contribution of the filtered TKN components, the particulate organic nitrogen (X_{ON}), and organic nitrogen associated with biomass components.

Full characterization of the wastewater in terms of model components was accomplished using the following sources of data:

- ***Long term data:*** The petrochemical facility conducts a regular sampling program to identify the concentrations of different components in the influent wastewater streams. These were collated to generate plots of the long term characteristics of the treatment plant influent streams. This was a valuable source of information for characterizing the influent streams. The long term data also provided data on the quantity and quality of the effluent discharged from the wastewater treatment system which also was necessary for the calibration procedure (see Appendix 4) .

- *Grab samples and daily monitored parameters:* During the experimental program designed to collect information on the kinetic behaviour of the system, grab samples were taken of the different influent streams. This provided information on the concentration of composite measures such as total COD and TKN (unfiltered and filtered) on any given day. These measurements were supplemented with daily monitoring of specific contaminants [i.e. alcohol P (S_{AP}), aliphatic amine P (S_{AAP}), phenolics (S_{PH}), and volatile organic compounds (S_V)], conducted by the plant personnel at the petrochemical facility. The daily readings enabled a more detailed description of the specific wastewater quality being treated in the batch test to be determined. This provided a more realistic simulation of the batch tests, and enabled the model to be calibrated more accurately.

- *Model Calibration:* The final refinements of wastewater characterization were conducted in conjunction with the calibration process itself. Certain constituents in the model were represented by bulk parameters such as inert material (S_I, X_I), particulate material (X_S), and hydrocarbons (S_{CH}). Specific measurements of these components were difficult to obtain directly, but could be estimated from the response of the activated sludge during the batch tests by monitoring OUR, COD, and TKN. For example, the inert COD (S_I) was assumed to be the residual COD left undegraded at the end of the batch tests. Refinements on these estimates were made by modifying the wastewater characteristics until model predictions were most comparable to observed results.

The above sources of information were used to determine the wastewater characteristics of the influent streams being treated by the activated sludge system at the petrochemical facility.

6.4.1 Composition of Individual Influent Streams

Each stream may contain any number of the different model components. However, certain streams tend to exhibit particular influent characteristics due to the processes which generate them. A general description of each of the streams is given below along with the source of the supporting information. Tables which quantify the different influent fractions are presented in Section 6.6 in conjunction with the batch test simulations.

One assumption made in analysing these wastewaters which should be noted here is that the removal kinetics of each compound did not depend on the other compounds present in the influent (i.e. no interactive affects). Therefore, the concentrations of each model component, and the response associated with it, could be determined independently of other compounds.

STREAM 1: The composition of Stream 1 includes alcohol P (S_{AP}), aliphatic amine P (S_{AAP}), volatile organics (S_V), hydrocarbons (S_{CH}), and inert organics (S_I). The alcohol P and aliphatic amine P concentrations in this stream are measured directly in the daily monitoring program. The aliphatic amine also contributes to the presence of TKN measured in this stream. The behaviour of the batch test confirmed the presence of these two compounds, as well as a small fraction of mixed soluble COD (S_M). These tests were used to estimate the quantities of each of these parameters, and the calibration process was used to refine the fractionation (see Table 6.4).

In terms of nutrients, the daily measurements indicated low levels of ammonia present in Stream 1. Sodium meta-bisulphite may also be present in this stream contributing to unusually high OUR readings over the first few minutes in the batch tests.

STREAM 2: The main components in Stream 2 are certain volatile organic compounds (S_V) based on results presented in a VOC study on this facility, plus a mixture of soluble mixed compounds (S_M), inert organic compounds (S_I) and some hydrocarbon material (S_{CH}). One particular VOC is nearly always present and measured daily in this stream [Due to proprietary reasons it cannot be identified]. Other parameters measured daily are found in small quantities and lumped into the soluble mixed category. The amount of soluble mixed COD present was determined by fitting model predictions to the initial response of the batch test. The presence of an unbiodegradable inert fraction was indicated in the batch test effluent. Similarly, the presence of some adsorbed or slowly biodegradable organic was determined in the batch tests. This was reflected in the prolonged OUR at levels greater than endogenous rates. The calibration process confirmed the presence of hydrocarbon material in this stream. Tables 6.5 and 6.6 lists the different wastewater fractions which apply to the batch tests conducted with this stream.

In terms of nutrients, low levels of ammonia are indicated in the daily monitoring of influent quality and in the grab samples. Sulphur compounds are also identified. The addition of sodium meta-bisulphite as an oxygen scavenger during upstream processing explains the initially large OUR at the start of the batch tests. Sulphite is oxidized to sulphate in the process.

STREAM 3: Daily monitoring of this stream indicates that the major component in this wastewater is the alcohol P (S_{AP}). Inert material (S_I), hydrocarbons (S_{CH}), and some remaining soluble mixed COD (S_M) were indicated in the batch test responses of this stream. Calibration of the batch test with this stream refined the actual fractionation of the different components (see Tables 6.7 and 6.8).

The batch tests also indicated potential nitrogen limitations preventing the complete removal of the organic material. Daily reports indicate the presence of ammonia in the influent, but in some instances another source of nitrogen may be necessary to ensure complete removal of the highly concentrated organics.

STREAM 4: This stream essentially is composed of phenolic compounds. Small quantities of residual resin also may be present contributing to the nitrogen levels in this stream. The batch tests indicated the presence of some inert organic material, as well as small quantities of mixed soluble COD. In some instances hydrocarbon COD may also be found. Hydrocarbon COD was noticed in the test using a 5 mL sample of Stream 4, but not in the test using a 1 mL sample. This is likely due to the fact that in the smaller sample it may be more difficult to detect hydrocarbon COD or differentiate it from the other compounds present. The controlling component in this stream, however, is the phenolic material. The component fractions used in the batch tests are listed in Tables 6.9 and 6.10.

STREAM 5: This stream is influent from a holding tank which varies widely in composition. It contains waste trucked from throughout the site, as well as diverted streams due to flow increases in the other streams. Therefore, the composition of this stream varies significantly and to predict accurately the response of the system to this stream, an updated estimation of its composition is important. The sample of trucked wastewater used in the batch test contained mainly alcohol P (S_{AP}) and aliphatic amine P

(S_{AAP}), along with some inert material (S_I). The presence of these components was confirmed during the model simulations of the batch test. Table 6.11 lists the influent fractions determined from the batch tests.

STREAM 6: This stream consists mainly of an unbiodegradable latex compound which is inert organic material (S_I) along with a combination of mixed soluble COD, slowly biodegradable hydrocarbon COD (S_{CH}), and some volatile organics (S_V). The large inert fraction is reflected in the high effluent COD values in the batch test results. Matching model simulations to observed batch test response in the calibration procedure confirmed the presence of the other organic components (see Table 6.12).

The descriptions given above indicate the nature of the different influent streams. The specific concentrations associated with each influent stream are identified in the following discussions on model simulations so are not reported here.

6.5 INITIAL MODEL SIMULATIONS OF FULL-SCALE PLANT

Before calibrating the petrochemical activated sludge model it was necessary to run some preliminary simulations of system behaviour. These were required to ensure that model predictions provided reasonable estimates of effluent quality and solids concentrations. This enabled the actual calibration procedure to proceed more quickly. Also, to initiate the batch test simulations, an initial estimate of the active biomass concentration in the treatment plant was necessary. The preliminary simulations of the petrochemical activated sludge plant were conducted using the following input:

- Default stoichiometric and kinetic coefficients from the petroleum refinery model.

- Long term average flowrates of the influent streams treated by the petrochemical facility (See Appendix 4).

- Estimates of the concentrations of different compounds present in each of the influent streams to approximate plant loadings. Interpretation of a number of different data sources provided this information. These included grab samples on each of the influent streams, daily monitored parameters recorded by plant personnel, and estimates of the influent fractions from interpretation of the batch tests themselves. The aim was to estimate the influent loadings to the system at the time of the batch tests so that information attained from these tests could be used in conjunction with full-scale operating data during the same period.

This information provided the required data to simulate the operation of the petrochemical plant and calculate an initial estimate of the active biomass concentration present in the reactors when treating the estimated flowrates and loadings of wastewater.

To estimate the influent loadings required for these preliminary simulations, the daily monitored parameters tabulated by the petrochemical facility indicated the concentrations of different model components likely to be present in a given stream. Table 6.1 gives a sample of this data for Streams 1 and 2 on February 9, 1993. The total COD present in the influent streams was estimated using grab samples of the different streams.

Table 6.1: Sampling Results for Streams 1 & 2 on February 9, 1993. These samples were taken and analysed by plant personnel.

STREAM	PARAMETERS	FEBRUARY 9, 1993	UNITS
Stream 1	DOC	96	mg C/L
	Alcohol P	8.1	mg AP/L
	Aliphatic Amine	203.1	mg AAP/L
	Phenol	0.15	mg PH/L
	Volatile Organic	-	mg/L
	NH3	3	mg N/L
Stream 2	DOC	31	mg C/L
	Alcohol P	3.7	mg AP/L
	Aliphatic Amine		mg AAP/L
	Phenol	0.9	mg PH/L
	Volatile Organic	44.8	mg/L
	NH3	1.8	mg N/L

This information was used in conjunction with the batch test responses to estimate the concentrations of compounds present in the influent streams when the batch tests were being conducted. For example, any readily biodegradable mixed COD (S_M) was consumed at the beginning of the batch test. The mass of oxygen consumed in this part of the test provided an estimate of the initial mixed COD concentration. If alcohol P (S_{AP}) occurred in a stream then the amount present in the batch test could be estimated from the response of the OUR curve in the middle portion of the test since it degrades at a slower rate. Hydrocarbons (S_{CH}) also are degraded slowly since they are adsorbed prior to degradation, so estimates of their concentration can be approximated from the response of the OUR curve as it drops to endogenous levels.

This influent characterization procedure was repeated for each of the soluble organic model components in each batch test. The results of this procedure are tabulated in Table 6.2. The particulate organic components also had to be estimated, but are considered after the initial simulations. For initial model simulations, these fractions were assumed to be zero.

Table 6.2: Influent Stream Fractionation used in Preliminary Simulations

Concen. (mg/L)	STM1	STM2	STM3	STM4	STM5
Total COD[1]	233	348	2152	250000	3318
Sol. COD[1]	216	249	2070	250000	3318
Alcohol[1]	94	0	1502	0	2900
AAP[1]	0	15	0	0	100
Sol. Mixed[1]	73	184	167	0	318
Sol. Inert[1]	50	50	400	0	0
TSS[2]	20	119	99	0	0
Slowly Bio. Part. COD[1]	4	5	29	0	0
Particulate Inert COD[1]	13	95	54	0	0
TKN[3]	5	5	3	0	26
Ammonia[3]	1.5	1	3	0	3
Phosphorus[4]	5	5	5	5	5
Sulphite[5]	25	25	50	5	5

[1] Concentrations in mg COD/L
[2] Concentrations in mg TSS/L
[3] Concentrations in mg N/L
[4] Concentrations in mg P/L
[5] Concentrations in mg S/L

Concentrations of inorganic compounds in the influent also were estimated. Influent TKN concentrations were based on the summation of typical ammonia values measured in the grab samples or in daily monitored data, plus the nitrogen component in the aliphatic amine associated with the influent stream. The phosphorus concentrations were assumed to ensure the system was not P limited and do not reflect any actual measured values.

These influent stream characteristics were input into the GPS-X^{TM} along with the long term average flowrates and model coefficients from the petroleum refinery model to simulate the behaviour of the full-scale plant. This provided initial estimates of the behaviour of the petrochemical system in terms of suspended solids concentrations and more specifically, the biomass concentrations.

With these preliminary estimates, model predictions of the volatile suspended solids (VSS) and total suspended solids (TSS) were compared to measured values to determine if these approximated values found in the actual activated sludge units. These estimates were modified to reflect the actual concentrations measured in the aeration basins in the following manner. The particulate fractions (X_I, X_S) in the influent streams had to be altered until the VSS and TSS concentrations were predicted adequately. Long term average concentrations for each stream were used as a basis for estimating the influent solids measurements (Appendix 4). Simulations indicated that most of the particulate COD in the influent tended to be inert. It was assumeu for purposes of further simulations that the slowly biodegradable particulate fraction of the influent COD was only two percent of the total if solids were present (TSS>0) and zero percent if no solids were present in the influent stream (Table 6.2). These assumptions provided reasonable estimates of VSS and TSS concentrations found in the actual plant.

At this point in the procedure, a number of other parameters were considered. The COD/VSS ratios of the slowly biodegradable particulate and the inert particulate fractions (X_S, X_I) were adjusted. The aim was to obtain model predictions of the sludge COD/VSS ratio which compared to experimental values measured in the aeration tanks. A COD/VSS ratio of 2.3 for the two particulate fractions was found to provide suitable estimates of experimental COD/VSS ratios measured on sludge removed from the aeration basins.

This procedure provided baseline estimates for all the model coefficients and provided initial estimates of system behaviour. Results of these steady state simulations are tabulated in Table 6.3.

The value of the active biomass concentration determined from these preliminary model simulations provided an estimate of the biomass concentrations in the RAS used in the batch tests. By approximating the active biomass likely to be present in the RAS, calibration of the model proceeded more effectively. The next stage in the calibration procedure was to refine these estimates using the batch test response curves.

Table 6.3: Results of the Steady State Simulations on the petrochemical plant using preliminary estimates of stream characteristics and kinetic coefficients. Model predictions are compared to measured values in the full-scale plant which were available.

	VSS (mg/L)		TSS (mg/L)		Heter. (mg/L)	sCOD (mgCOD/L)	
	Model	Actual	Model	Actual	Model	Model	Actual
AT1	2682	1662	4568	2799	627	831	117
AT2	2200	1811	3748	3123	532	126	75
AT3	2201	N/A	3750	N/A	530	80	
AT4	2192	1690	3733	2757	512	65	63
RAS	5463	3624	9256	5845	1269	65	97
Effluent	15.6		26.5		3.6	65	82

6.6 MODEL CALIBRATION USING BATCH TEST DATA

6.6.1 Example to Demonstrate Considerations in Model Calibration

As described previously, the aerobic batch tests were performed by individually mixing each of the influent streams with return activated sludge (RAS) from the petrochemical unit and measuring the response of certain parameters (soluble COD, soluble TKN, OUR). Calibration of the model involved assigning a set of values to the various stoichiometric and kinetic model parameters. The overall outline of the calibration procedure using data from the first set of batch tests has been presented in Section 6.2. As noted there, calibration involved an iterative procedure using the results from all of the six batch tests in the first series. The objective was to determine *a single set of stoichiometric and kinetic parameters* which would provide reasonable predictions of the observed behaviour in all six of the batch tests.

Before discussing the calibration procedure an example of a batch test is presented to illustrate some of the issues in model calibration. For purposes of illustration one of the batch test response curves on Stream 2 is used. Depending on what part of the batch test was being considered, different model coefficients were adjusted. This was because various organic components dominated different parts on the calibration plot. In order to optimize the calibration process it was useful to understand which organic fractions dominated each section of the curve. Figure 6.3 illustrates the four main areas of interest when simulating behaviour in this batch test.

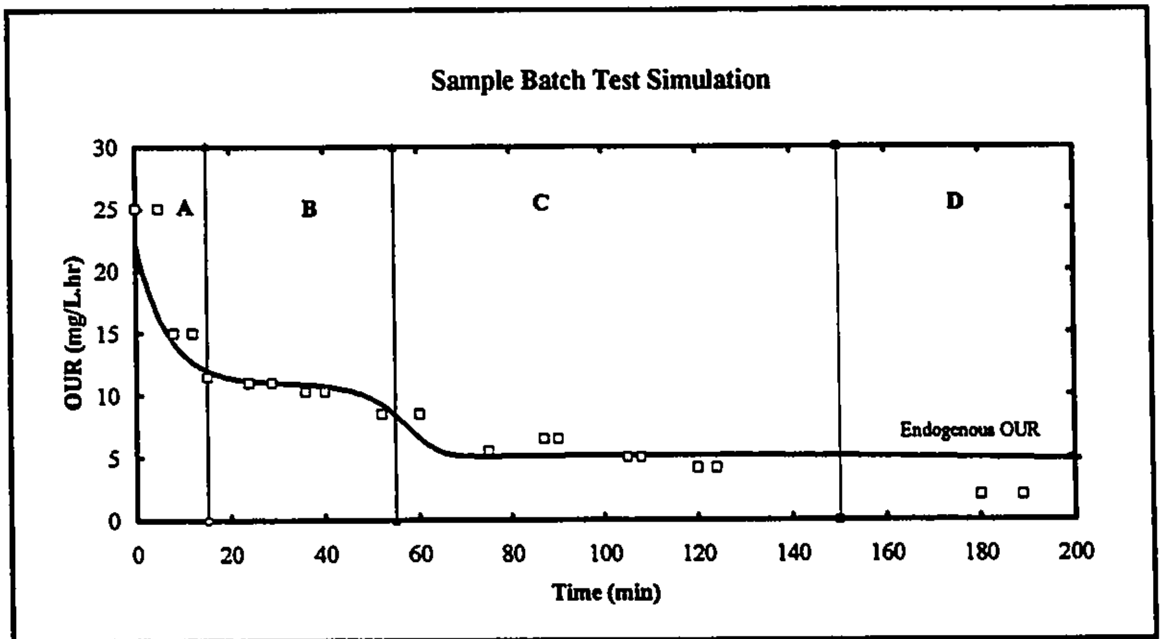

Figure 6.3: A batch test simulation on Stream 2 illustrating the dominating species of COD in different areas of the curve.

In area A of Figure 6.3, the readily biodegradable mixed COD component (S_M) dominated the behaviour of the batch test because it was rapidly utilized. Therefore, while this component was consumed the OUR level was high. Also, in this initial section of the response chemical oxidation of sulphite perhaps contributed to the overall oxygen consumed. Oxidation of reduced sulphur species demands significant oxygen consumption. Both these processes occur rapidly resulting in the high OUR levels. Once these compounds were consumed, the OUR dropped to a lower level.

The next area in the batch test response is indicated by section B. The behaviour in this region was dominated by more slowly biodegradable COD such as alcohol P (S_{AP}) which is present in Stream 2. With an estimate of the concentration of alcohol P, the maximum growth rate on alcohol P was adjusted to correspond to response in this portion of the curve.

Area C on the plot was influenced by a number of factors. As alcohol P (S_{AP}) was present in the stream the shape of the drop in OUR to the lower level was influenced by the half-saturation coefficient of growth of organisms on the alcohol (K_{sPH}). In this situation this parameter was adjusted to correspond to this response. In other tests this region was influenced by the volatile fraction (S_V) in the influent which also tended to be slowly biodegradable. Altering the fraction of volatile COD illustrated this influence in this portion of the curve.

Finally, Area D on the plot corresponds to the endogenous oxygen utilization rate of the organisms. In this portion of the test the only source of organic material is the organism mass itself. All remaining influent organic components have been utilized.

Other factors also influence the overall response of the batch test and should be identified. For example, the presence of hydrocarbon COD (S_{CH}) which acts as slowly biodegradable COD influences the overall OUR in the system. It serves to increase the OUR throughout the latter stages of the test. Its influence is most obvious in Area D of the plot if incorrectly specified. If the hydrocarbon COD is overestimated the model predictions of the OUR in the batch test will be higher than the endogenous levels. This fraction would have to be adjusted accordingly. Furthermore, an incorrect estimate of the inert COD (S_I) in the influent would alter the OUR level in the batch test since this fraction does not consume oxygen. Its greatest influence is indicated by an incorrect estimate of the final COD concentration. Again, modification of the organic fractions during calibration would identify any discrepancies.

The different points identified in the above discussion assisted in determining the best estimates for the model coefficients for the petrochemical model. Understanding which portion of the curve was dominated by which organic component in a particular batch test enabled the constants to be adjusted accordingly.

6.6.2 Estimation of Model Component Concentrations at the Start of the Batch Tests

In order to simulate the response of the batch tests using the GPS-X^{TM} model, it was necessary to specify values of each model component at time zero in the batch test. This posed two types of problem:

- For certain model parameters which were measured directly, such as ammonia (NH_3), the concentration at time zero should have been equal to the value calculated by mixing the RAS and the influent stream, for which individual ammonia measurements had been made. The calculated value and the measured values at time zero did not always match exactly.
- For the COD components, it was necessary to establish the division of the measured soluble COD into model components e.g. S_{AP}, S_{AAP}, etc. However, the individual component concentrations were not measured on the samples used in the batch tests.

In resolving the problem of (1) the differences between the calculated and observed time equal zero values for certain components, and (2) the deficiency in data for individual COD component concentrations, it was necessary to use some reasonable approximation approach. To do this consideration was given to:

- Measurements on the separate influent streams and RAS before mixing;
- Measurements at the start of the batch test;
- Data reported in the plant records for grab samples on the influent streams and RAS for that day.

It was not expected that the grab samples taken by the plant personnel would be equal to the grab samples taken in conjunction with the batch tests due to potential differences in sampling and analysis procedures, and the different sampling times. However, necessarily the composition of the grab samples had to be considered since measurements of individual compounds e.g. aliphatic amine P and alcohol P, were not made on batch test grab samples. For the division of soluble COD into S_{AP}, S_{AAP}, etc. to give the initial composition of each COD component at time zero in the batch test, consideration was given to:

- Typical proportions of each component in the various streams from historical plant records;
- The proportions in the plant grab sample for that day;
- The soluble COD measured on the stream sample used for the batch test;
- Factors such as the proportions of ammonia, soluble TKN, and soluble COD. This could sometimes be used as an indication of S_{AAP} concentrations, for example.

The process of estimating the initial batch test model component concentrations did lead to some anomalies. For example, when the various COD components were added together, the total did not always necessarily match the soluble COD concentration at the start of the batch tests calculated for the mixed RAS and influent stream. It was not possible to resolve all of these differences due to insufficient data and/or experimental error in the measured data. However, it would appear that the procedure which was followed did provide reasonable initial estimates of model component concentrations.

Tables 6.4 to 6.12 tabulate the characteristics of the influent stream assumed in each of the batch tests. Data collected on the various influent streams from all the different information sources is tabulated as well. This was the data used to estimate the initial concentrations of COD and nitrogen model components. As indicated above, some of the differences could not be resolved with available data. Plausible explanations of the deficiencies are presented.

Included in the tables are six categories of measurements. The first two columns provide information on the RAS stream. Column 1 lists measured values on the RAS taken from the different sources. The only assumed value for this stream is the concentration of active biomass present in the batch test. This concentration is the same for each batch test and was determined during the model calibration procedure. The third and fourth columns list the characteristics of the influent streams. The top portion of the table lists the measured values for the influent from various sources. These were measured in terms of bulk parameters such as unfiltered and filtered COD and TKN, although some ammonia values were available. The lower portion of these columns lists the estimated values of the different model components. Any measured data available is indicated in the "Measured" column whereas the values "Assumed" to be present in the influent used in the batch tests are listed in column 4. These values were calculated by taking the component fractions determined during characterization of the batch tests and accounting for the impact of dilution in the batch test. The last two columns (5 and 6) list the characteristics of the batch test mixture of RAS and the influent stream under consideration. Column 5 lists the initial values which should be present in the batch test if the value of the grab sample is assumed, whereas column 6 reflects the values which corresponded more closely to the actual response of the batch test. This is where some of the discrepancies arose. These points should assist in understanding the information presented in the tables.

In terms of units, the biomass measurements are given in mg VSS/L, the total and soluble COD components are measured in terms of mg COD/L, the nitrogen compounds are measured in mg N/L, phosphorus is measured in terms of mg P/L, and sulphur compounds are in units of mg S/L.

Problems with specific influent streams are discussed in the next section. Several general comments should be made, however, with regards to experimental problems:

- Analysis of Stream 4 was very difficult due to the large experimental errors associated with the dilution of the sample to levels which could be measured by the experimental analyses. In order to conduct COD and TKN tests, samples had to be diluted up to four hundred times. As a result, significant errors were introduced into measured values which makes analysis of stream characteristics difficult. For example, any measurement of COD made on high range vials had an error of ±18 mg COD/L. For a dilution of 400 times this automatically introduced an error of 7200 mg COD/L without consideration of any sampling errors. This was evident in the tables.

Table 6.4: Influent characterization of Stream 1 - February 24, 1993

Parameter	**RAS 125 ml**		**INFLUENT STREAM 900 ml**		**BATCH TEST INITIAL CONC.**	
Gross	Measured	Calibrated	Measured	Calibrated	Calculated from Measured Values	Calibrated t = 0
Total TKN	1.69		5.3	10.9		7.5
Sol. TKN	1.69		5.3	9.8	4.88	6.0
NH3	1.83 (3.6)		0.72 (11.8)	1.7	0.86	1.0
Total COD			129	170	121	
Sol. COD	59.7		101	142	98	131
Part. COD			28	28		
Estimated Model Component Concentrations						
Z_{BH}		860.0			104.9	
X_S				0		3.5
X_{CH}				0		
X_I				28		
S_{AP}			(50)	11		10
S_{AAP}			(8.4)	11		10
S_{PH}			(0.2)	0		0
S_V				11		10
S_M				2.8		2.5
S_{CH}				68		60
S_I				36		38
X_{ON}				1.1		1.5
S_{NH}				1.7		1.0
S_{ON}				5.7		5.0
S_P						5.0
S_{SR}				3.4		3.0

NOTES: **(1) Shaded area indicates the influent fractionation assumed for the batch test.**

(2) Bracketed values indicate values measured by petrochemical plant and recorded in daily records.

Table 6.5: Influent characterization of Stream 2 - February 25, 1993

Paramcter	RAS 125 ml		STREAM 850 ml		BATCH TEST INITIAL CONC.	
Gross	Measured	Calibrated	Measured	Calibrated	Calculated from Measured Values	Calibrated t = 0
Total TKN	1.37		3.6	5.8	3.31	5.0
Sol. TKN	1.34		3.5	3.5	3.05	3.0
NH3	0.58 (0.6)		2.35 (1.6)	2.3		2.0
Total COD			180	150		
Sol. COD	55.0		172	150	155	138
Part. COD				0		
Estimated Model Component Concentrations						
Z_{BH}		860.0			110.3	
X_S				0		3.7
X_{CH}				0		
X_I				0		
S_{AP}			(0)	0		0
S_{AAP}			(0)	0		0
S_{PH}				0		0
S_V			(146)	63		55
S_M				20		18
S_{CH}				23		20
S_I				44		45
X_{ON}				2.3		2.0
S_{NH}				2.3		2.0
S_{ON}				1.2		1.0
S_P						5.0
S_{SR}				3.4		3.0

NOTES:
(1) Shaded area indicates the influent fractionation assumed for the batch test.
(2) Bracketed values indicate values measured by petrochemical plant and recorded in daily records.

Table 6.6: Influent characterization of Stream 2 - June 16, 1993

Parameter	**RAS 125 ml**		**STREAM 850 ml**		**BATCH TEST INITIAL CONC.**	
Gross	Measured	Calibrated	Measured	Calibrated	Calculated from Measured Values	Assumed t = 0
Total TKN			6.9	5.9		5.0
Sol. TKN	1.06		6.3	4.7	5.5	4.0
NH3	(0.1)		(3.8)	3.5		3.0
Total COD			474	252		
Sol. COD	119.2		435	213	3886	188
Part. COD						
Estimated Model Component Concentrations						
Z_{BH}		860.0			129	
X_S				0		4.4
X_{CH}				0		
X_I				39		
S_{AP}			(0)	0		0
S_{AAP}			(0)	0		0
S_{PH}			(0)	0		0
S_V			(75)	88		75
S_M				3		2.5
S_{CH}				12		10
S_I				110		100
X_{ON}				1.2		1.0
S_{NH}				3.5		3.0
S_{ON}				1.2		1.0
S_P						5.0
S_{SR}				3.5		3.0

NOTES: (1) Shaded area indicates the influent fractionation assumed for the batch test.
(2) Bracketed values indicate values measured by petrochemical plant and recorded in daily records.

Table 6.7: Influent characterization of Stream 3 - February 24, 1993

Parameter	**RAS 700 ml**		**STREAM 100 ml**		**BATCH TEST INITIAL CONC.**	
Gross	Measured	Calibrated	Measured	Calibrated	Calculated from Measured Values	Calibrated t = 0
Total TKN	1.69		37.5	23.2	6.2	4.5
Sol. TKN	1.69		36.8	15.2	6.0	3.5
NH3	1.83 (3.6)		34.8 (42)	7.2	5.9	2.5
Total COD			2023	2354		
Sol. COD	59.7		1831	2162	281	314
Part. COD						
Estimated Model Component Concentrations						
Z_{BH}						
X_S				0		25.4
X_{CH}				0		
X_I				192		
S_{AP}			(2900)	1440		180
S_{AAP}			(6)	0		0
S_{PH}				0		0
S_V				0		0
S_M				160		20
S_{CH}				560		70
S_I				2		44
X_{ON}				8.0		1.0
S_{NH}				7.2		2.5
S_{ON}				8.0		1.0
S_P						5.0
S_{SR}				0		0.0

NOTES: (1) Shaded area indicates the influent fractionation assumed for the batch test.
(2) Bracketed values indicate values measured by petrochemical plant and recorded in daily records.

Table 6.8: Influent characterization of Stream 3 - June 15, 1993

Parameter	**RAS 900 ml**		**STREAM 100 ml**		**BATCH TEST INITIAL CONC.**	
Gross	Measured	Calibrated	Measured	Calibrated	Calculated from Measured Values	Calibrated t = 0
Total TKN			14.8	8.2		2.0
Sol. TKN	1.35		14.2	8.2	2.64	2.0
NH3	(0.2)		(16)	8.2		1.0
Total COD			690	403		
Sol. COD	97.6		637	350	152	125
Part. COD						
Estimated Model Component Concentrations						
Z_{BH}		860			774	
X_S				0		26.1
X_{CH}				0		
X_I				53		
S_{AP}			(52)	100		10
S_{AAP}				0		0
S_{PH}				0		0
S_V				0		0
S_M				100		10
S_{CH}				100		10
S_I				60		95
X_{ON}				0		0
S_{NH}				8.2		1.0
S_{ON}				N/A		1.0
S_P						5.0
S_{SR}				0.0		0.0

NOTES: (1) Shaded area indicates the influent fractionation assumed for the batch test.
(2) Bracketed values indicate values measured by petrochemical plant and recorded in daily records.
(3) N/A indicates that reasonable values could not be determined.

Table 6.9: Influent characterization of Stream 4 - February 25, 1993

Parameter	**RAS 940 ml**		**STREAM 5 ml**		**BATCH TEST INITIAL CONC.**	
Gross	Measured	Calibrated	Measured	Calibrated	Calculated from Measured Values	Calibrated t = 0
Total TKN	1.37		513	1054		7.0
Sol. TKN	1.34		490	776	4.2	5.5
NH3	0.58 (0.6)			76		1.0
Total COD			138000	151000		
Sol. COD	71.5		133000	146000	757	820
Part. COD						
Estimated Model Component Concentrations						
Z_{BH}		860			855	
X_S				0		29
X_{CH}				0		
X_I				5200		
S_{AP}				0		0
S_{AAP}				0		0
S_{PH}				123000		650
S_V				0		0
S_M				13200		70
S_{CH}				9500		50
S_I				50		50
X_{ON}				278		1.5
S_{NH}				76		1.0
S_{ON}				700		4.5
S_P						5.0
S_{SR}				0		0.0

NOTES: (1) Shaded area indicates the influent fractionation assumed for the batch test.
(2) Bracketed values indicate values measured by petrochemical plant and recorded in daily records.

Table 6.10: Influent characterization of Stream 4 - June 15, 1993

Parameter	**RAS 1900 ml**		**STREAM 1 ml**		**BATCH TEST INITIAL CONC.**	
Gross	Measured	Calibrated	Measured	Calibrated	Calculated from Measured Values	Calibrated t = 0
Total TKN			560	N/A		6.0
Sol. TKN	1.35		510	N/A	1.86	1.0
NH3	(0.2)			N/A		1.0
Total COD			190000	205000		
Sol. COD	103		198000	205000	301	305
Part. COD						
Estimated Model Component Concentrations						
Z_{BH}		860			859	
X_S				0		29
X_{CH}				0		
X_I				0		
S_{AP}				0		0
S_{AAP}				0		0
S_{PH}				185000		185
S_V				0		0
S_M				20000		20
S_{CH}				0		0
S_I				0		100
X_{ON}				N/A		5.0
S_{NH}				0		1.0
S_{ON}				N/A		0.0
S_P						5.0
S_{SR}				0		0.0

NOTES:

(1) Shaded area indicates the influent fractionation assumed for the batch test.

(2) Bracketed values indicate values measured by petrochemical plant and recorded in daily records.

(3) N/A indicates that reasonable values could not be determined due to large dilution factors.

Table 6.11: Influent characterization of Stream 5 - February 26, 1993

Parameter	RAS 940 ml		STREAM 100 ml		BATCH TEST INITIAL CONC.	
Gross	Measured	Calibrated	Measured	Calibrated	Calculated from Measured Values	Calibrated t = 0
Total TKN	3.4		260.5	81.3		8.5
Sol. TKN	0.72		109	81.3	11.1	8.5
NH3	0.71 (0.8)		(8.0)	10	1.4	1.0
Total COD	94.9		918	1284		
Sol. COD	61		882	1247	145.5	175
Part. COD						
Estimated Model Component Concentrations						
Z_{BH}		860			777	
X_S						
X_{CH}				0		26.2
X_I				37		
S_{AP}			(262)	624		60
S_{AAP}			(131)	0		0
S_{PH}			(43)	0		0
S_V				0		0
S_M				364		35
S_{CH}				0		0
S_I				259		80
X_{ON}				0		0.0
S_{NH}				10		1.0
S_{ON}				71.3		7.5
S_P						5.0
S_{SR}				0		0.0

NOTES: **(1) Shaded area indicates the influent fractionation assumed for the batch test.**

(2) Bracketed values indicate values measured by petrochemical plant and recorded in daily records.

Table 6.12: Influent characterization of Stream 6 - June 16, 1993

Parameter	**RAS** **900 ml**		**STREAM** **85 ml**		**BATCH TEST** **INITIAL CONC.**	
Gross	Measured	Calibrated	Measured	Calibrated	Calculated from Measured Values	Calibrated t = 0
Total TKN			104.3	231.6		
Sol. TKN	1.06		93.3	231.6		21
NH3				220		20
Total COD			2077	2359		
Sol. COD	122.4		1958	2240	277	305
Part. COD						
Estimated Model Component Concentrations						
Z_{BH}		860			786	
X_S				0		27
X_{CH}						
X_I				119		
S_{AP}				0		0
S_{AAP}				0		0
S_{PH}				0		0
S_V				116		10
S_M				232		20
S_{CH}				1160		100
S_I				732		175
X_{ON}				0		0.0
S_{NH}				220		20.0
S_{ON}				11.6		1.0
S_P						5.0
S_{SR}				0		0.0

NOTES: **(1) Shaded area indicates the influent fractionation assumed for the batch test.**

(2) Bracketed values indicate values measured by petrochemical plant and recorded in daily records.

- Problems with the dilution of samples also was apparent when analysing other high strength influent streams such as Streams 3, 5, and 6, but to a lesser extent. The high strength of these wastewaters necessitated that samples had to be diluted significantly for analysis procedures. This introduced increased experimental error to the measured values and made resolution of the model components more difficult.
- In conducting the analyses of TKN there were difficulties with the analytical procedures. While the samples were being digested, there was extensive foaming of the samples. It was difficult to determine if any sample was lost as a result of the foaming, but it did introduce potential uncertainty in the TKN readings.

These points explain some of the experimental limitations in the characterization of the influent streams. Other reasons relating to the model development are identified in the next section. Despite these discrepancies, the procedure did provide reasonable estimates of the influent composition so that the model could be calibrated.

6.6.3 Calibration Against Batch Test Responses

This section presents the experimental results for each of the six batch tests used to calibrate the model together with model predictions for the three observed parameters: oxygen utilization rate (OUR), filtered COD, and filtered TKN. To calibrate properly the model using the batch tests, information on the full-scale plant operation was required (plant SRT, the volatile suspended solids concentrations in the reactors, and effluent COD) to assist in determining the active biomass concentration in the RAS resulting from treatment of wastewaters at the flowrates and loadings characteristic of that period. Therefore, it was necessary to have full-scale data which was measured at the same time as the batch tests were conducted. For this calibration procedure, batch tests conducted in February were used for model calibration and complimented with data on full-scale plant operation during February. For two influent streams it was necessary to make exceptions to this procedure and utilize batch response data from the June test period. The reasons for selecting these particular batch test results are discussed in the relevant sections, but for purposes of model calibration it was assumed that using this data would have negligible impact on overall system response because of the low flowrates associated with each stream. The results are presented in Figures 6.4 to 6.9. The solids lines in each figure represent the calibrated model predictions of response.

The main purpose of this section is to discuss the response in each batch test of the first series, comparing the observed and predicted behaviour. The following section (6.7) presents the results of the verification phase where the calibrated model was applied to prediction of the response observed in the second series of batch tests. A comprehensive discussion of the magnitudes of the stoichiometric and kinetic parameters is presented later in Sections 6.8 and 6.9, respectively.

Stream 1: The experimental results of the batch test on Stream 1 are illustrated in Figure 6.4. Plots are presented which show the changes in OUR, filtered COD, and filtered TKN during the test. The model predictions compare reasonably well to observed values. Characterization of the wastewater indicated that all the model components contributed to the loading of this stream and needed to be considered during model calibration.

The OUR curve dropped rapidly in the initial stages. The final OUR level predicted by the model corresponds closely to that in the actual system. Similarly, the COD decline of the batch tested was followed appropriately by the model, as well as the slight accumulation of TKN in the system. This accumulation was likely due to the addition of nitrogen to the system through organism decay at a rate faster than that utilized by the biomass for growth processes. The hydrolysis of the aliphatic amine P may also have contributed to this slight increase in TKN/ammonia. The experimental system indicated a bit more accumulation of nitrogen than the model, but in general the experimental results from the batch tests were predicted adequately by selecting appropriate values of model coefficients.

Stream 2: Figure 6.5 illustrates the results of the batch test conducted on Stream 2 in terms of the change in OUR, COD, and TKN. The wastewater characterization indicated that this stream is composed of mixed COD, volatile COD, hydrocarbons, and inert COD. This information assisted in determining the fractions of the different components and their associated kinetics.

The initial drop in OUR reflected the use of the mixed COD component, while the next step change reflected the use of the remaining COD (volatile and hydrocarbon). Once all these COD components were consumed, the OUR dropped to endogenous levels. The model predictions matched the experimental results with the exception of the final OUR level which was overestimated by the model. This may be a result of slightly overestimating the fraction of the hydrocarbon COD component or underestimating its utilization rate, both which could cause the OUR to remain above endogenous levels for longer than expected. In general, the model predictions of the OUR correspond closely to the OUR of the experimental system.

The COD response curve predicted by the model followed the drop in COD monitored in the experimental system. There appeared to be slightly more COD removed initially from the laboratory system than the model predicted. This could be a result of more volatile COD being removed from the batch test than accounted for in the model. Since the OUR of the system is predicted adequately this was likely the situation.

Finally, the TKN changes in the experimental system responded rather differently than the model predicted. The actual response suggested an accumulation of TKN was occurring in the batch test which the model did not mimic. There appears to be a process or source of nitrogen which is not accounted for in the model i.e. perhaps the presence of a compound similar to the aliphatic amine which releases ammonia. Additional information would be necessary to determine the exact nature of this discrepancy. This point illustrates the fact that any model formulation is a building process; the key removal processes are identified and supporting processes continually are being refined.

Stream 3: Figure 6.6 illustrates the results of the batch test operated with Stream 3 and the corresponding model predictions. This stream consisted mainly of the alcohol P COD. Adjusting the growth rate and half-saturation constant for this component enabled the model predictions indicated in Fig. 6.6 to be attained. The change in OUR of the batch test was monitored adequately in the model. Adjusting the growth rate allowed the OUR level in the middle of the test to be quantified. The final step change was modelled by altering the half-saturation constant until the model corresponded to the experimental response. The model also predicted the appropriate drop in total filtered COD. The slight deviation in COD values about the 40 minute mark was likely a result of more volatile

COD being stripped from the system than the model predicted. As was the case with the petroleum refinery system, quantifying the fraction and kinetics of the volatile organic COD is an important step in correctly predicting system behaviour.

The TKN change in this system suggested an inadequacy in the model formulation which has already been identified in the petroleum refinery application i.e. the need to include an unbiodegradable soluble TKN fraction among the nitrogen components. For this test, the current response predicted by the model matches the pattern generated in the batch test, but at a lower concentration. Therefore, it appeared that the rate at which the TKN was consumed was predicted adequately by the model. If the assumed concentrations of nitrogen present in the influent were increased, the pattern of the response curve was altered and did not match the actual response. These observations are potentially the result of an unbiodegradable fraction of TKN measured in the influent which is utilized in the model system, but which is not actually available in the laboratory test. By assuming in the model that all the measured TKN in the laboratory is biodegradable the situation illustrated in Figure 6.5 arises. This further illustrates the importance of including an unbiodegradable soluble fraction of TKN in the influent streams rather than simply assuming that it passes through the system unchanged with no impact on system behaviour.

Stream 4: The results of a batch test conducted with Stream 4 is illustrated in Figure 6.7. The data presented in these plots was collected in the June test period. These plots indicate the inhibitory nature of the phenolics compounds when present at high concentrations which the data collected in February did not clearly illustrate. In February, the sample volume of influent Stream 4 for the biomass present in the batch test was too large so the inhibition affects could not be monitored. Therefore, to establish the kinetic constants associated with inhibitory growth processes it was necessary to use the June response data. It was assumed that this approach was justified since Stream 4, although highly concentrated, is a low flow stream, and changes in stream characteristics would not have a significant influence on the overall behaviour of the full-scale plant in terms of biomass concentration. Biomass concentration is the main parameter required from full scale-operation for the calibration procedure.

As indicated previously, growth on inhibitory compounds can be represented by the Haldane equation. The response associated with the Haldane equation was evident in this batch test with the activity of the organisms (indicated by the drop in OUR) decreasing initially with the high concentrations of phenolic COD. This was a result of the phenolic compounds inhibiting growth processes, and therefore less oxygen being consumed. Once the phenolic COD concentration dropped there was less inhibition, and the OUR gradually increased indicating increased biodegradation. As the phenolics concentration continued to drop below inhibitory levels, the growth processes could proceed at maximum rates. Therefore, the OUR increased rapidly to a maximum rate as the remaining phenolic material was consumed. Once the phenolics were utilized, the OUR dropped rapidly to endogenous levels. By adjusting the growth rate on phenolic COD, the half-saturation constant, and the inhibition coefficient the shape of the curve can be altered to generate an OUR response which best approximates the experimental results. The model prediction plotted in Figure 6.7 was the best compromise.

The COD drop in phenolics was predicted adequately by the model. Both the experimental results and the model indicated a gradual decline in COD. The TKN concentrations predicted by the model varied somewhat from the experimental results, the main problem being data scatter. It is difficult to determine from the given data exactly what is occurring so an estimate had to be assumed. The current model prediction indicates the accumulation of TKN, while potentially, the actual batch test response could reflect a more constant concentration. [Towards the end of the test, however, there seems to be a slight increase in TKN.] Assuming the model does reflect system response, the system behaviour can be explained as follows. The degradation process continues throughout the batch test which would release nitrogen to the liquid. If growth is occurring at a decreased rate due to inhibition influences, then less TKN than expected would be used resulting in an accumulation. Also, the presence of a certain amount of particulate nitrogen was assumed which must be hydrolysed to the soluble form prior to use. Each of these processes would contribute to the pool of soluble nitrogen.

Stream 5: The batch test conducted with the trucked wastewater stream (Stream 5) is illustrated in Figure 6.8. The difficulty with this stream is that it is constantly changing in composition so determination of its influent characteristics on any given day were extremely important for proper calibration of this batch test. Mixed COD (S_M) and the alcohol P COD (S_{AP}) were established as the main organic components in the stream on the testing day. Based on this assumption, the model predictions of the OUR, COD, and TKN were reasonably accurate when compared to the experimental response. There is some uncertainty in the initial stages of the OUR response when the experimental response and model estimates are compared. The initial high level may be overestimated based on the first two data points, but it follows the remaining points effectively. The initial discrepancy may be a result of inappropriate selection of influent components and neglecting to include the removal process associated with the compound in the model. Without more detailed data this discrepancy cannot be resolved.

The drop in TKN and COD was predicted by the model. The slight overestimation of the TKN at time zero may be a result of measuring the TKN on the pure influent stream rather than the mixture of RAS and influent. This created a potential source of experimental error which needed to be considered during analysis of these results. Despite the uncertainty in the specific influent composition, the model provided good overall estimation of the batch test response.

Stream 6: Figure 6.9 illustrates the OUR, COD, and TKN response during a batch test of a latex stream (Stream 6) which is piped from an off-site facility. This stream had a significant fraction of inert COD, along with mixed, volatile, and hydrocarbon COD. The batch test on this influent was conducted in June since this was the only information available on this stream. Stream 6 was not being treated by the plant during the February test period. Again, since this stream is a low flow stream it would not significantly influence the overall solids production in the treatment plant. Use of this data for model calibration could be assumed with negligible impact.

The pattern generated by the change in OUR during the batch test was predicted by the model with the OUR initially being high, followed by a slow, gradual drop to the endogenous levels. The initial COD drop was slightly overestimated by the model, however. One potential explanation for this discrepancy is that the volatile COD fraction in the influent is greater than estimated or it is not being stripped as quickly as predicted by the model. Since the OUR curve is adequately predicted, the discrepancy is likely related to the volatilization rate.

The TKN predicted by the model slightly underestimates the consumption rate of nitrogen in the batch test. This may be related to the overpredicted drop in COD i.e. the loss of COD is connected to the loss of TKN. Potentially, there is a process occurring in the actual batch test not accounted for in the model. As in any initial modelling efforts, further analysis of the system will refine the model to predict these slight discrepancies.

6.7 MODEL VALIDATION USING SECOND SET OF BATCH TEST DATA

Using the first set of batch tests presented in Section 6.6, the stoichiometric and kinetic parameters in the model were estimated. The next stage in the process was to verify that the constants which were selected were capable of predicting system behaviour under a different set of conditions. This involved obtaining data on batch tests on wastewater from a second set of conditions i.e. the activated sludge system is operating under different conditions such as a change in loading. The batch tests run in June were used for this purpose, with the exception of Stream 4. The data collected during February was used for Stream 4 since the June data was used for calibration. The same justification was applied i.e. the impact of changes to stream characteristics on overall biomass production is minimal. Figures 6.10 to 6.12 illustrate the application of the calibrated model to these batch tests. The following discussion presents the results of this procedure.

Stream 2: A second batch test was performed using influent Stream 2 and the results are illustrated in Figure 6.10. The OUR curve is predicted with reasonable accuracy. The model simulates the rapid drop in OUR at the beginning of the test which was associated with the oxidation of sodium meta-bisulphite and some mixed COD. The rate of oxygen consumption then was maintained at a fairly consistent level in both the laboratory test and in the model simulation.

The COD changes predicted by the model indicated a discrepancy with the experimental results. The model underestimated the drop in COD when compared to the actual batch test. Since the appropriate OUR pattern was simulated in the model, one possible explanation for this discrepancy is that there is a large component of the influent soluble COD which is adsorbed onto the sludge, but is not actually utilized. This would result in the COD of the batch test dropping rapidly as observed in the experiment, but not

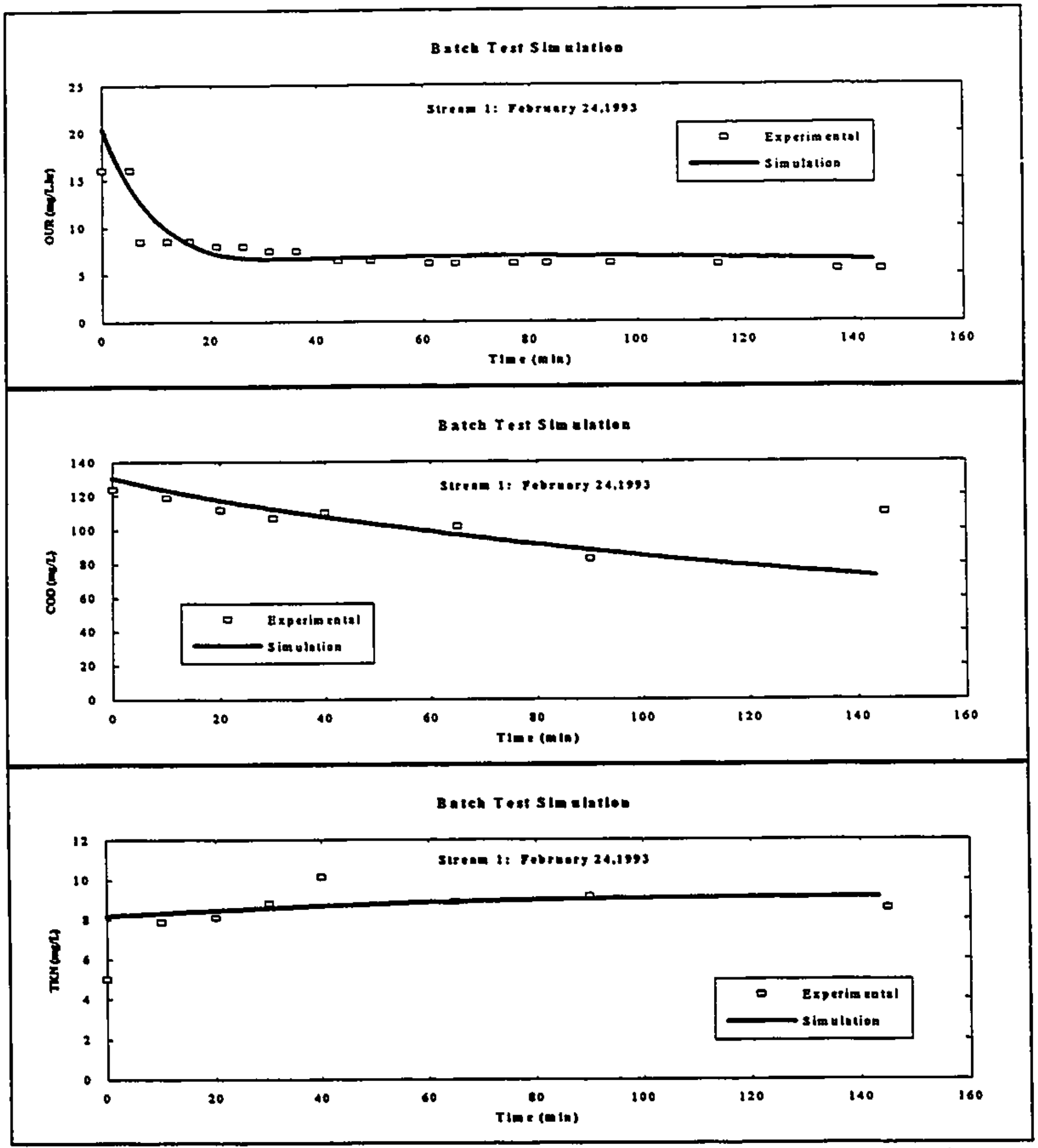

Figure 6.4: The results of the batch test on Stream 1 (February 24, 1993) are illustrated. OUR, COD, and TKN were monitored during the batch test and the model parameters adjusted until model simulations predicted the experimental results. The predicted responses of the batch tests simulated in the GPS-X^{TM} model are indicated by the solid line on the plots above.

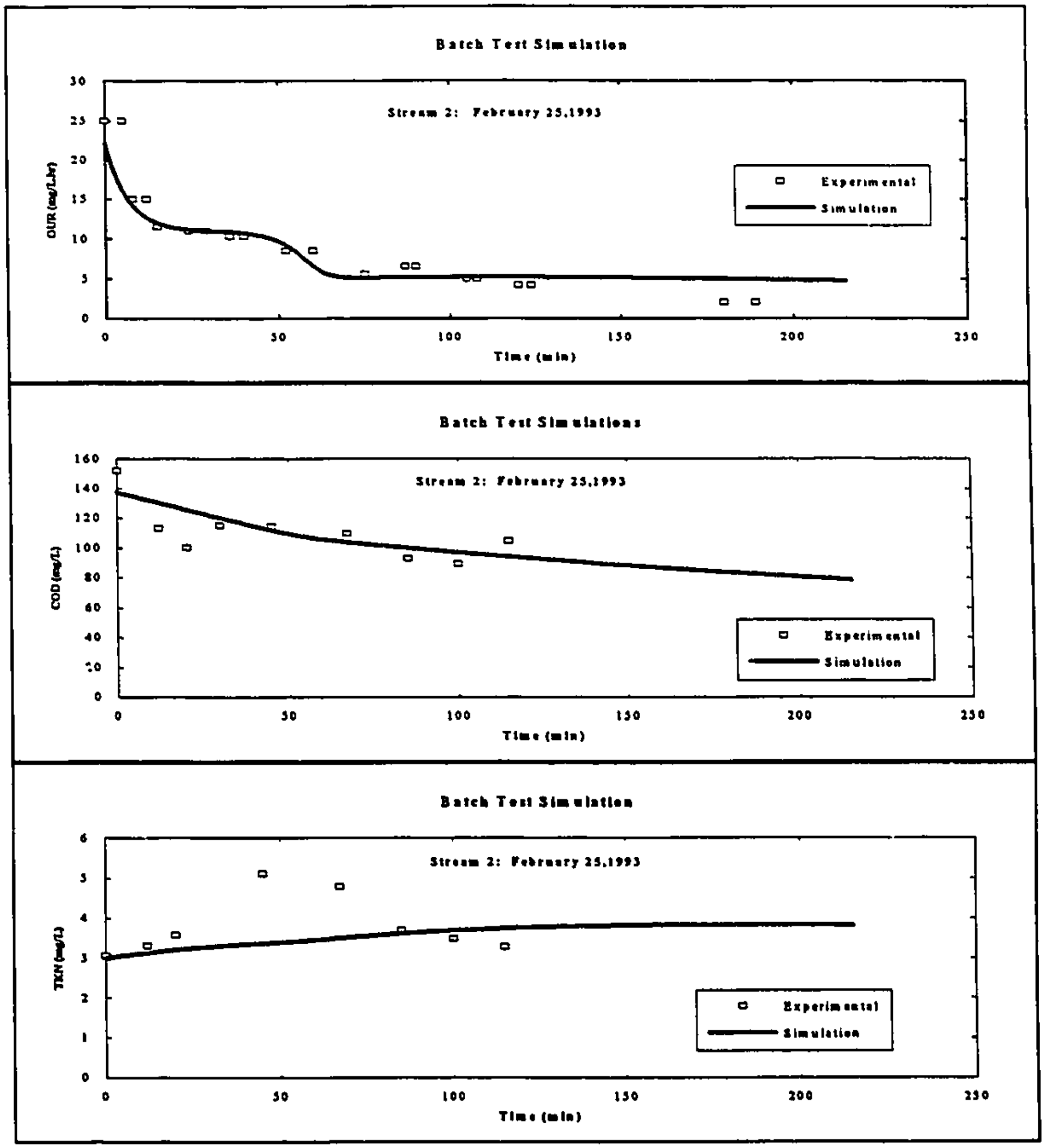

Figure 6.5 : The results of the batch test on Stream 2 (February 25, 1993) are illustrated. OUR, COD, and TKN were monitored during the batch test and the model parameters adjusted until model simulations predicted the experimental results. The predicted responses of the batch tests simulated in the GPS-X^{TM} model are indicated by the solid line on the plots above.

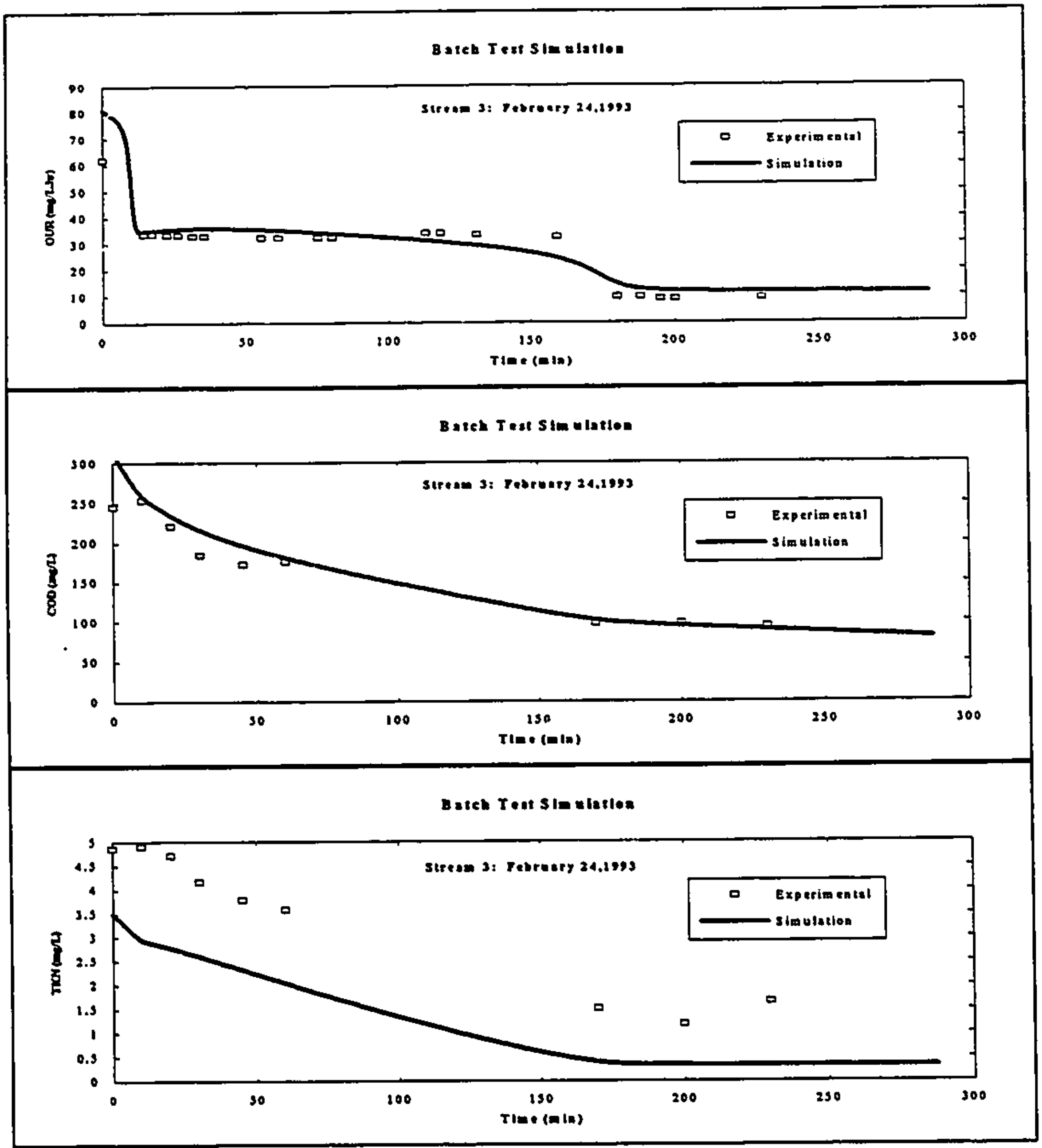

Figure 6.6: The results of the batch test on Stream 3 (February 24, 1993) are illustrated. OUR, COD, and TKN were monitored during the batch test and the model parameters adjusted until model simulations predicted the experimental results. The predicted responses of the batch tests simulated in the GPS-X^{TM} model are indicated by the solid line on the plots above.

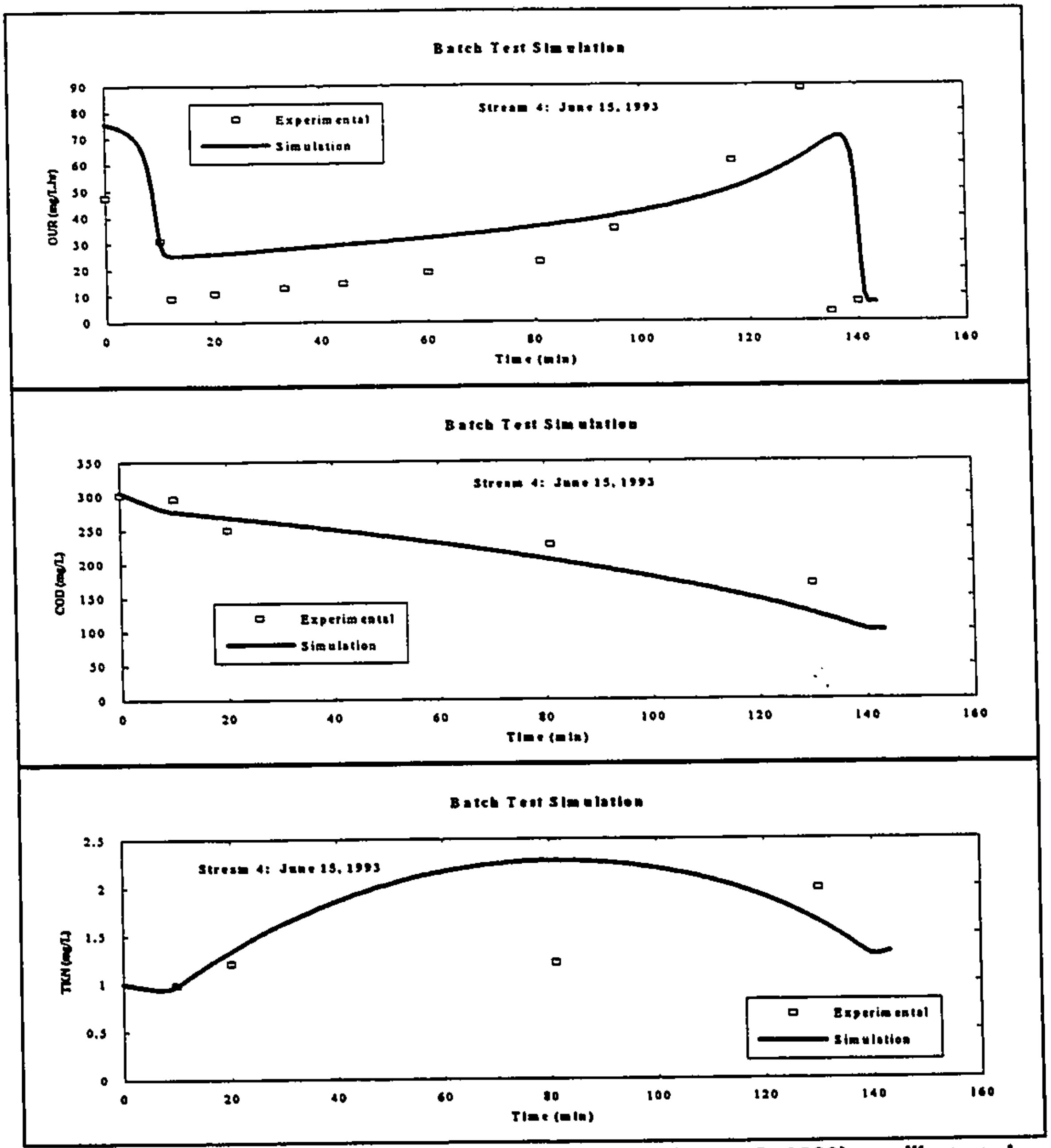

Figure 6.7: The results of the batch test on Stream 4 (June 15, 1993) are illustrated. OUR, COD, and TKN were monitored during the batch test and the model parameters adjusted until model simulations predicted the experimental results. The predicted responses of the batch tests simulated in the GPS-X^{TM} model are indicated by the solid line on the plots above.

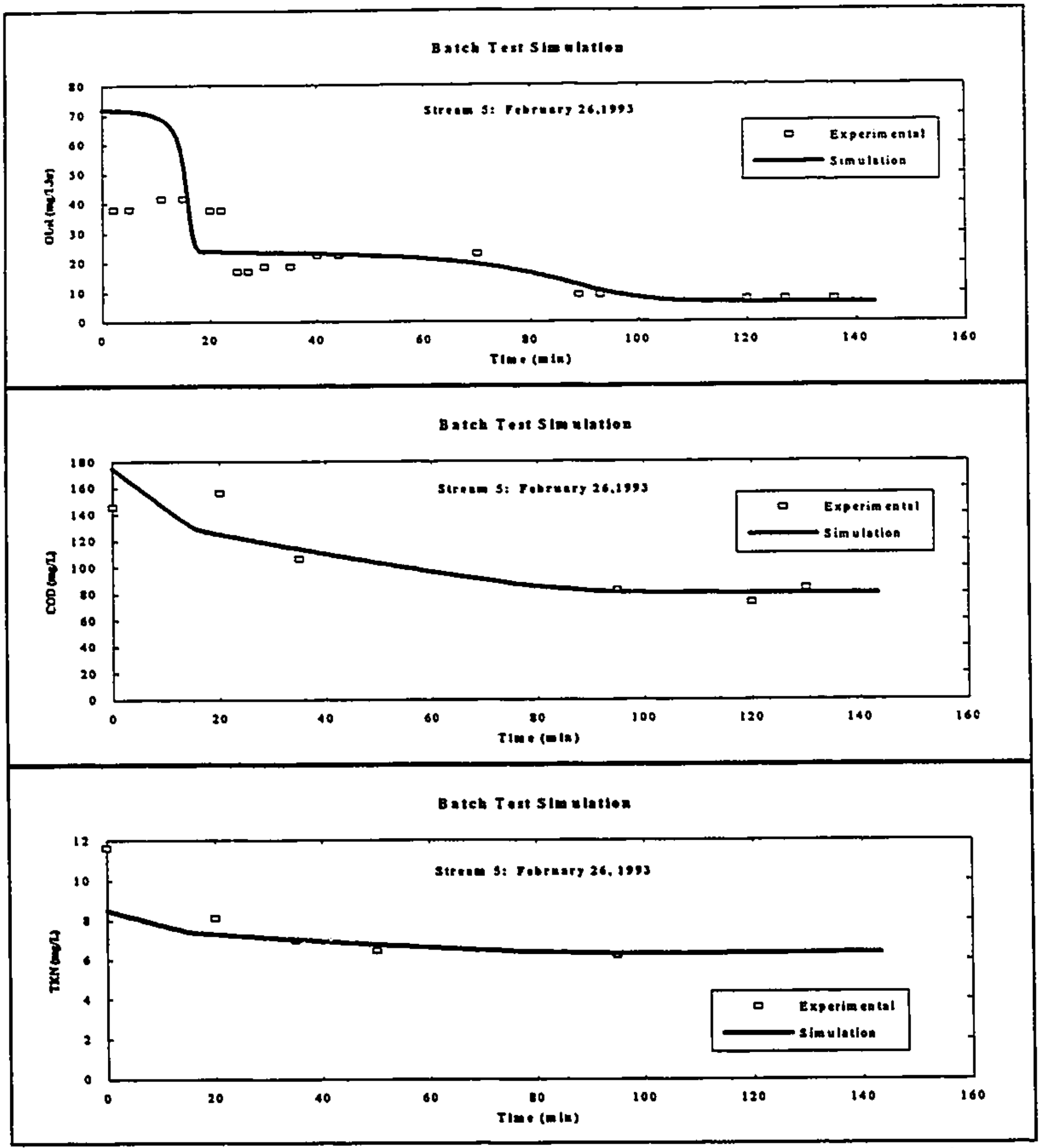

Figure 6.8: The results of the batch test on Stream 5 (February 26, 1993) are illustrated. OUR, COD, and TKN were monitored during the batch test and the model parameters adjusted until model simulations predicted the experimental results. The predicted responses of the batch tests simulated in the GPS-X^{TM} model are indicated by the solid line on the plots above.

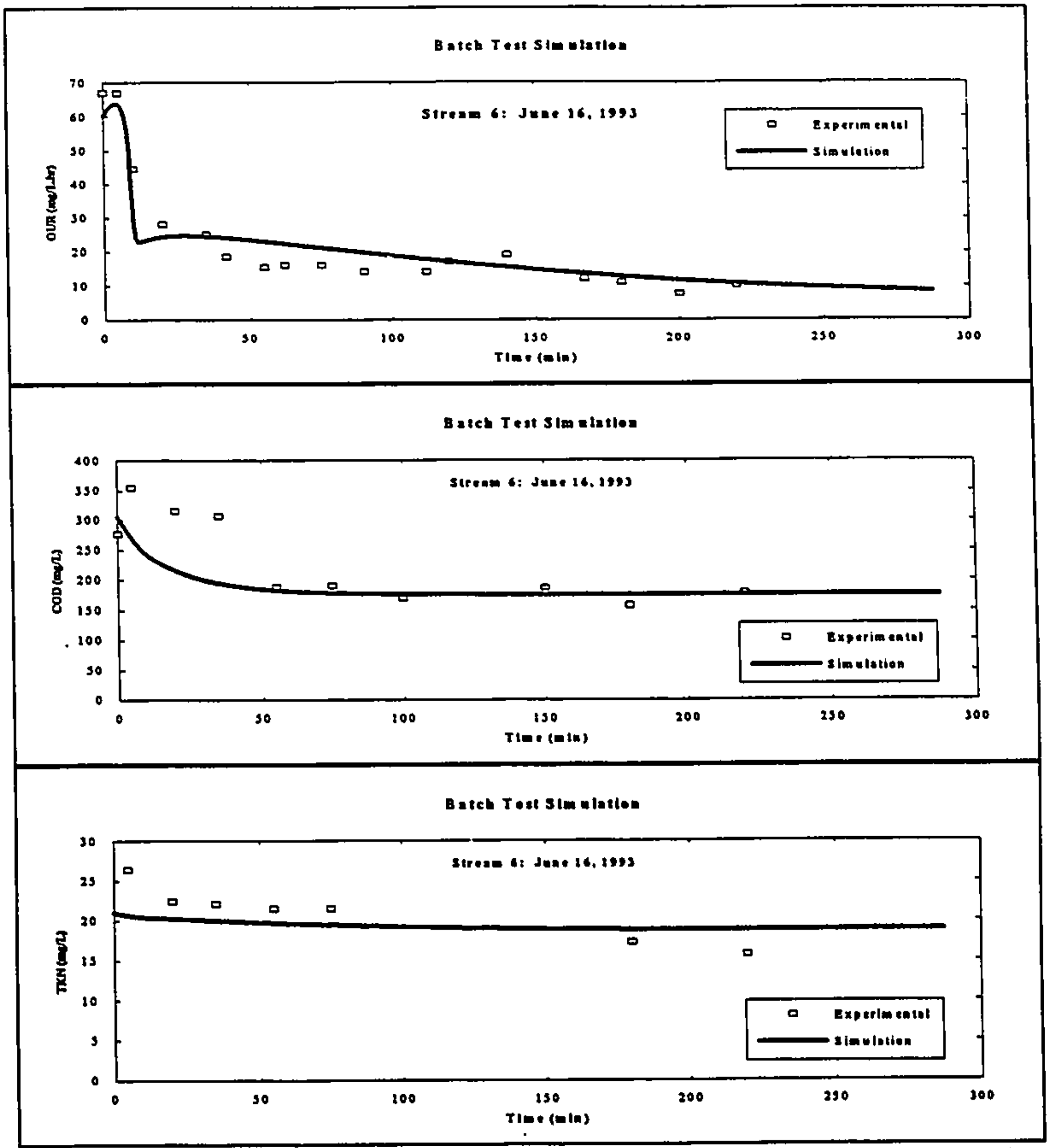

Figure 6.9: The results of the batch test on Stream 6 (June 16, 1993) are illustrated. OUR, COD, and TKN were monitored during the batch test and the model parameters adjusted until model simulations predicted the experimental results. The predicted responses of the batch tests simulated in the GPS-X^{TM} model are indicated by the solid line on the plots above.

modelled accordingly, while the model predictions follow the observed values of the OUR response curve.

There was also the possibility that a volatile COD component was being stripped from the system that was not considered in the model. For purposes of calibration it was assumed that one particular VOC was the main volatile component as identified by the VOC study. The behaviour of the batch test suggested that perhaps another volatile compound should be considered. The final COD estimated by the model was predicted successfully, indicating that the remaining processes monitored in the model are appropriate.

Finally, the TKN in this batch test illustrates the same discrepancy between model predictions that was identified in the initial batch test on Stream 2. There appears to be some accumulation of filtered TKN initially in the batch test which is not predicted by the model. Again this may be related to the hydrolysis of the aliphatic amine or some similar compound present in the system. For example, the process may be releasing ammonia faster than the nitrogen can be utilized. There is also the possibility that another reaction is associated with this influent batch which should specifically be considered when modelling this stream behaviour. However, the initial and final TKN concentrations are predicted adequately by the model suggesting the overall mechanisms adequately represent system behaviour. The subtle changes in system behaviour require more detailed experimental work.

Stream 3: Figure 6.11 presents the results of the second trial using Stream 3 in the batch test. The OUR, COD, and TKN changes predicted by the model generally reflected the changes monitored during the experiment. These observations suggest that the process equations and values selected for the different model coefficients associated with alcohol P are adequate for representing the growth processes on this compound.

One comment should be noted based on observations made during calibration of the petrochemical model. It was evident from batch test simulations that the organism growth on Stream 3 was very close to being nitrogen limited. Using the model for the June 15, 1993 test, it was apparent that organism growth in the batch test was potentially nitrogen limited. If insufficient nutrients were present then the biodegradable COD could not all be utilized. This situation would influence the apparent biodegradable COD in the batch system. Observations such as this illustrate the advantages of modelling as a diagnostic tool for these systems.

Stream 4: The results of another batch test operated using the phenolics stream (Stream 4) are illustrated in Figure 6.12 and indicate that the model is successful at predicting the changes in OUR, COD, and TKN associated with growth processes on this compound. The OUR at the beginning of the test is slightly underestimated by the model. In the actual batch test the presence of an easily degradable compound in the wastewater could have caused this slightly higher OUR. The model predictions quickly aligned with the experimental results once this initial compound was consumed. This suggests that in general the model was capable of simulating the behaviour of the actual system.

One other comment which should be made is the discrepancy in the initial TKN reading. As mentioned earlier, the initial readings were taken on the pure influent sample rather than a filtered sample directly from the batch test. The actual measurement in the mixture of RAS and influent may be slightly different. Therefore, the initial reading at time zero had an inherent error so that if it was somewhat different than the remaining samples it was not a major concern. The remaining portion of the TKN curve was predicted successfully in model simulations.

The discussion presented above illustrates the ability of the model of the petrochemical activated sludge model to simulate the overall behaviour of such a system treating wastewaters generated at a petrochemical facility. As is the case with all models, however, some of the subtle changes are difficult to account for especially when the systems are prone to the dynamics associated with the operation of a full-scale industrial system. This situation is magnified when trying to simplify a model to account for the multitude of components associated with any petrochemical facility. In analysing the application of the model predictions it was evident that the major trends in the petrochemical activated sludge system could be tracked with reasonable accuracy using the model. This suggests that the model developed for the petrochemical system activated sludge system based on the petroleum refinery model was adequate for predicting system behaviour. It was difficult to track some of the minor changes in system behaviour, but the overall behaviour was adequately represented. In order to identify some of these changes more experimental studies would have to be conducted. The aim with this portion of the research was to illustrate that with limited experimentation a model could be developed which adequately predicted the behaviour of the petrochemical system. The graphs presented throughout the discussion illustrated that the changes in OUR, COD, and TKN which occurred during batch tests of the different streams can be simulated successfully using the model formulated to represent this particular activated sludge system.

The values assigned to the various stoichiometric and kinetic parameters as a result of the calibration and verification procedures are described in Sections 6.8 and 6.9. A sensitivity analysis was performed and is presented in Section 6.10 to confirm the selection of the best estimates for the various model constants. When calibrating any model a series of compromises often have to be made in order to obtain reasonable predictions for all sets of data. The sensitivity analysis indicates the impact of changing the value of a given model parameter on the actual prediction. For each process considered this provided a range of values which were capable of predicting the response of a given batch test. Establishing these ranges minimized the impact of the compromises which must be made when trying to simulate the behaviour of different influent streams. In summary, model coefficients must be selected to maximize the success of the model in predicting the behaviour of all the influent streams. As a result, an individual stream may be predicted with more accuracy by adjusting the model constants, but only at the cost of poorer simulations for a different stream. The objective of any calibration exercise is to minimize the discrepancy between the model predictions and experimental results for all the different cases. Since a model produces a representation of system response rather than a definitive output, these considerations are important to remember when analysing the success of a model and the selection of model constants.

6.8 STOICHIOMETRIC COEFFICIENTS

Using the plots discussed in Section 6.6, in conjunction with information sighted in the literature, the model coefficients were determined. In this section values assigned to the stoichiometric coefficients are presented along with the data supporting each selection. These values were reported in Table 5.3 in Chapter 5 which presented the petrochemical model.

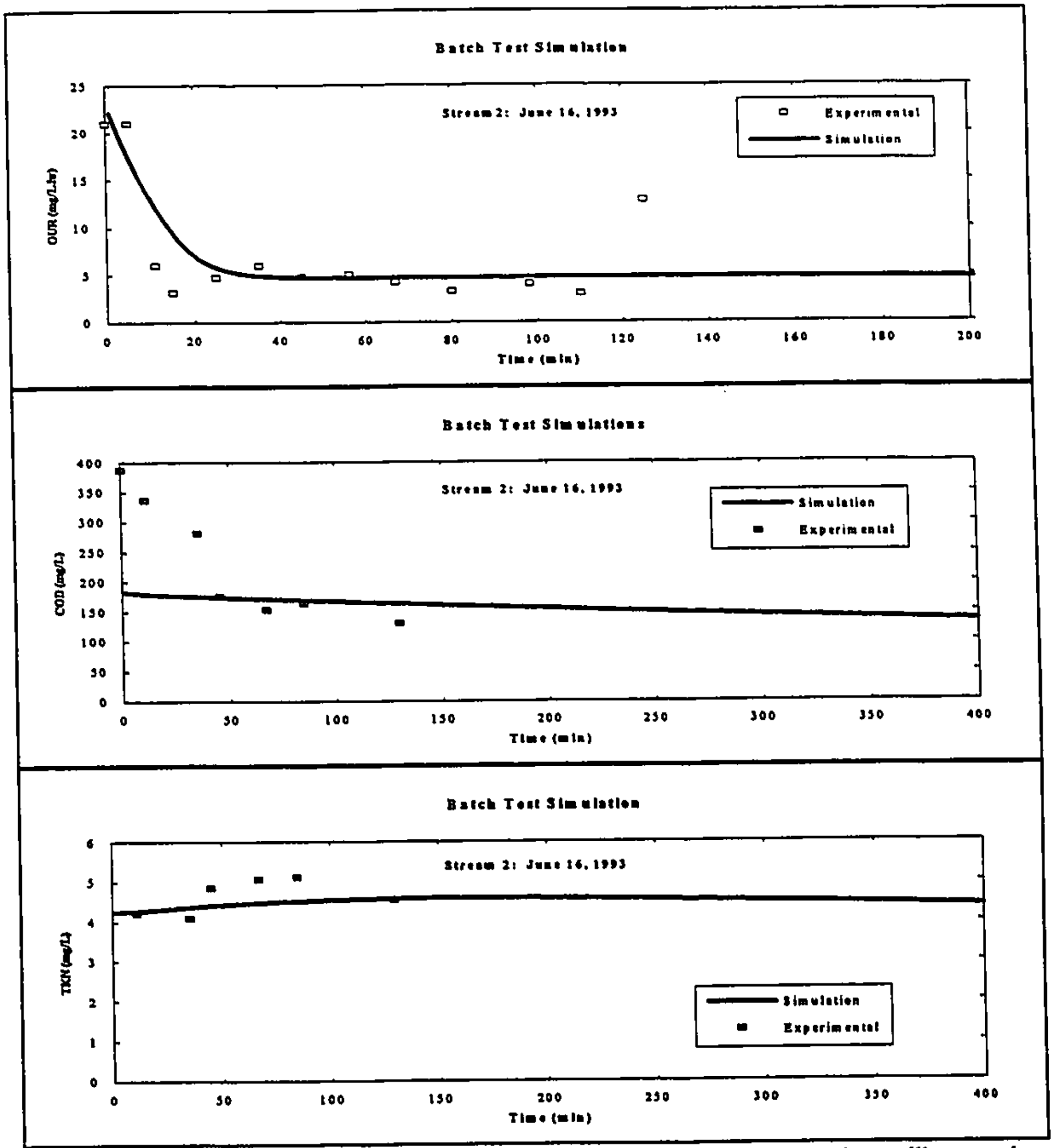

Figure 6.10: The results of the batch test on Stream 2 (June 16, 1993) are illustrated. OUR, COD, and TKN were monitored during the batch test. The predicted responses of the batch tests simulated in the GPS-X^{TM} model using the model coefficients determined during calibration are indicated by the solid line on the plots above.

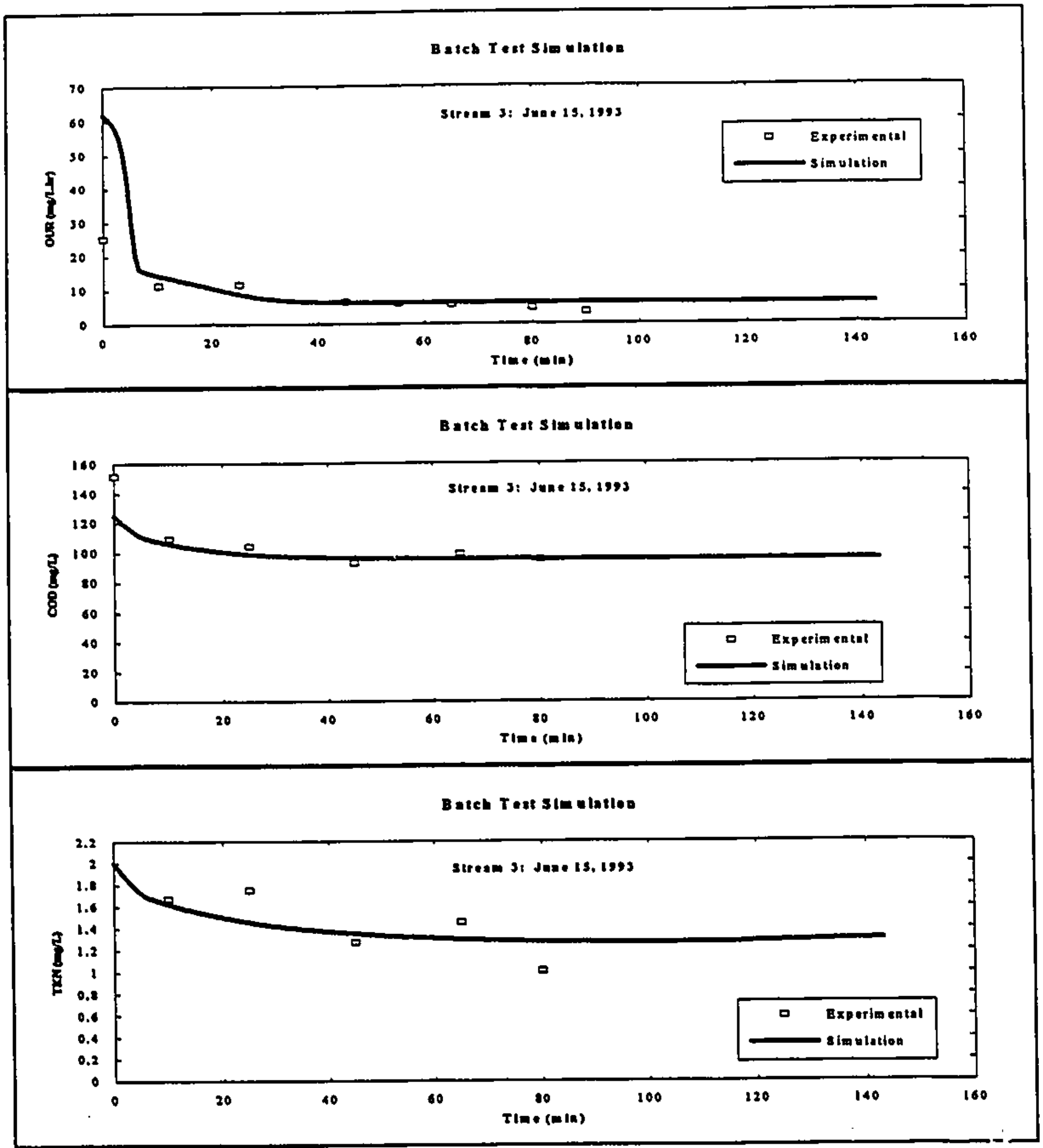

Figure 6.11: The results of the batch test on Stream 3 (June 15, 1993) are illustrated. OUR, COD, and TKN were monitored during the batch test. The predicted responses of the batch tests simulated in the GPS-X^{TM} model using the model coefficients determined during calibration are indicated by the solid line on the plots above.

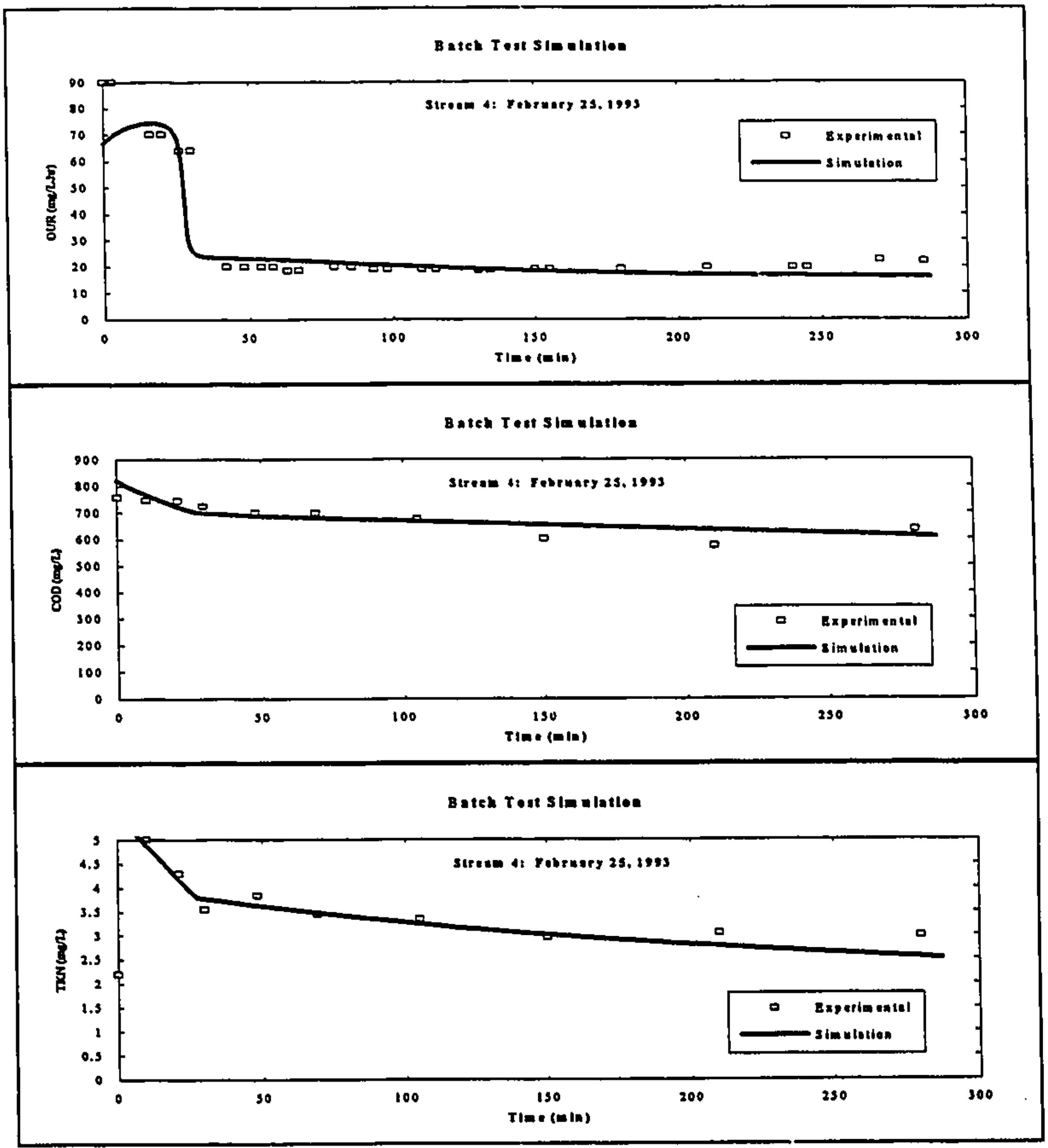

Figure 6.12: The results of the batch test on Stream 4 (February 25, 1993) are illustrated. OUR, COD, and TKN were monitored during the batch test. The predicted responses of the batch tests simulated in the GPS-X™ model using model coefficients determined during calibration are indicated by the solid line on the plots above.

6.8.1 Yield Coefficients

The yield coefficients for microbial growth on the different organic components were obtained from a number of sources. The literature provided valuable insight into the types of value to expect. Comparison of model predictions with actual response in the batch test played a significant role in quantifying these coefficients.

The yield of organisms on hydrocarbon material is reported in the literature as 0.555 gCOD $(gCOD)^{-1}$ (Payne, 1970). This is the value used in the petroleum refinery model since the majority of the contaminants treated are hydrocarbon in nature. Growth on hydrocarbons in the petrochemical system also was assumed to have the low yield. Results of the calibration procedure supported this assumption.

The three groups of organic compounds were assumed to have the same yield: (1) alcohol P (S_{AP}), (2) phenolics (S_{PH}), and (3) volatile organics (S_V). It was assumed that the nature of these compounds was quite similar in terms of their impact on the degradation processes. A range of yield coefficients were evaluated to include the low yield values associated with the growth on hydrocarbons (0.555 g COD/gCOD) and the yield coefficients normally associated with growth on mixed COD in municipal systems (0.666 gCOD/gCOD). By observing the response of the OUR curves in the different batch tests, the best estimate for the yield was 0.600 gCOD $(gCOD)^{-1}$.

The readily biodegradable mixed COD (S_M) was assumed to behave in a similar fashion to that of readily biodegradable COD found in municipal systems. Therefore, the yield was assigned a value of 0.666 gCOD$(gCOD)^{-1}$. Since this component was a small contribution of the total influent COD, the value associated with it did not have a significant impact. Furthermore, if the aliphatic amine contributes to the mixed COD fraction by being hydrolysed to a fatty acid, then this is a readily degradable compound common to the energy pathways in a municipal system. When these coefficients were used in the steady state simulations the volatile solids generated in the model system were comparable to full-scale measurements. This supports the choice of the above parameter values.

6.8.2 COD/VSS and TKN/VSS Ratios

The COD/VSS and TKN/VSS ratios quantify the COD and nitrogen associated with particulate matter in this particular petrochemical activated sludge system. These ratios are required to quantify stoichiometric coefficients.

Sludge usually has a COD/VSS ratio of approximately 1.42 gCOD $(gVSS)^{-1}$. Values significantly greater than this tend to suggest the presence of adsorbed degradable compounds or inert particulates with a high COD to mass ratio. This was the case in the petrochemical system. The measured COD/VSS ratios were simulated through adjustment of the COD/VSS ratios of the different influent particulate compounds. The particulate inert fraction had the most significant impact. This was a result of the particulate inert fraction accumulating in this system at a high SRT. This inert fraction was assumed to have a high COD to mass ratio based on consultation with plant staff (i.e. the compound in this system has COD/VSS =3.31).

The TKN/VSS ratio is required to determine the nitrogen requirements for growth in the system. Knowledge of the minimum amount of nitrogen needed for growth enables the risk of nutrient limited growth to be predicted by the model. For the petrochemical system both the COD/VSS ratio 2.3 of and TKN/VSS ratio of 0.1 were determined by direct measurement on the sludge from the different aeration tanks.

6.9 KINETIC CONSTANTS

When it was possible to isolate a single component in one stream, the ability to identify the growth kinetics was simplified. The kinetic constants of the reaction associated with the compound were adjusted until model predictions corresponded to the behaviour of the single batch test. In cases where a compound was present in more than one stream, the kinetics of the reaction were determined iteratively by adjusting the kinetic parameters within the different batch tests until reasonable predictions were obtained for all tests. Finally, some values of the model coefficients were based on experience with municipal activated sludge systems or the petroleum refinery activated sludge system. These included the following reactions:

- Autotrophic growth kinetics
- Growth kinetics on hydrocarbons
- Hydrolysis reactions
- Anoxic reactions
- Switching function values

The kinetic coefficients determined in the calibration process of the petrochemical activated sludge system are described below. Values for the model kinetic coefficients for the petrochemical model were listed in Table 5.4 in the preceding chapter.

6.9.1 Kinetic Coefficients for Growth on Mixed COD

The kinetics of organism growth on mixed COD (S_M) were determined by altering the maximum growth rate, μ_{maxM}, and the half-saturation constant, K_{sM}, until the model simulations of the initial stages of each batch test corresponded to responses in the experiments. The mixed COD treated in this system was assumed to be readily biodegradable organic compounds. As a result these are utilized quickly in the system. Similarly, in the batch tests consumption of these compounds corresponded to high OUR readings in the initial stages of the experiment when the compound was degraded rapidly. Therefore, the kinetics of this removal process were determined by matching the initial decline of the OUR and COD in each batch test. The concentration of the mixed COD compounds consumed was approximated in the wastewater characterization process. The kinetic parameters were adjusted until the behaviour of the mixed component in all the influent streams was predicted adequately. The values obtained were $\mu_{hM} = 4.0$ day^{-1} and $K_{sM} = 1.0$ g COD m^{-3}.

6.9.2 Kinetic Coefficients for Growth on Alcohol P

Growth kinetics of the alcohol P (S_{AP}) used in the petrochemical facility were determined largely from the behaviour of the batch tests conducted on Stream 3. Alcohol P is the main component in this influent stream so the growth behaviour was associated with the response of this stream when in contact with activated sludge. The maximum growth rate, μ_{hAP}, and the half-saturation constant, K_{sAP}, were determined by changing the values of these two parameters until the simulated response predicted by the model matched the experimental response. The maximum growth rate impacted the level of the OUR, while the half-saturation constant impacted the rate at which growth declines at low concentrations of the compound. Using these relationships appropriate values for the constants could be determined.

The alcohol P also was found in the trucked wastewater samples used in the batch tests. Therefore, the constants determined in the Stream 3 batch tests also had to predict the behaviour of the batch test treating the alcohol P in the trucked wastewater (Stream 5). This provided a check on the ability of the selected kinetic coefficients to predict growth behaviour on the alcohol. The kinetic constants were determined by ensuring that both these streams could be simulated. The value determined for μ_{hAP} was 1.1 day^{-1} and the value for the half-saturation constant, K_{sAP}, was 5.0 g COD m^{-3}.

6.9.3 Inhibition Growth Parameters for Phenolic Compounds

Batch tests of the phenolics stream (Stream 4) were used to determine the inhibition kinetics describing the degradation of phenolics (S_{PH}). The Haldane Equation was used to model growth on phenolics as indicated in Table 5.2. Three coefficients needed to be calibrated in this equation :

- Maximum growth rate (μ_{hPH}),
- Half-saturation constant (K_{sPH}), and
- Inhibition constant (K_I)

In order to quantify these parameters, estimates were obtained from the literature to establish a range of values which were reasonable (Rozich, 1985). Using these values as preliminary estimates, the actual response of the Stream 4 batch test could be simulated adequately in the model by adjusting the coefficients. This determined the constants which applied to the petrochemical system. The values established in this procedure were:

- μ_{hPH} = 4.3 day^{-1}
- K_{sPH} = 1.0 gCOD m^{-3}
- K_I = 60 gCOD m^{-3}

6.9.4 Volatilization Rate Constant, K_V

A first order relationship with respect to the concentration of volatile organic compounds (S_V) was used to describe the rate of stripping from this petrochemical system. The volatilization rate constant, K_V, was determined using a full-scale study conducted on volatile organic compounds at the petrochemical facility. This study identified that the stripping of VOC's from the petrochemical activated sludge system occurs mainly from the pretreatment tank.

A relationship for determining the removal rate of VOC compounds in subsurface aerated wastewaters is discussed in Matter-Muller *et al.* (1981). It relates the volatilization rate to the air flow rate, the volume of wastewater in the system, Henry's Law coefficient, the concentration of the volatile compound, and the mass transfer coefficient, k_La, of the compound through the liquid film. Munz & Roberts (1984) extended this research to include the influence of both liquid and gas transfer resistance on mass transfer. A further extension of this approach was described in Hsieh *et al.* (1994), but the more simplified approach was used in this study. A more detailed description of the equations required to estimate K_V is presented in Appendix 7.

For determining the value for K_V in the petrochemical model, estimates of the above parameters were required.

- According to previous studies the stripping of volatile compounds is related to the transfer of oxygen through the system by a factor ψ, usually ranging from 0.5 to 0.7 (i.e. $k_{Lav} = \psi \; k_{LaO2}$). Therefore, using the characteristics of the aeration equipment, the mass transfer rate of oxygen can be determined so the corresponding transfer of volatile organic compounds can be estimated.
- The air flow was estimated from preliminary model predictions by assuming that sufficient air was supplied to maintain a dissolved oxygen concentration in the pretreatment tank of 2 mg/L. The model predicted an air flow requirement of 15500 m^3/day which lies between the low and high air flow rates used in the VOC study.
- The GPS-X^{TM} used a k_La value of 11 day^{-1} which is comparable to typical values presented in the literature (Melcer *et al.* 1993; Metcalf & Eddy, 1991). This value

was used to estimate a mass transfer rate coefficient for the volatile organic compounds using a value of $\psi=0.6$ in the relationship indicated above.

- The VOC study was used to obtain values of Henry's Law coefficients. The Henry's Law Coefficient was reported to range between 0.033 and 0.170 L_{gas}/L_{liq} in the study.

Using these estimates and assuming the pretreatment tank was full ($V=3206$ m^3), K_V was determined to range between 0.16 day^{-1} ($H=0.033$) and 0.82 day^{-1} ($H=0.17$) [see Appendix 7]. Using this range as a guide, the batch tests were simulated. A value of 0.4 day^{-1} for K_V produced good model simulations of the observed measurements.

6.9.5 Kinetic Coefficients for Growth on Volatile COD

The influent streams which contribute the most significant levels of volatile organics (S_V) are Streams 1 and 2. The concentration of volatile organic compound identified as the major contributor was used as a key indicator of the amount of volatile organic COD present. Daily measurements of the concentration of this VOC compound in the influent were available. Using estimates of the volatile fractions in conjunction with the volatilization rate determined above, the growth kinetics were adjusted until the model simulations matched the observed batch test responses for these two streams. The values which provided the best estimates for growth on volatile organics were μ_{hV} equal to 1.5 day^{-1} and the half-saturation constant, K_{sV}, equal to 30.0 g COD m^{-3}. The low growth rate was expected since the major portion of the volatile fraction consists of chlorinated organics which are more difficult to degrade.

6.9.6 Ammonification Rate

The ammonification rate impacts the rate that soluble organic nitrogen (S_{ON}) is converted to ammonia (S_{NH}), which is subsequently available for organism growth or for nitrification. It was determined by adjusting the value of K_N until the response of the filtered TKN concentration in the batch tests were simulated. This process involved iterative consideration of the ammonification rate until all influent stream batch tests were simulated correctly. The ammonification rate was determined to be 0.06 m^3 g COD^{-1} d^{-1}.

6.9.7 Nitrification Kinetics

In the petrochemical facility there was no evidence of nitrification which is surprising given the long sludge retention time of this system. This is likely the result of inhibition of nitrification due to the presence of certain inhibitory compounds. Consequently, it was not possible to determine the growth rate of the nitrifiers, μ_N. The growth rate of nitrifiers is small, however.

6.9.8 Sulphite Oxidation Rate

This value was determined by estimating an oxidation rate which mimicked the rapid drop in OUR during the first few minutes of the influent stream batch tests known to contain sodium meta-bisulphite. These were Streams 1 and 2. A rapid oxidation rate parameter of 200 day^{-1} was obtained.

6.10 BATCH REACTOR SIMULATION SENSITIVITY ANALYSIS

This subsection illustrates how variation of specific model parameters and model wastewater characteristics impact the predictions of the aerobic batch reactor test results. This was important for determining the range of certainty which can be associated with a given set of model predictions. It also provided guidelines for calibrating the model with the appropriate model coefficients. A range of values was chosen for the key stoichiometric and kinetic coefficients to determine how these influence model response. By altering the values of the different coefficients the influence on model predictions could be identified.

Some coefficients have a greater influence on system response than others. The influence of varying those coefficients which show appreciable impact on model predictions are illustrated graphically throughout the following discussion.

- Overestimation of the hydrocarbon component concentration (S_{CH}) generated an overestimation of the OUR which is most noticeable in the later stages of the batch test (Figure 6.13). In this scenario it appeared that there was more organic material being utilized than was actually present. If the material thought to be hydrocarbon was actually inert material then the final COD concentration was underestimated.

- Overestimation of the volatile component concentration (S_V) influenced the model predictions of the OUR. If a higher volatile component was assumed, the OUR later in the test remained higher for a prolonged time (Fig. 6.14), but dropped off slowly. This may at first appear contradictory. However, assuming a higher volatile fraction meant that the inert COD was decreased to keep the total COD constant. The volatile COD consumes oxygen, whereas the inert COD does not. Therefore, increasing the VOC concentration increases the organic material which is available for degradation. On the other hand, an underestimation of S_V resulted in a more rapid drop to endogenous levels.

  Overestimation of the volatile component (S_V) in a waste stream resulted in the model predictions underestimating the final COD concentration. The reverse is true for an underestimation of the volatile fraction.

- If a key heterotrophic growth rate (μ_{hM} , μ_{hAP} , μ_{hPH} , μ_{hV} ,or μ_{hCH}) is high, the model will overestimate the OUR and the COD uptake rate. The model will also predict an earlier decline in the OUR to endogenous levels. For example, in Figure 6.15 illustrating the influence of the growth rate on alcohol P, a μ_{hAP} of 2.0 d^{-1} overestimated the OUR during utilization of the alcohol P substrate and caused it to drop off earlier than observed in the test.

- The half-saturation coefficients in the growth equations (K_{sM}, K_{sAP}, K_{sPH}, K_{sV}, or K_{sCH}) impacted the rate at which the OUR curve declined to endogenous levels (Figure 6.16). In this figure a value of K_S which was too high prolonged the time required for the OUR to drop to endogenous levels.

- If the heterotrophic yield coefficient on mixed COD (Y_{hM}) is low, the model will overpredict the initial OUR in the sludge decay rate test (Figure 6.17).

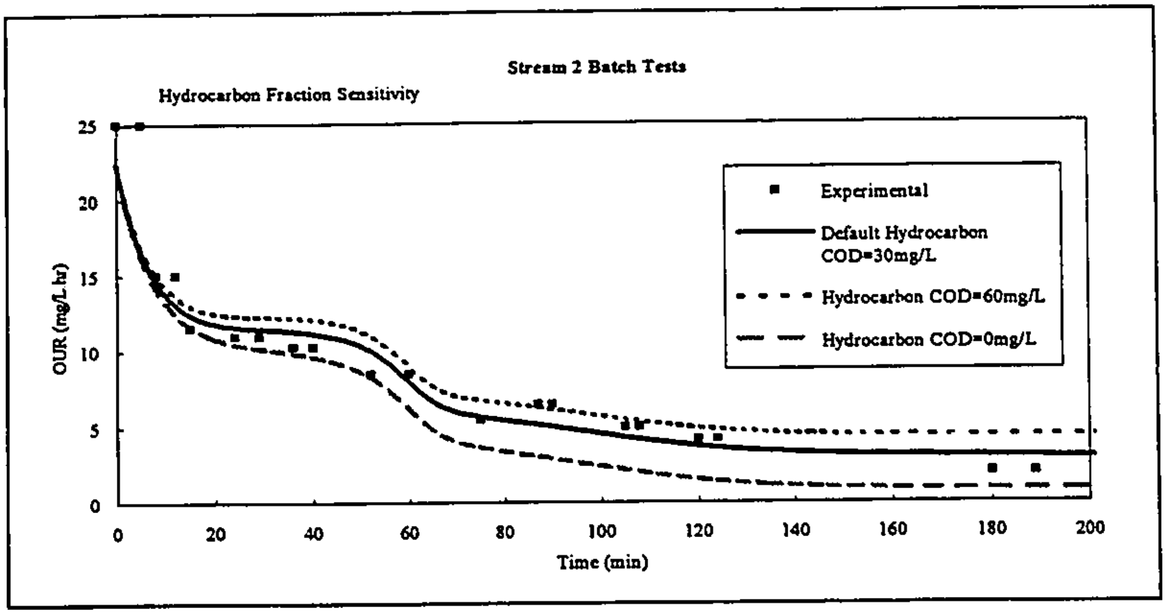

Figure 6.13: Impact of the fraction of hydrocarbon COD in Stream 2 on the behaviour of the batch test OUR.

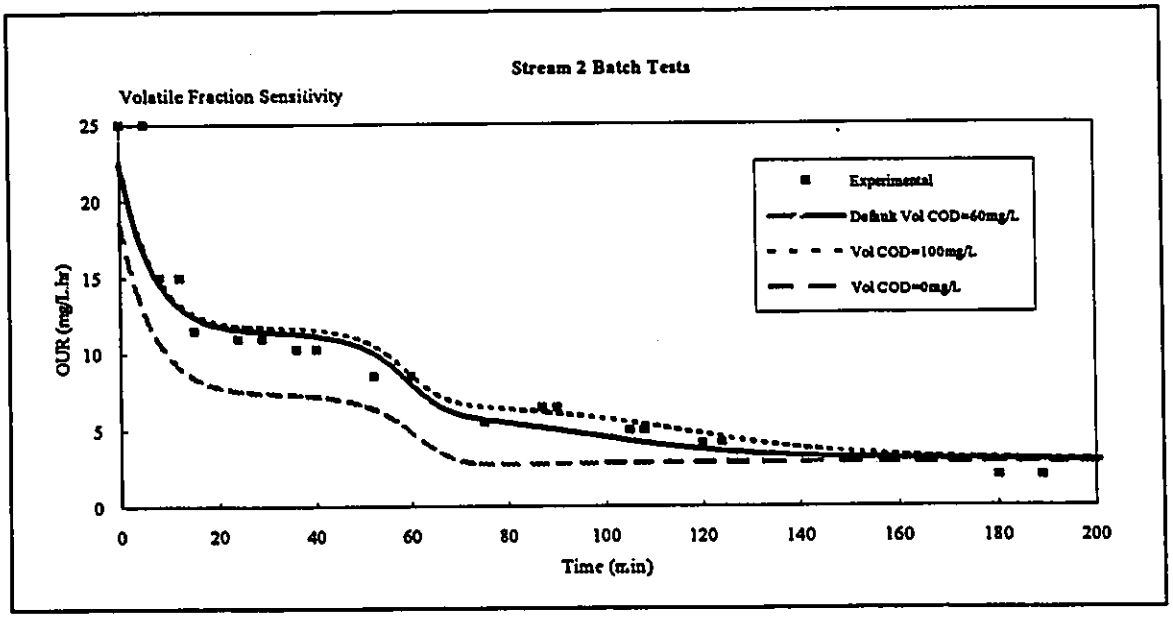

Figure 6.14: Impact of the volatile organic compound fraction in Stream 2 on the behaviour of the batch test OUR.

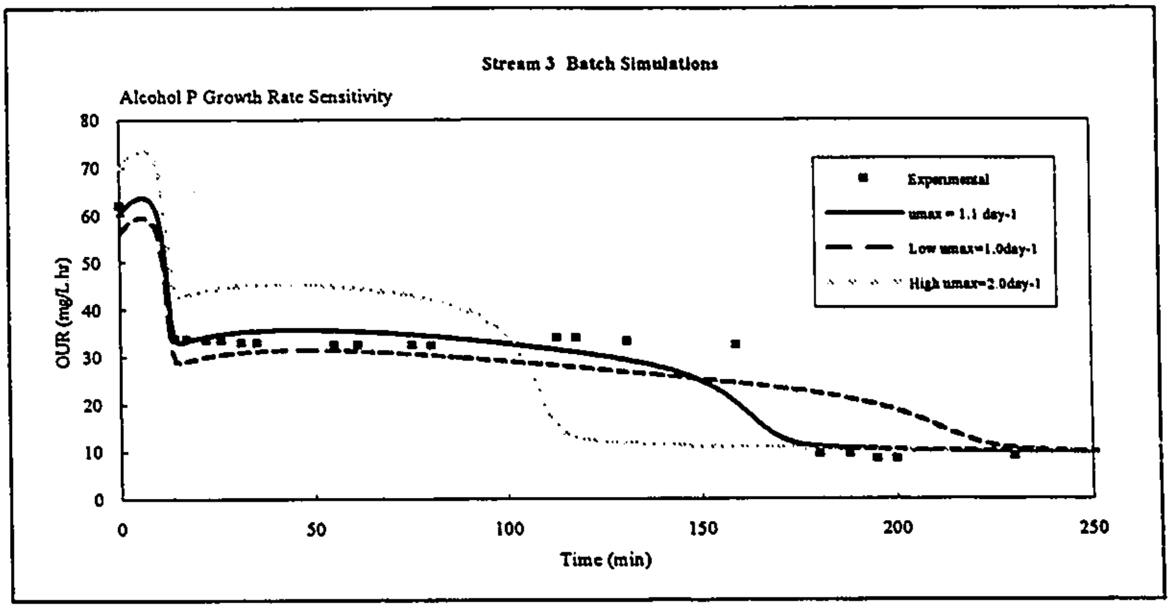

Figure 6.15: Impact of the maximum growth rate of organisms on alcohol P in Stream 3 on the behaviour of the batch test OUR.

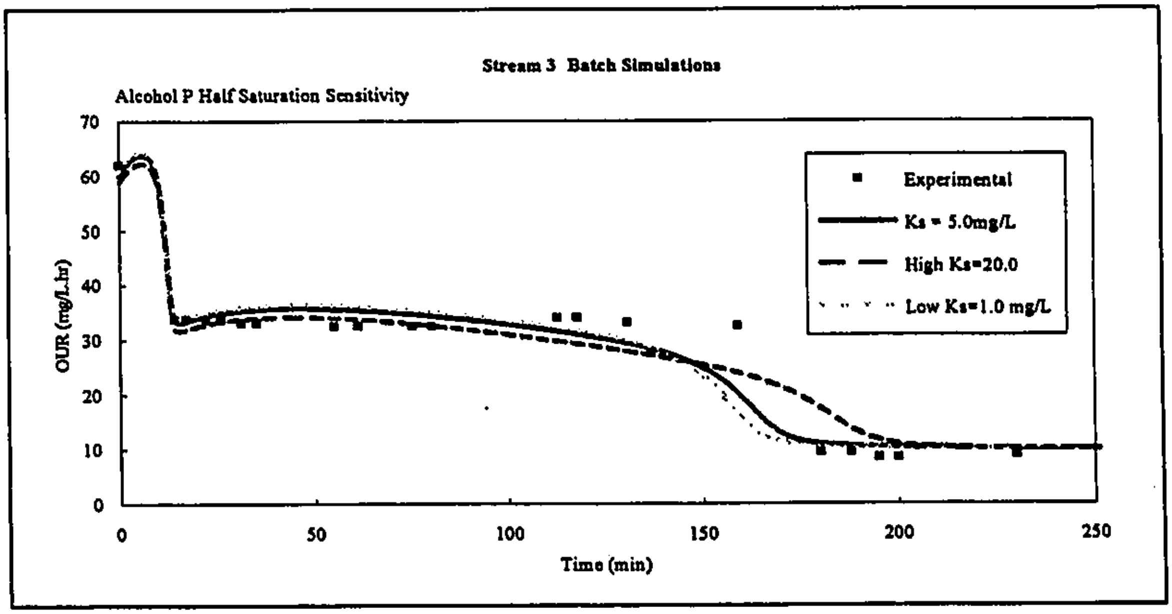

Figure 6.16: Impact of the half-saturation constant of the growth of organisms on alcohol P in Stream 3 on the behaviour of the batch test OUR.

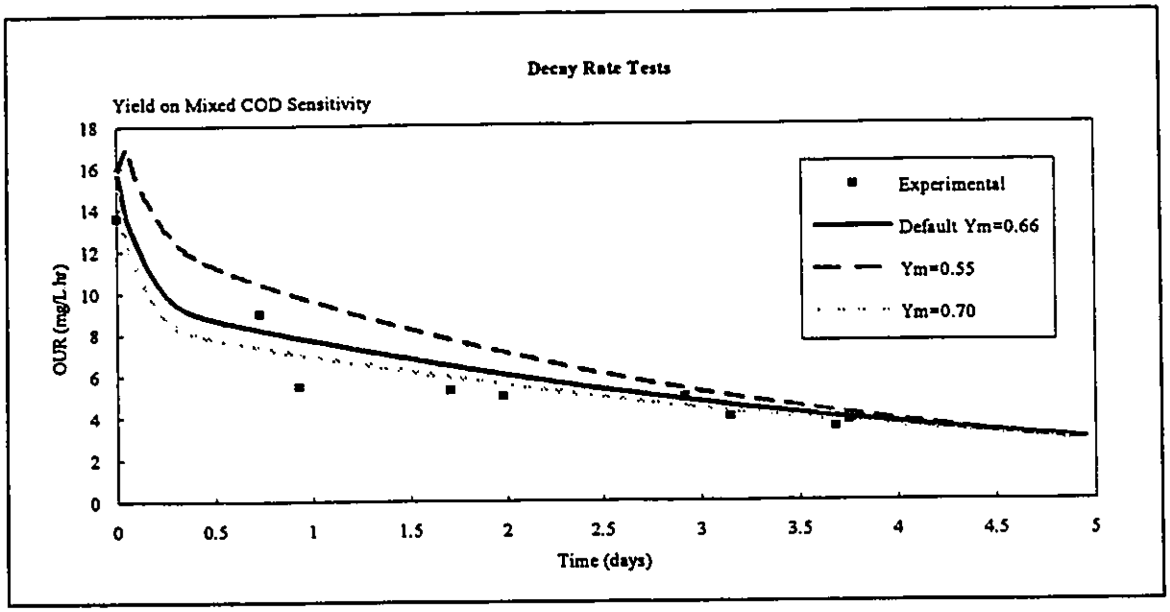

Figure 6.17: Impact of the yield coefficient on the behaviour of the OUR response in a decay rate test.

- The model predictions of the batch test results for the Stream 4 are extremely sensitive to the value of the inhibition coefficient for phenolics (K_I). If the value for K_I is overestimated, the OUR is too high initially and then drops off early (Figure 6.18). The COD removal is also overestimated and drops off too quickly. If the value for K_I is too low then the increase in OUR through the middle portion of the batch test is underpredicted and the COD removal is underestimated.

  The model predictions for this stream also are extremely sensitive to the value of the half-saturation coefficient, K_{sPH} and the heterotroph maximum specific growth rate on phenolics (μ_{hPH}). The half-saturation coefficient influences system behaviour by determining the rate of decrease of OUR to endogenous levels (Figure 6.19). For example, selecting a value of K_{sPH} which is too high results in a gradual decline to endogenous OUR levels.

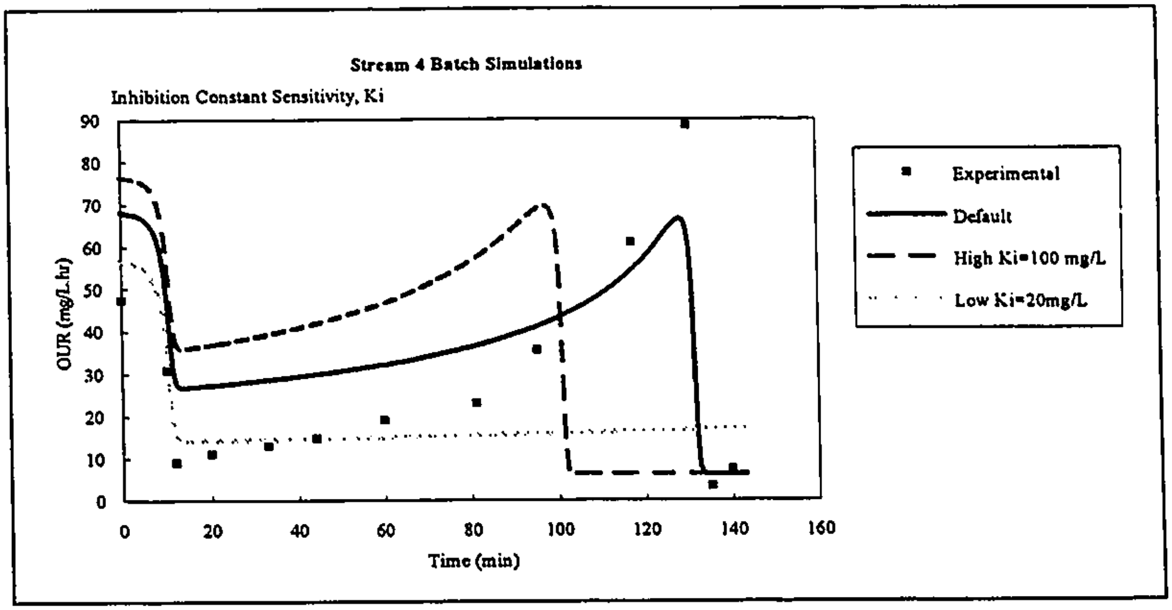

Figure 6.18: Impact of the inhibition constant, K_I, associated with inhibitory growth of organisms on phenolic compounds in the phenolics stream on the behaviour of the batch test OUR.

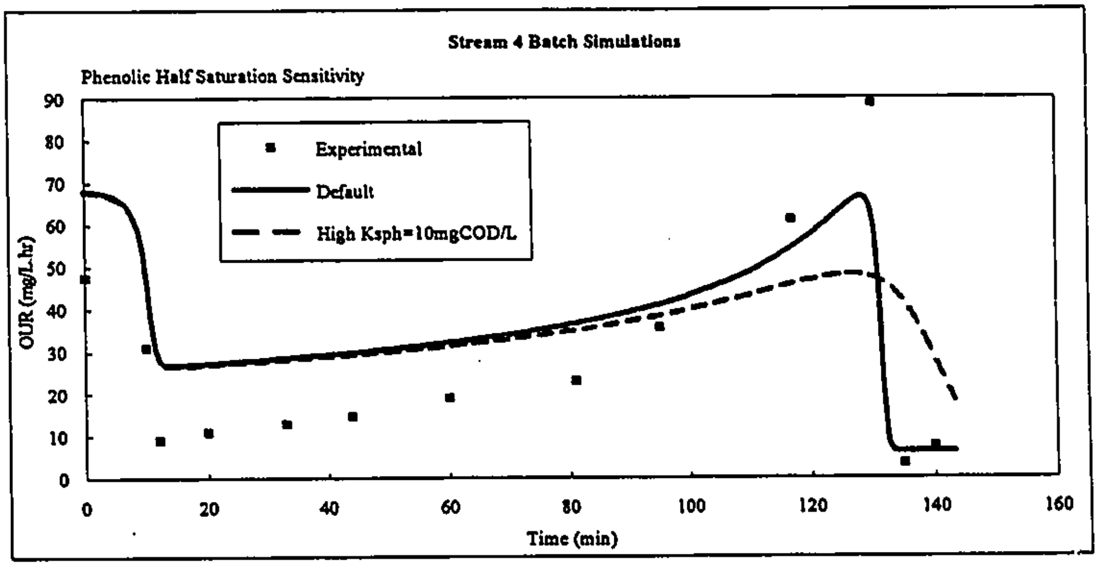

Figure 6.19: Impact on the behaviour of the batch test OUR of the half-saturation constant, K_{sPH} of organisms on phenolics in the phenolics stream.

If μ_{hPH} is too high, then the OUR is initially overestimated and then drop off too soon in the batch test. If μ_{hPH} is too low, the model will underpredict the dramatic increase in OUR as the phenols are degraded to less inhibitory levels. The oxygen consumed for phenolic growth is prolonged in this case and remains above endogenous levels much longer than actually observed.

- Underestimation of the rate of volatilization, K_V, in a waste stream results in an overestimation of the OUR (Figure 6.20) and an underestimation of the initial drop in COD in the model predictions. The reverse is true for an overestimation of the volatilization rate.

- The value of the hydrolysis rate constant, K_H, impacts the concentration of slowly biodegradable particulate material in the system. Changing the value of K_H appeared to have no impact on model predictions of the batch tests on the influent wastewater streams. The impact of K_H was more significant in decay rate batch tests on the sludge where the concentration of slowly biodegradable particulate is significant (Figure 6.21). Therefore, if a significant fraction of slowly biodegradable particulate were present in a given stream, the impact of changing K_H on the individual batch tests with the influent streams would likely be observable.

- In the batch reactor tests on sludge, an overestimation of the decay rate (b_H) results in an overprediction of the initial OUR by the model (Figure 6.22). There is minimal impact on the model predictions of the COD concentration. The decay rate also has an impact on the final solids concentration.

- Underestimation of the inert soluble COD (S_I) fraction results in the model predictions of the OUR being too high (i.e. more soluble mixed COD) and the final COD concentration being too low. The reverse is true for an overestimation of the inert fraction.

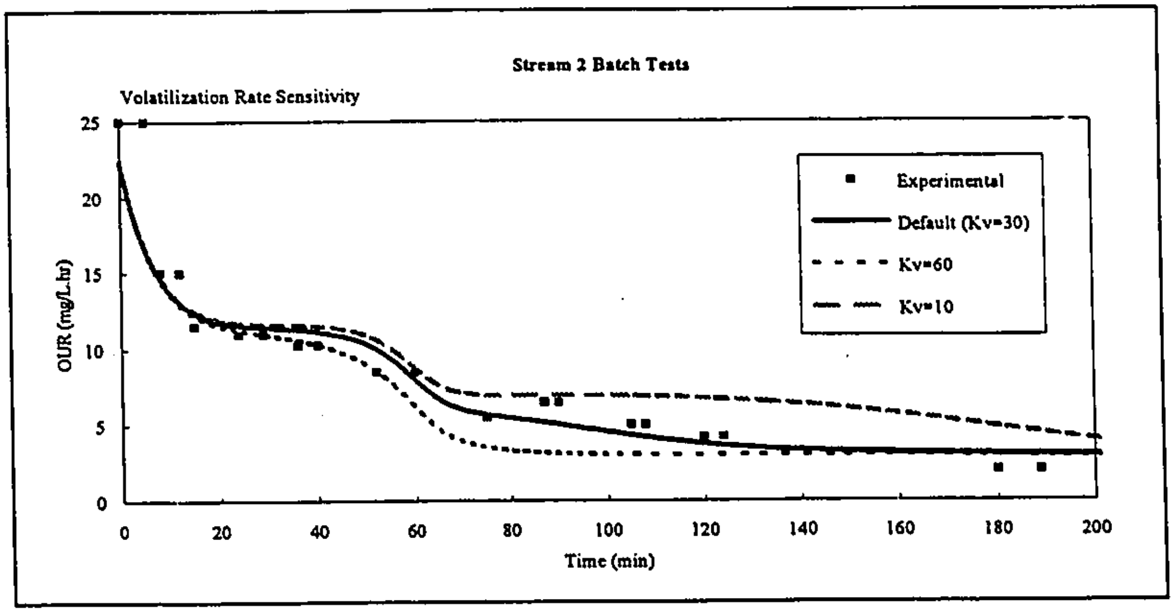

Figure 6.20: Impact on the behaviour of the batch test OUR test of the volatilization rate (K_V) of volatile organic compounds in Stream 2.

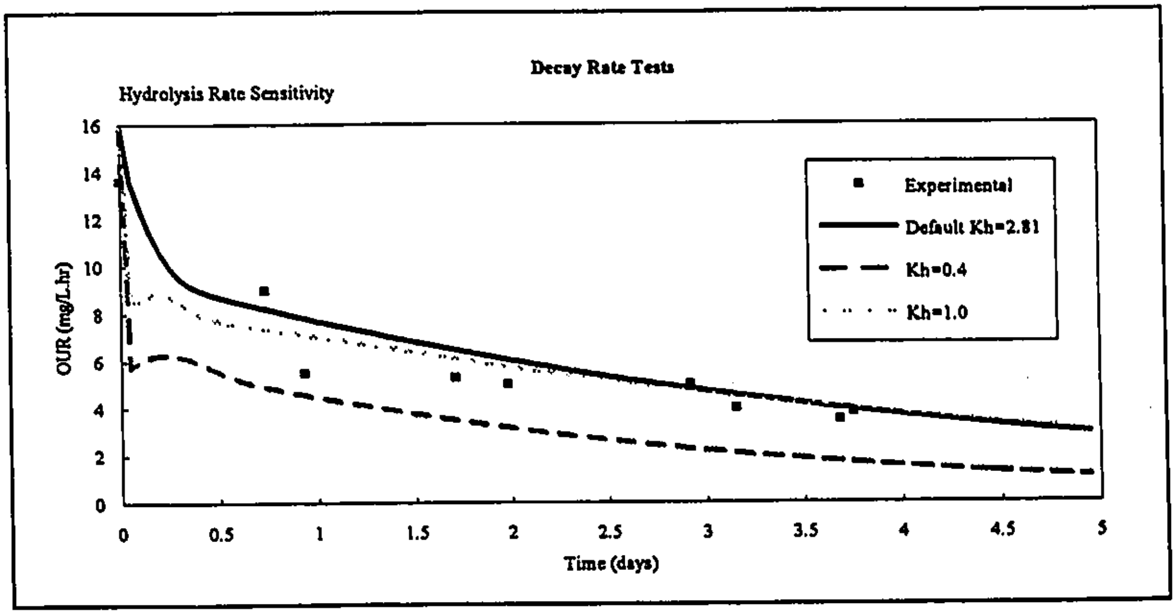

Figure 6.21: Impact on the behaviour of the batch test OUR in the decay rate test of the hydrolysis rate of slowly biodegradable particulate COD.

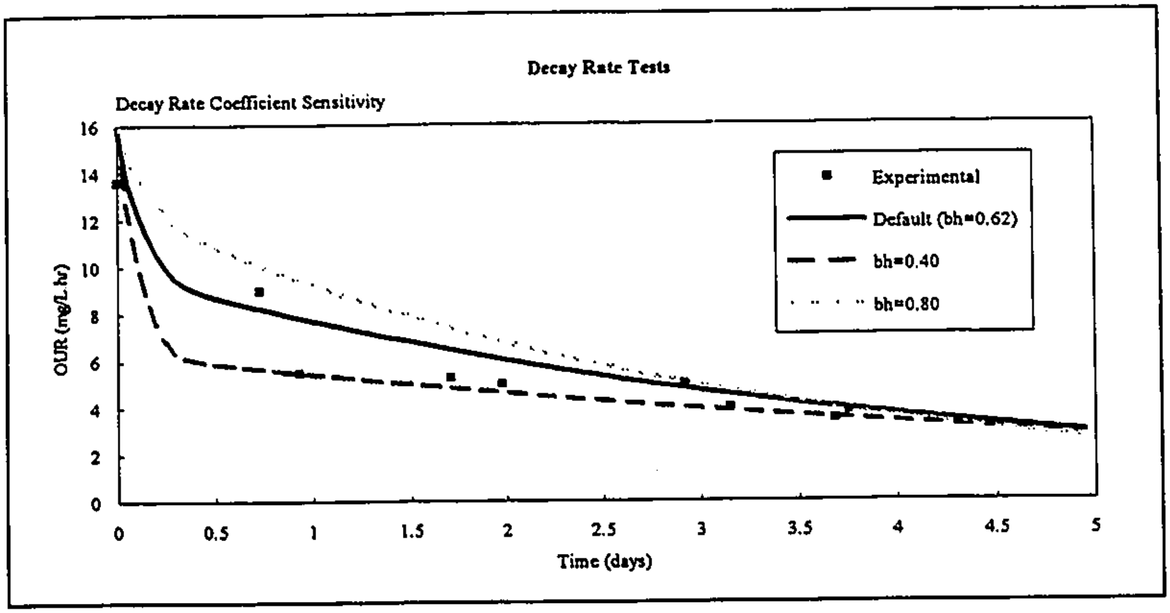

Figure 6.22: Impact of the decay rate on the behaviour of the OUR during the batch test conducted to determined the decay rate of the organisms.

- Nitrogen limitations can impact the levels of removal of a particular compound since organisms need nitrogen for growth. This may be reflected in the batch tests by a shift in the drop off point in the OUR curve to endogenous levels.

- Model predictions are sensitive to the value for the fraction of active mass which remains as endogenous residue following decay ($f_{Ep,H}$). Decreasing this value causes the model to overpredict the OUR, whereas an increase in this fraction decreases the OUR.

In summary, the sensitivity analysis indicated a wide variation in the sensitivity of model output predictions to any one specific parameter. The relationships described above were utilized to calibrate the model. By adjusting the various parameters according to these guidelines the model predictions could be improved to correspond with the observed results. Performing a sensitivity analysis on the model ensures that the best estimates for the model coefficients have been determined for the given data.

A point which becomes evident in performing these analyses is that the coefficients used in the model are not absolute, but are considered the best estimates. Calibrating a model is often a series of compromises to achieve the best value for all situations being considered. The task of deciding on one value of a coefficient is difficult, but for the applications considered, optimum choices have been identified. Further experimentation would assist in fine tuning these values.

6.11 SUMMARY OF THE CALIBRATION AND VERIFICATION PROCESS

The process used to calibrate and verify the activated sludge model describing the behaviour of the activated sludge system operating at the petrochemical refinery has been presented. The approach used to calibrate the model using a series of batch tests treating different influent streams was identified and successfully applied. These batch tests formed the basis for determining the stoichiometric and kinetic coefficients which describe the reactions occurring in the system. The values of the coefficients were altered until the model predictions of OUR, COD, and TKN matched the experimental observations. This process was performed for each influent stream. In some cases, the constants could be determined by calibrating the batch test of a single stream, while in other instances, an iterative process which provided the best fit for multiple streams was required (e.g. alcohol P kinetics were calibrated on influent Streams 3 & 5). The result was quantification of the stoichiometric and kinetic coefficients which describe the specific removal mechanisms occurring in the petrochemical activated sludge system. The values established during this procedure were applied to a separate set of data in order to verify that the model was capable of predicting system response under a different set of conditions. This constituted the verification stage of model development.

An important part of the calibration analysis involved determining the characteristics of the influent wastewater streams which enter the petrochemical activated sludge plant. In order to determine correct values for the removal mechanism coefficients, the wastewater had to be characterized. Preliminary wastewater quality was assumed from long term data, while the final fractionations were refined during the calibration procedure. A description of the characteristics of the influent streams was provided, as well as the justification for the assumptions.

A sensitivity analysis was performed to determine the influence of different values of the coefficients on model predictions. This enabled the best estimate of each stoichiometric and kinetic coefficient to be determined. It also allowed the degree of certainty associated with the model predictions to be established.

The result of the entire calibration/verification process is a calibrated model capable of providing estimates of the behaviour of the activated sludge system treating the wastewaters generated at the petrochemical manufacturing site or piped to the system from outside industries.

CHAPTER 7

APPLICATION OF MECHANISTIC MODELS TO PROCESS OPTIMIZATION

7.1 INTRODUCTION

The preceding chapters described the formulation and calibration of mechanistic models for activated sludge systems treating petroleum and petrochemical wastewaters. One of the major advantages sighted in the application of mechanistic models of municipal activated sludge systems is the ability to optimize system performance. The models can be used to simulate a range of operating modes to establish which conditions tend to maximize system performance, and also which conditions tend to upset system behaviour. Another application is the use of the model for designing new systems. In order to illustrate the capabilities of these petroleum-based models to evaluate the performance of existing systems, the petrochemical wastewater treatment system was selected.

As previously described, the petrochemical activated sludge system consists of four aeration tanks which operate at different hydraulic residence times with multiple feed points into the system depending on the source of the influent stream (Figure 7.1). A pretreatment tank at the head of the system serves as an equalization and pH balancing tank. Three clarifiers currently operate to settle the suspended solids. The complexity of this treatment system provided a suitable illustration of the ability of a mechanistic model, when used in conjunction with a simulator, to predict system performance. By running different model simulations, an optimum operating strategy could be suggested. Simulation of the system also enabled a better understanding of system behaviour to be developed and identified the limitations of the treatment system. This information is invaluable for averting potential instabilities in the system and maintaining a high level of effluent quality. The following discussion illustrates the application of the model to optimize the performance of the activated sludge system operating at the petrochemical facility.

7.2 CASE STUDIES

The petrochemical activated sludge mechanistic model was used in the GPS-X^{TM} simulator to evaluate two aspects of concern in the operation of this petrochemical facility. These concerns were identified by plant operations staff:

- The issue of volatile organic emissions from the system was evaluated due to the increasing concern about air quality in regulatory agencies. In the current system, studies have indicated that the majority of VOC emissions from this facility originate from the pretreatment tank at the head of the plant. Therefore, methods of reducing the VOC emissions from this section of the plant were of interest.

- The impact of transient shock loadings of alcohol P (S_{AP}) to the system was considered. The concern with spike loadings is the potential degradation of effluent quality if the spike cannot be attenuated in the treatment system. Alcohol P is often discharged in Stream 3 as a spike loading to the activated sludge system during certain processing stages and adequate treatment before discharge is essential.

In evaluating each of these aspects of plant performance, the approach was to simulate the performance of the existing system, as well as a number of alternative system configurations. These alternatives all involve using the existing plant tankage, but making changes to either (1) the points of input of the six influent streams, (2) the RAS recycle flow distribution, of (3) the routing of flows from reactor to reactor. The various alternative schemes were selected for evaluation because each one could be implemented quite easily within the existing system.

The following section (7.3) presents the various configurations. Section 7.4 evaluates the VOC issue, and Section 7.5 considers the impacts of a spike loading of S_{AP} on system performance.

7.3 OPERATING CONFIGURATIONS

The activated sludge system at the petrochemical facility currently treats six different wastewater streams. Five different operating configurations of the petrochemical activated sludge system were simulated in the GPS-X^{TM} to evaluate system performance for the treatment of these six streams. For purposes of describing the different configurations, the pretreatment tank in the system is referred to as PT and the four aeration basins are referred to as AT1, AT2, AT3, and AT4, respectively.

Configuration 1 - Present Configuration: Figure 7.1 outlines the present configuration of the system.

- Streams 1 and 2 enter PT.
  Streams 3, 4, 5, and 6 enter AT1.
- RAS is split between AT1 (5%) and AT2 (95%).
- Internal flow pattern is from AT1 to AT2 to AT3 to AT4.
  PT flow directed to AT2.

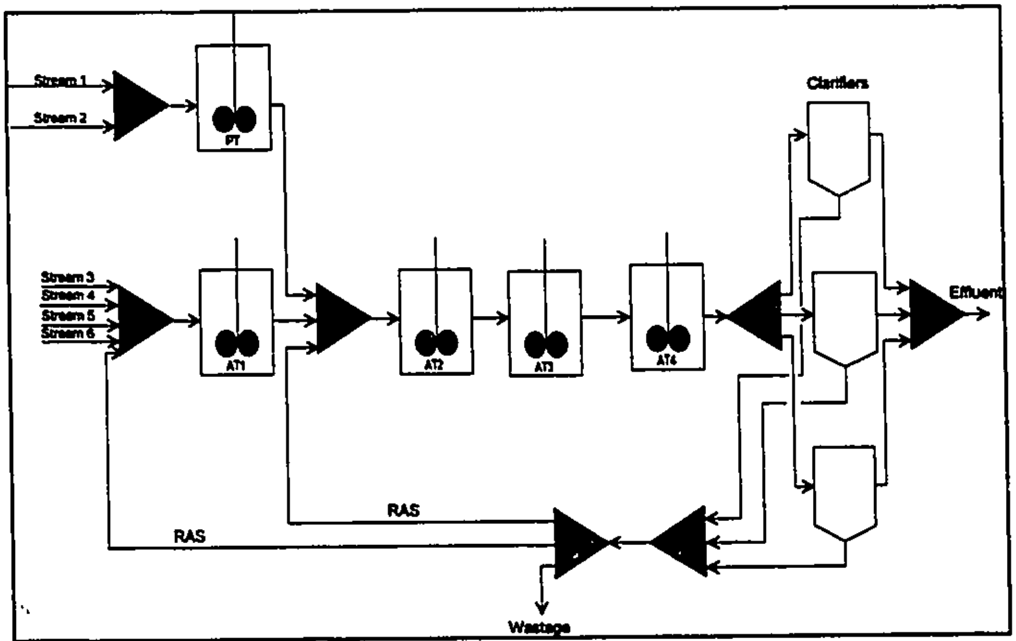

Figure 7.1 : Configuration 1: The configuration of the petrochemical activated sludge system in its present operating mode.

Within this configuration, an important aspect is the large hydraulic retention time (HRT) in AT1. This is evident from Table 7.1 which lists the daily mean flowrates (Q), DOC concentrations, and DOC loading rates of the six streams (Note: DOC values are reported because long term average values were available). The four high strength streams (Streams 3, 4, 5, & 6) are discharged into the first aeration tank (AT1). Due to the low flow rates of these high strength streams, the result is a longer hydraulic residence time in AT1 than the other three tanks (AT2, AT3, AT4). The rationale for this operating scheme is that the highly concentrated and difficult-to-degrade components in the influent wastewater are exposed to the biomass for a longer period. Since the components in the petrochemical wastewater streams are generally soluble COD an increased hydraulic residence time is required to provide the extended contact time and not just an increased sludge age.

The lower strength, high flow influent streams (Streams 1 & 2) are combined in the pretreatment tank (PT) at the head of the plant and discharge into the second aeration tank (AT2). This pretreatment tank contains no biomass, serving only as an equalization and pH balancing tank. The lower hydraulic residence times operating in tanks AT2, AT3, and AT4 generally are sufficient for proper treatment of the remaining contaminants.

Table 7.1: Summary of long term average flowrates, DOC concentrations, DOC loadings and percentage loadings to the petrochemical activated sludge plant.

STREAM #	FLOW (ML/d)	DOC Conc. (mg/L)	DOC LOAD (kg/d)	% OF DOC LOAD
1	4.24	31	135	8.2
2	12.60	47	589	35.9
3	0.76	440	313	19.1
4	0.002	81000	162	9.9
5	0.5	884	442	26.9
6	< 50 L	Variable	-	-
TOTAL	18.1		1641	100

Configuration 2 - All feed treated in first aeration tank (AT1); RAS to AT1: Figure 7.2 illustrates this operating configuration.

- Streams 1 and 2 entered PT.
  Streams 3, 4, 5, and 6 directed into AT1.
- RAS recycle stream recirculated to AT1 (100%).
- Internal flow from AT1 to AT2 to AT3 to AT4.
  Streams 1 and 2 initially entered PT and then flowed into AT1.

The objective of this operating scheme was to evaluate if reducing the hydraulic residence in AT1 significantly influenced effluent quality. It also increased the time Streams 1 and 2 were in the activated sludge system. Therefore, the two streams with the greatest mass loadings received increased treatment, whereas the low flow streams (3, 4, 5, 6) with high COD concentrations were in the system for less time overall. The concern with this configuration was the potential for negative impacts on effluent quality during a spike loading of alcohol P (S_{AP}) from Stream 3.

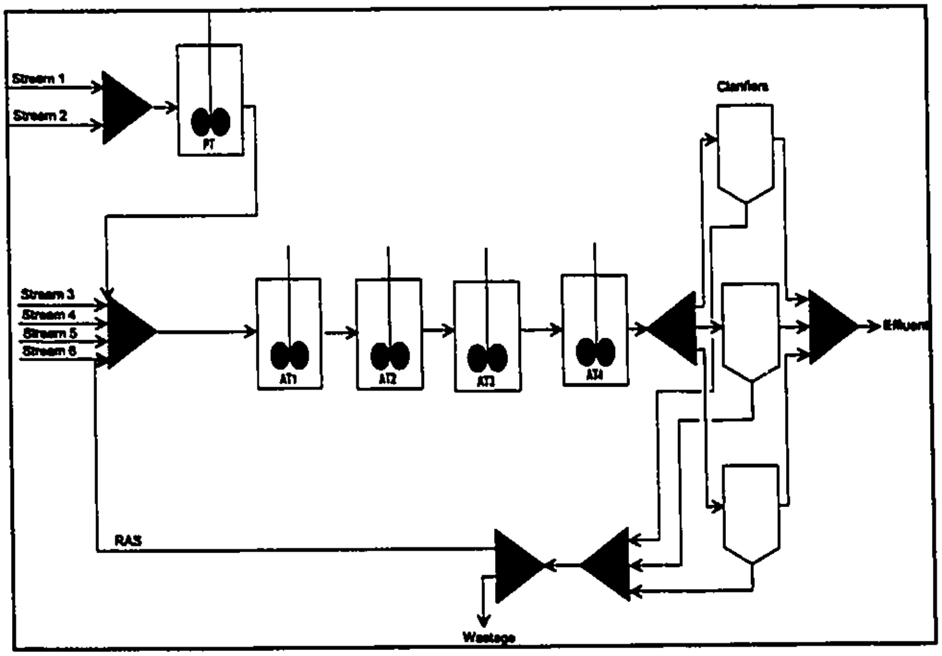

Figure 7.2: Configuration 2 - The petrochemical activated sludge plant was operating with all feed directed through the first aeration basin (AT1).

Configuration 3 - Conversion of the pretreatment tank (PT) to an aeration basin in the present operating configuration: The outline of this operating configuration is illustrated in Figure 7.3.

- Streams 1 and 2 entered PT which was converted from an equalization basin to an aeration basin containing biomass.
  Streams 3, 4, 5, 6 entered AT1.
- RAS recycle stream split between AT1 (5%) and PT (95%).
- Internal flow from AT1 to AT2 to AT3 to AT4.
  Streams 1 and 2 initially entered PT and then were directed into AT2.

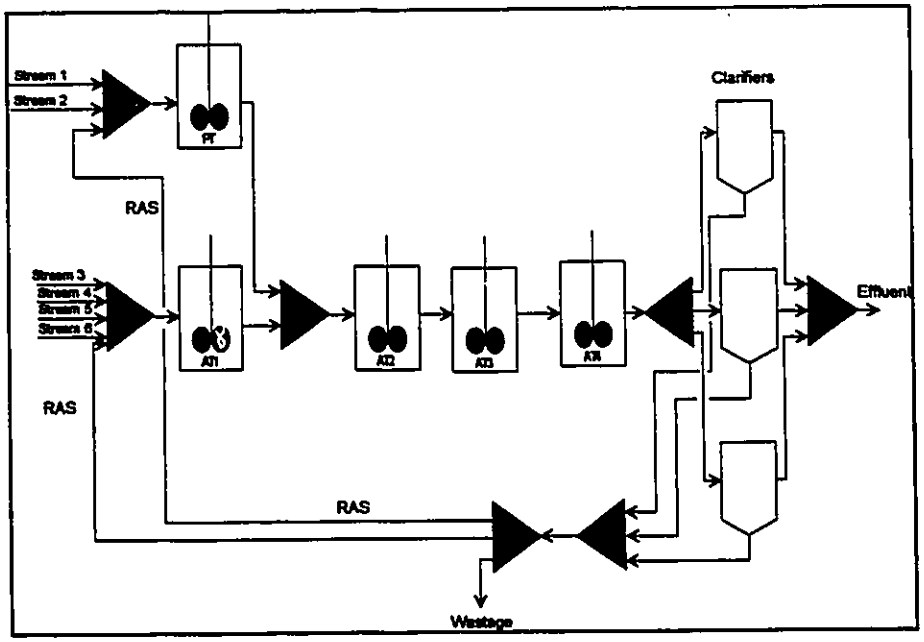

Figure 7.3: Configuration 3 - The petrochemical activated sludge plant was operating with the pretreatment serving as an aeration basin. Wastewater from the pretreatment tank was directed to AT2. AT1 continued to operate at the longer HRT.

This configuration aimed to reduce the emission of volatile organic compounds from the plant by utilizing the pretreatment tank as another aeration basin. Since the majority of the VOC's are stripped from this basin, it was expected that the VOC emissions could be reduced by degrading the organics instead of giving them the opportunity to be stripped.

Since the high strength influent streams continued to be directed to AT1 for treatment at the longer hydraulic residence time, there was minimal concern for a decrease in effluent quality, especially during spike loads.

Configuration 4 - Conversion of the pretreatment tank (PT) to an aeration basin; All feed treated in AT1: This operating strategy also converted PT into an aeration basin, but combined this operation with Configuration 2 by treating all influent in AT1 (Figure 7.4).

- Streams 1 and 2 entered PT which was converted from an equalization basin to an aeration basin containing biomass.
  Streams 3, 4, 5, 6 entered AT1.
- RAS recycle stream split between AT1 (5%) and PT (95%).
- Internal flow from AT1 to AT2 to AT3 to AT4.
  Streams 1 and 2 initially entered PT and then were directed into AT1.

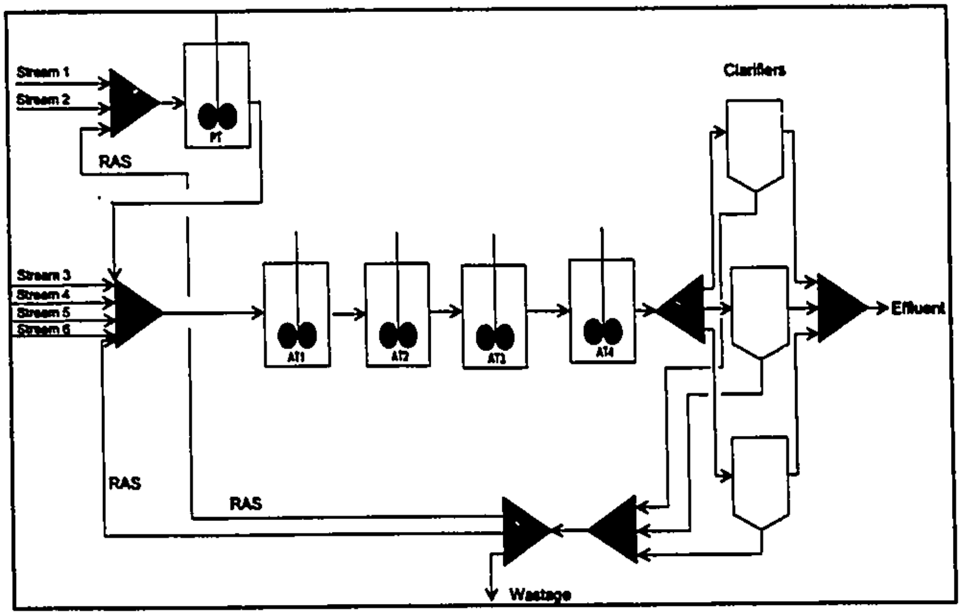

Figure 7.4: Configuration 4 - The petrochemical activated sludge plant was operating with the pretreatment serving as an aeration basin. All wastewater streams, including those in the pretreatment tank, were directed to AT1.

The aim of this configuration was to evaluate system performance when combining Configurations 2 and 3. As in configuration 2, this scheme increased the time the two streams (Streams 1, 2) with the greatest mass loadings were in contact with biomass, but decreased the time that the high strength waste was treated (Streams 3, 4, 5, & 6). This was combined with the desire to reduce VOC emissions from the pretreatment tank. Again, the potential for problems when a spike loading of alcohol P was discharged into AT1 from Stream 3 was a concern due to the reduction in overall hydraulic residence time.

Configuration 5 - Two sets of two tanks in series: Figure 7.5 illustrates the petrochemical activated sludge system operating in this mode.

- Streams 1 and 2 entered PT.
  Streams 3, 4, 5, and 6 combined with PT flows and entered AT1 or AT3.
- RAS recycle stream directed to AT1 (50%) and AT3 (50%).
- Total flow split between AT1 and AT3.
  AT1 flowed to AT2 and then to clarifiers.
  AT3 flowed to AT4 and then to clarifiers.

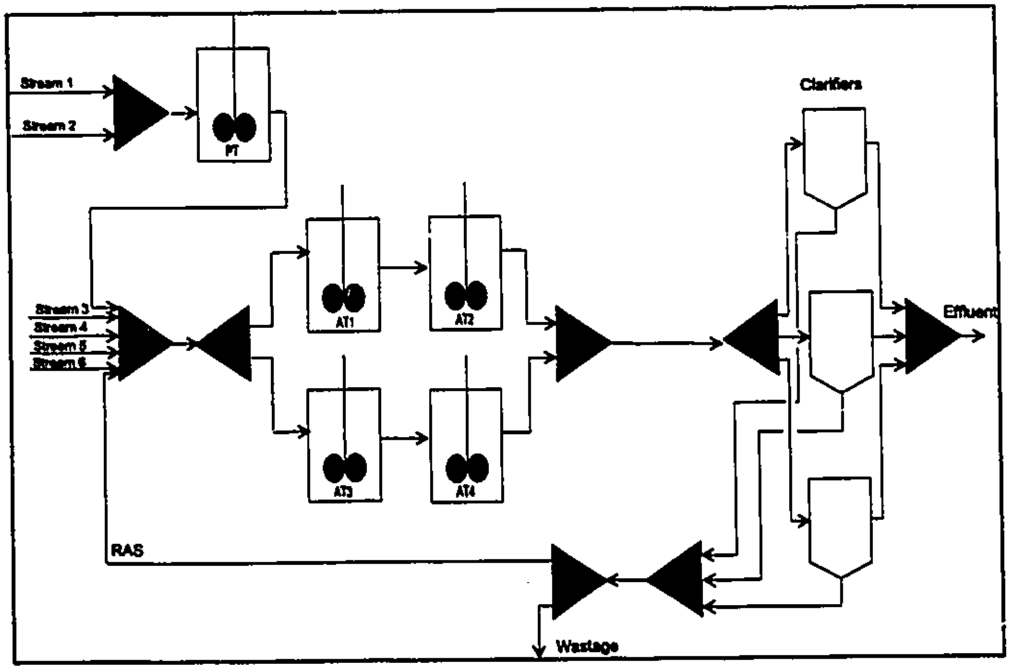

Figure 7.5: Configuration 5 - The petrochemical activated sludge plant was operating as two sets of two tanks in series.

The objective of evaluating this operating mode was to determine if doubling the hydraulic residence time in each reactor improved system performance. Operating two sets of tanks in series doubled HRT in each reactor, but the wastewater was treated in only two tanks instead of four. This configuration was similar to treating all the influent streams in all four aeration basins (i.e. directing pretreatment tank flows to AT1) in terms of the overall hydraulic residence time of the wastewater in the system. Again, the concern was the ability of the system to attenuate spike loads of alcohol P from Stream 3.

The two aspects of plant operation under consideration were evaluated in each of the five plant configurations.

7.3.1 Problems Encountered in Operation of the Petrochemical Treatment Plant

Before discussing the results of the individual simulations conducted on the different operating modes some general observations should be noted.

- Petrochemical wastewaters generally tend to contain low concentrations of the important nutrients, nitrogen and phosphorus. In this particular plant, the system apparently operated very close to nitrogen limited growth conditions. This was evident during model simulations of the different system configurations. When a spike loading of alcohol was discharged to the first aeration basin there was insufficient nitrogen for the organisms to degrade the additional substrate. As a result, the first aeration basin became nitrogen limited so only a certain amount of excess substrate could be utilized. This in turn influenced the nitrogen concentrations in subsequent reactors. More nitrogen was removed from these reactors and in certain instances caused these aeration basins to be nutrient limited. The level of organic material which could be removed then became limited with the result being an increase in effluent COD or in VOC emissions, or both.

- The amount of volatile organic compounds which were degraded *versus* the amount that was volatilized was a function of the relative rates of these two processes, as well as the nutrients available for growth. If nutrients were limited, then more VOC's tended to be volatilized since they would remain in the system longer in the volatile form without being degraded. In the volatile form they continued to be stripped and added to the total VOC emissions from the facility. It is often difficult to determine which of these removal pathways the VOC compounds follow at a given time.

7.4 CASE STUDY 1: INFLUENCE OF OPERATING CONFIGURATION ON VOC EMISSIONS

In the current operating scheme of the petrochemical activated sludge system, return activated sludge (RAS) is returned to the first and second aeration tanks (AT1, AT2). As tabulated in Table 7.2, model simulations of this operating mode predicted VOC emissions at an estimated rate of 75.0 kg COD per day. With the increased concern over air emissions a method of reducing this loading to the atmosphere is advantageous. Four alternatives were considered.

The main area of concern for air emissions was from the surface of the pretreatment tank (PT). During a study of volatile organic compound emissions conducted at the petrochemical facility, this portion of the wastewater treatment system was identified as the main generator of air emissions. In order to address this situation it was suggested that biomass be directed to the pretreatment tank. Instead of only being stripped from the system, a portion of the VOC's would be biodegraded by the organisms present in the tank. Stripping of VOC'S would continue, but at a much reduced rate. Simulation enabled prediction of the changes to VOC emissions under these alternate strategies. Table 7.2 summarizes the results of the simulations. The impact on effluent soluble COD (mg/L) and effluent TSS (mg TSS/L) also are tabulated and indicate minimal affect.

The values tabulated in Table 7.2 indicate that significant improvements can be achieved in terms of air emissions when return activated sludge is directed into the pretreatment tank. In the two operating scenarios where the pretreatment tank was converted into another aeration basin, the VOC emissions were reduced by 73 percent from 75.0 kg COD per day to 20 kg COD per day. This suggests that this mode of operation is highly advantageous if the mass of organics stripped from the activated sludge system is a major concern.

Table 7.2: Impact of operating configuration on the air emissions of volatile organic compounds and on the effluent COD.

		SYSTEM RESPONSE		
	CONFIGURATION	AIR EMISSIONS (kg COD/day)	EFFLUENT COD (mg COD/L)	EFFLUENT TSS (mg TSS/L)
1	Present Configuration	75.0	51.3	27.5
2	All feed through AT1	101.4	51.1	27.5
3	RAS to PT instead of AT2; PT effluent discharged to AT2	20.3	51.1	27.5
4	RAS to T5; All feed discharged to AT1	20.4	51.0	27.4
5	2 sets of 2 tanks in series	74.2	51.4	27.5

One comment which should be made is that with degradation of organic compounds, the nutrients such as nitrogen and phosphorus must be present in sufficient levels to ensure that growth is not limited. As an example, nitrogen limitations result in increased VOC emissions from the system when all feed is directed into AT1. The VOC concentration leaving the pretreatment tank is the same regardless of whether the stream is fed into the second tank (AT2) in the present operating configuration or whether it is directed into AT1. This indicates that the change in conditions in the first tank, when it receives all the feed, influences the air emissions. In the present operating configuration the ammonia concentrations in AT1 and AT2 are 0.02 mg N/L and 0.5 mg N/L, respectively. AT2 receives the combined influent streams from the pretreatment basin, including the volatile organic compounds, and there appears to be sufficient nitrogen to generate some organism growth. When the system is operated such that all feed goes into AT1, the nitrogen in the tank is only 0.2 mg N/L and that in AT2 is only 0.3 mg N/L. This is getting closer to nutrient limiting growth conditions in both tanks, reducing the removal rate of the volatile organic compounds via the degradation route. Therefore, more of the volatile organic compounds have time to be stripped from the system. This simulation illustrates the interrelationships that can be determined using a model that would otherwise be very difficult to quantify.

Observing the response of the activated sludge system treating petrochemical wastewaters illustrates the significant role that volatile organic compounds have in determining the behaviour of these systems. It is important that the fraction of volatile organic compounds in the influent wastewater is determined and the stripping rates associated with the different compounds are quantified. These characteristics influence the air emissions from the plant, as well as the amount of organic material available for growth given sufficient nutrient levels. This in turn impacts the oxygen utilized in the activated sludge system and the amount of volatile suspended solids generated. The discussion above also illustrates that when a plant has the potential for nutrient deficiency, the amount of volatile organic compounds which can be degraded in a given time frame may be limited. In summary, the case study on the petrochemical system shows the importance of understanding the processes associated with the removal of volatile organic compounds

7.5 CASE STUDY 2: INFLUENCE OF OPERATING CONFIGURATION ON SYSTEM RESPONSE TO A SPIKE LOADING OF ALCOHOL P TO AT1

This case study involved disturbing the petrochemical activated sludge system by discharging a spike loading of alcohol P (S_{AP}) used in the petrochemical refinery to the first aeration tank (AT1). Alcohol P constitutes the main component in influent Stream 3 which discharges into AT1 in the current mode of operation. Due to its application in upstream processing, spike loads of the compound are a regular occurrence. Therefore, the activated sludge system must be operated in a mode which attenuates these spikes when they occur.

The spike load simulated in the model of the system was a discharge of 5000 mg DOC/L over a period of 2.4 hours from a baseline concentration of 345 mg DOC/L. This represents approximately a fifteen fold increase in concentration. In terms of daily loading rates, this spike represents an increased organic loading of 41 percent to AT1 and a 23 percent increase in loading rate to the overall plant. Five different operating strategies were evaluated in the model to identify the operating scheme which minimized the impact on effluent quality.

Initially the spike was simulated in the present operating configuration to establish current characteristics of system response. Figure 7.6 illustrates the response in the four aeration tanks in terms of soluble COD (mg/L). At the onset of the spike into AT1 the soluble COD increased dramatically due to the discharge of the highly concentrated alcohol P. For the duration of the spike the concentration of COD in AT1 continued to increase. A slight increase in soluble COD concentration was evident in AT2, but there was no impact in the third and fourth reactors. Once the influent spike ceased, the COD concentration in AT1 gradually decreased to original levels. The same situation is illustrated in AT2, but to a much lesser degree. From this plot it can be concluded that the present operating configuration is capable of attenuating a spike loading of alcohol P to the first aeration tank with no impact on effluent quality. The long hydraulic residence time of the influent in AT1 plays a significant role in the ability of this operating strategy to handle the transient loadings.

The response of the different operating configurations to a spike loading of alcohol P is illustrated in Figure 7.7 in terms of the final effluent COD. As the graph indicates, only the present configuration and the modifications which send RAS to the pretreatment tank successfully attenuated the loading. In these scenarios the high strength streams, which include the alcohol stream, had an extended hydraulic residence time in the system in AT1 which the alternative scenarios do not incorporate. Therefore, the alcohol P spike was in contact with the biomass for a longer time. This provided the extra time required to degrade the high concentrations of this more slowly degradable compound.

The specific response of each of the alternative operating scenarios is now outlined. The importance of having sufficient nutrients such as nitrogen is prevalent throughout the discussion of these simulations.

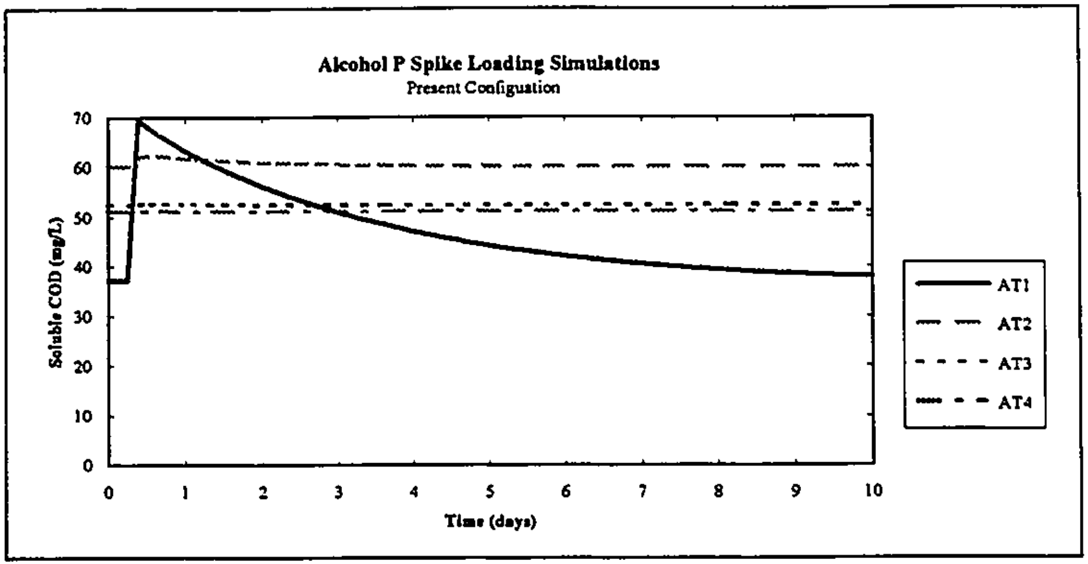

Figure 7.6 : The response of the petrochemical activated sludge system in its present operating configuration during a spike loading of alcohol P. The graph illustrates the change in effluent soluble COD (mg/L) in each of the four aeration tanks in the system.

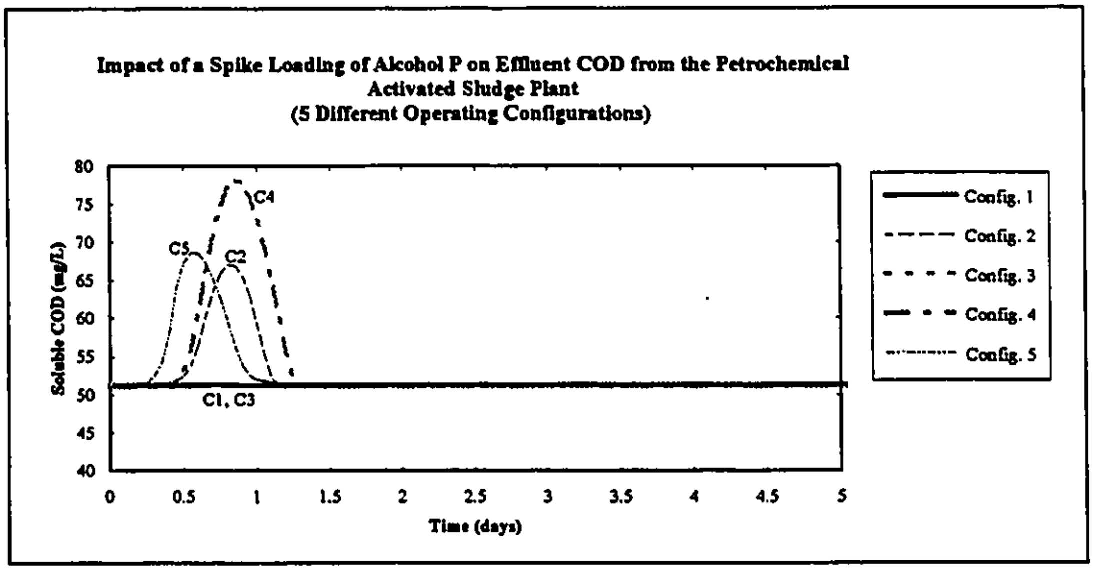

Figure 7.7: The response of the petrochemical activated sludge system during a spike loading of alcohol P for the different operating conditions. The graph illustrates the change in effluent soluble COD discharged from the system. Only the current operating mode or a mode which involves rerouting the return activated sludge stream to the pretreatment tanks are capable of attenuating a spike loading of alcohol.

7.5.1 Response of Present Configuration to an Alcohol P Spike

Figure 7.6 illustrated that the present configuration was capable of attenuating a spike of alcohol P with no impact on the final effluent soluble COD. This was despite the concentration of the compound in reactor AT1 approximately doubling to about 70 mg COD/L. Simulations indicated that it would require about 10 days for the conditions in the first tank to return to normal operating values under such a spike. This was largely a result of the lengthy hydraulic retention time of the wastewaters in AT1. The impact on soluble COD reaching AT2, AT3, and AT4 was minimal. Since the effluent from AT1 mixed with 90 percent of the fresh feed, dilution played a significant role in minimizing the impact in subsequent tanks. Due to both dilution and degradation influences, the influent soluble COD to the second aeration basin only increased by 2 mg/L. Negligible impact was observed in the final two aeration basins in terms of soluble COD.

The responses of other system parameters in the model simulations also were reviewed and are presented in Figures 7.8(a) to (c). The response which most clearly illustrates behaviour of the system under the spike loading to AT1 is that for ammonia [Figure 7.8(c)]. Even prior to the spike AT1 apparently is close to being nitrogen limited, with an ammonia concentration of only 0.02 mg N/L *versus* approximately 0.4 mg N/L in the other aeration tanks. Examination of the model output indicated that most of the degradable substrate was being removed in AT1, however. Therefore it would be anticipated that there would be minimal degradation in AT1 of additional substrate entering AT1 with the spike. This additional substrate would have to pass through AT1 into the downstream aeration tanks where nitrogen limitation was less severe. The anticipated system response was confirmed in the simulations. From Fig. 7.6, integration of the area under the AT1 soluble COD curve (above the baseline level before the spike) indicated that the major portion of the spike loading passed from AT1 undegraded as a result of the nutrient limitation. This is substantiated by the observation that there was almost no increase in OUR predicted in AT1 after the spike load even though the COD concentration was elevated for a period of several days.

Figure 7.8(c) shows a decrease in ammonia concentrations in AT2, AT3, and AT4 immediately following the spike. This decrease is a result of the increased nitrogen requirements as additional undegraded substrate passed out of AT1. [The predicted small spike in ammonia concentration in AT1 should be explained. The spike should not occur given that no additional ammonia enters with the alcohol P shock load to AT1. Rather the "predicted" spike is an artifact of the instability in the numerical integration procedure used in the simulator package, and would not occur in practice. The OUR response in AT1 [Fig.7.8(a)] also shows some instability as a result of the small ammonia spike. Both of these anomalies should be ignored in the interpretation of response. Similar minor integration instabilities also are evident in the ammonia responses shown in Figs 7.9(d), 7.10(d), 7.11(d), and 7.12(d).]

In all four aeration basins the spike resulted in a slight increase in the volatile suspended solids concentrations due to the additional substrate available for growth. The response of the suspended solids concentration in model predictions of AT1 also was impacted by the behaviour of the simulator. The spike load caused an increase in biomass concentration due to increased substrate available for growth. The controller for the SRT in the simulator responded by increasing the wastage rate to remove the extra solids and maintain the sludge retention time. This decreased the rate of return of RAS. Since the inflow to AT1 is nearly all RAS, any change in its characteristics is reflected in the characteristics in AT1. Therefore, the changing flow and concentration of RAS resulted in this initial drop in suspended solids in AT1. As the simulation continued and more substrate was utilized, the suspended solids slowly increased to a level higher than that before the spike. This sensitive response is unlikely to be seen in a full-scale system.

In the model simulation there was also a slight increase in VOC emissions from the system. This was likely the result of the nutrient deficiency in the wastewaters. With an increased organic load during the spike loading more nutrients were required for substrate utilization so any nutrients in the wastewaters were used rapidly. Nutrients continued to be consumed until all the additional substrate was consumed. However, because VOC's can be stripped from the system, the stripping rate was such that the compounds were stripped before the necessary nutrients became available. In nutrient deficient conditions more VOC compounds are likely to be stripped.

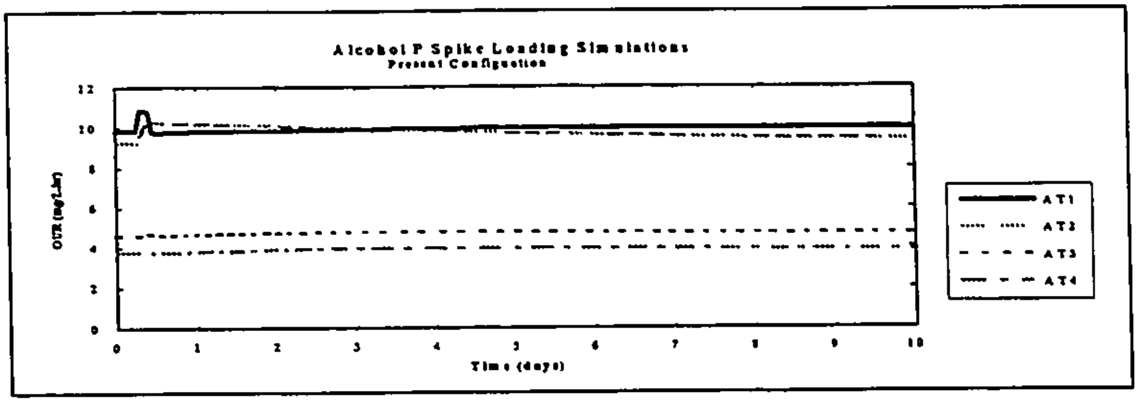

Figure 7.8a : The response of the petrochemical activated sludge system (Present Configuration) during a spike loading of alcohol P. The graph illustrates the change in OUR (mg/L/hr) in each of the 4 aeration tanks in the system.

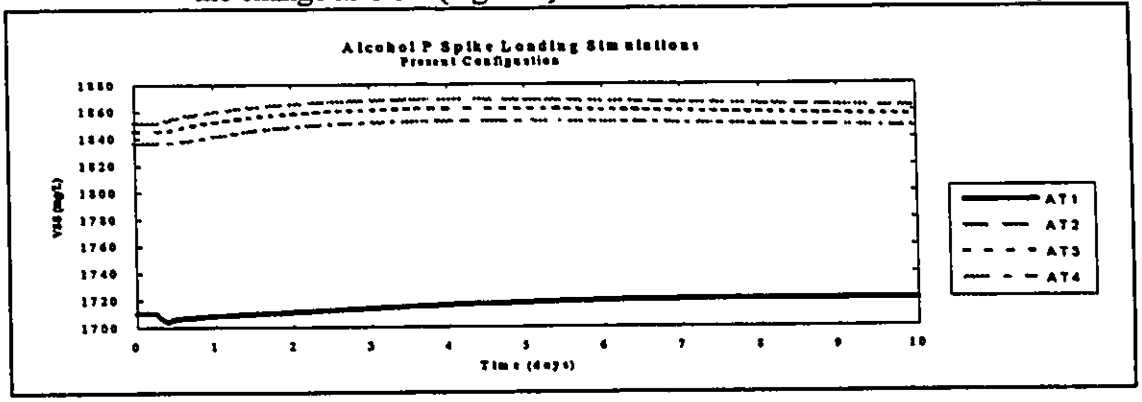

Figure 7.8b: The response of the petrochemical activated sludge system (Present Configuration) during a spike loading of alcohol P. The graph illustrates the change in VSS (mg VSS/L) in each of the 4 aeration tanks.

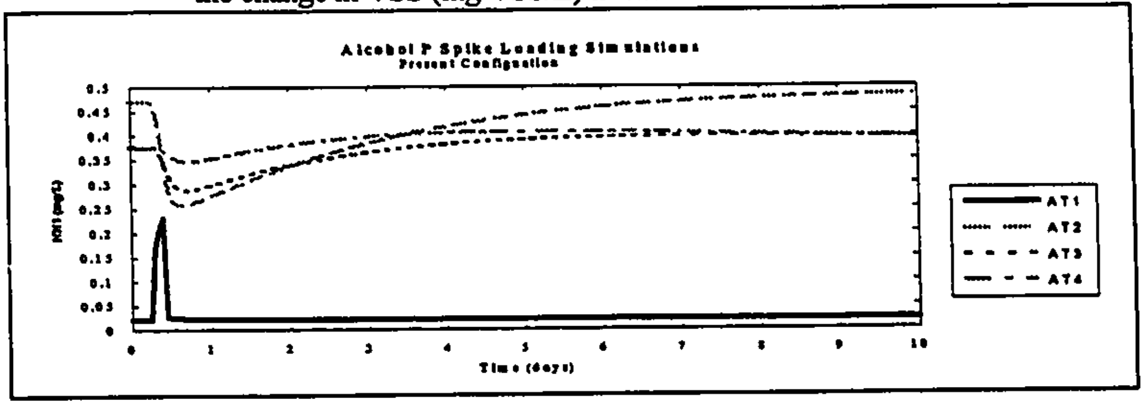

Figure 7.8c : The response of the petrochemical activated sludge system (Present Configuration) during a spike loading of alcohol P. The graph illustrates the change in effluent ammonia (mg N/L) in each of the 4 aeration tanks.

7.5.2 Response of Configuration 2 to an Alcohol Spike

The model simulations of operating the petrochemical activated sludge system in this operating model are illustrated in Figure 7.9(a) to (d). By sending all influent streams in the system through the first aeration basin (AT1), the system was unable to attenuate a shock loading of the alcohol compound. The concentration of the soluble alcohol COD increased in all aeration tanks including the final aeration tank [Figure 7.9(a)]. In the first aeration basin (AT1) the concentration in the reactor increased from 50 mg COD/L to over 300 mg COD/L. The final effluent concentration increased by 18 percent to 67 mgCOD/L. This observation indicated that the long hydraulic retention time in the first aeration basin was required to degrade the shock loadings of this particular compound.

Since the COD increased in each of the aeration basins there was more substrate available for organism growth, and therefore, higher nutrient requirements. Both the VSS concentration [Figure 7.9(c)] and the oxygen utilization rate [Figure 7.9(b)] in each tank initially increased, but gradually decreased as the influence of the spike diminished. [The spike in OUR in AT2 is related to the instability of the numerical integration discussed in Section 7.5.1.] The impact of nutrient limited growth was reflected in the lower than expected changes in OUR in the first two aeration basins. The OUR increased due to the increased organic loading, but with sufficient nitrogen would be expected to increase more significantly.

The ammonia concentration response also reflected the additional substrate, and the subsequent increase in nutrient requirements for growth. As previously mentioned in Section 7.5.1, the spike of ammonia which apparently occurred in AT1 was a result of instability in the numerical integration procedure. Therefore, it should not be included in interpretation of the system behaviour. The drop in ammonia to lower concentrations than prior to the spike is a more realistic response. Once the spike had passed through the tank the ammonia concentration gradually returned to normal levels. In the remaining three aeration basins (AT2, AT3, AT4) the onset of the shock load also resulted in a significant drop in ammonia concentration to very low levels in all tanks. The ammonia concentration dropped rapidly due to the extra nitrogen required for growth, and remained at these extremely low concentrations until the spike passed through the system. With nitrogen continuing to enter in the influent streams and being generated from decay processes, the nitrogen levels eventually increased. Initially, the ammonia returned to concentrations greater than original levels due to the increased contribution from decay processes (i.e. the VSS concentration was greater due to increased growth from the additional substrate; therefore, there were more organisms to decay). As the VSS concentration returned to pre-spike levels, the ammonia concentrations in the reactors all returned to normal levels.

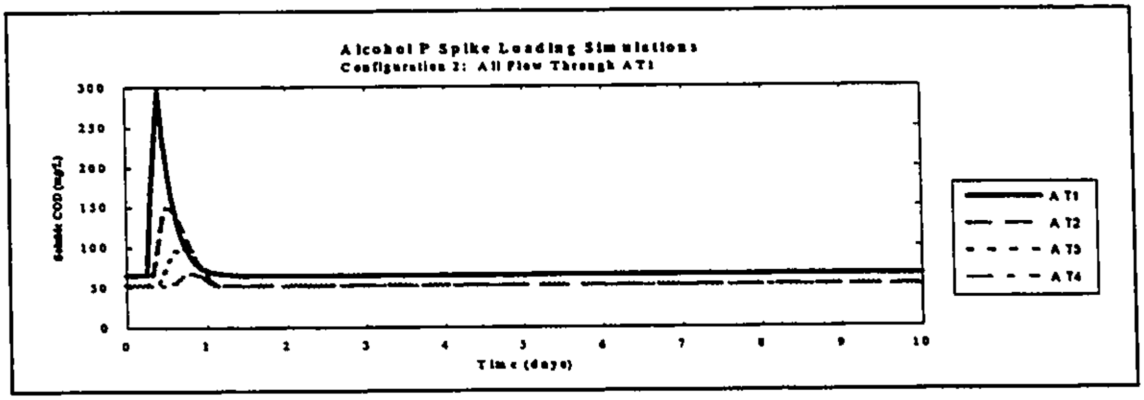

Figure 7.9a : Configuration 2: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in effluent soluble COD (mg/L) in each of the four aeration tanks in the system.

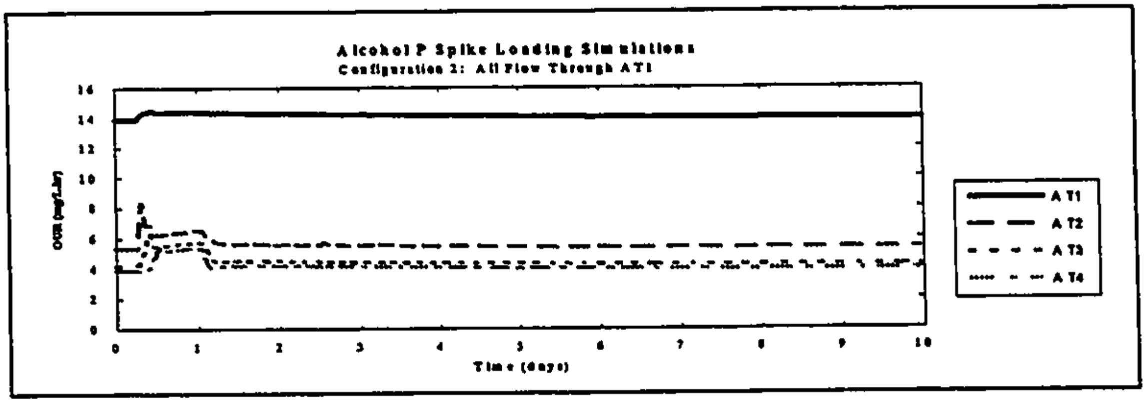

Figure 7.9b: Configuration 2: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in OUR (mg/L/hr) in each of the four aeration tanks in the system.

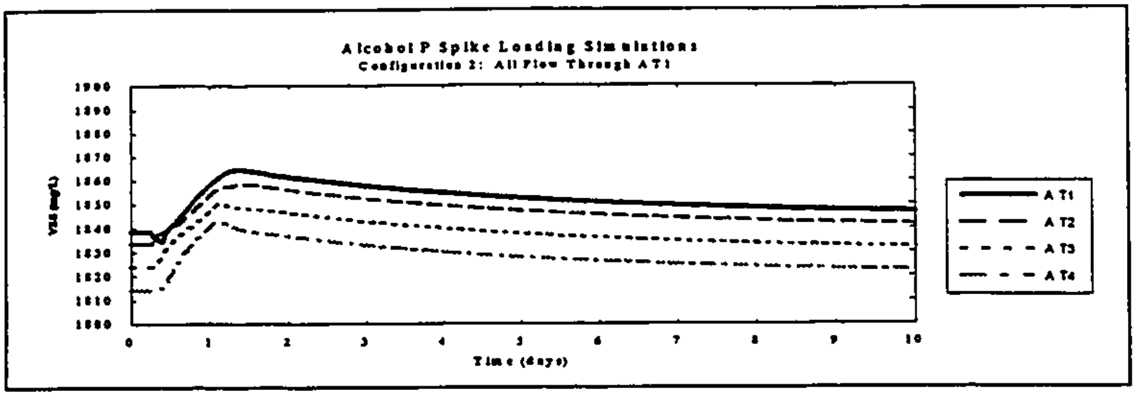

Figure 7.9c: Configuration 2: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in VSS (mg VSS/L) in each of the 4 aeration tanks in the system.

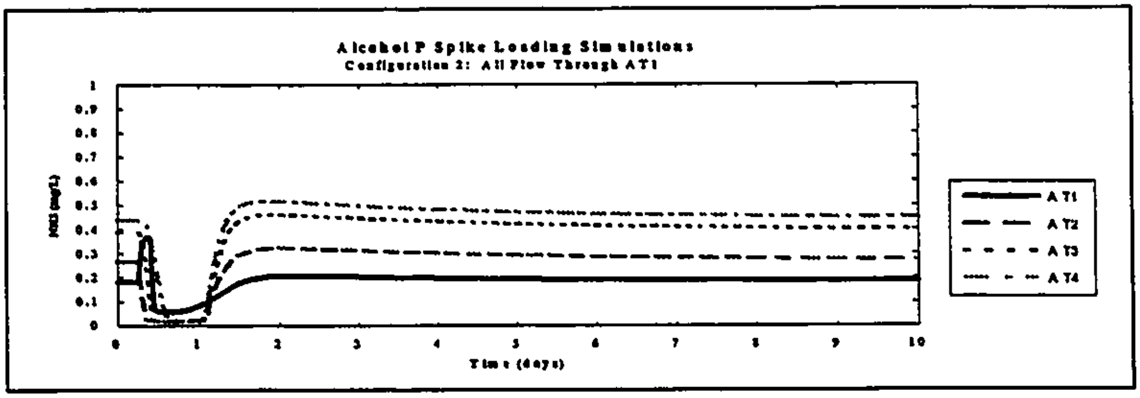

Figure 7.9d: Configuration 2: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in ammonia (mg N/L) in each of the 4 aeration tanks in the system.

7.5.3 Response of Configuration 3 to an Alcohol Spike

In this operating configuration RAS is redirected to the pretreatment basin instead of the second aeration tank (AT2) to minimize the volatile organic compound emissions from the system. Since this flow scheme did not impact the retention time of the shock load in the first aeration basin there was no change in the final effluent soluble COD. The soluble COD in AT1 and AT2 increased initially under the shock loading conditions as it did under the present operating configuration, but gradually returned to pre-shock loading concentrations. Similarly, the ammonia concentrations were influenced by the increased organic load and decreased in each of the tanks during the shock load concentrations, but eventually returned to original levels once the additional COD was consumed. Due to the nutrient limiting conditions imposed during a shock load, there was an increase of about 2 kg COD/day in the VOC emission loading. For the remaining system parameters, the response in this configuration was similar to the response of the present configuration.

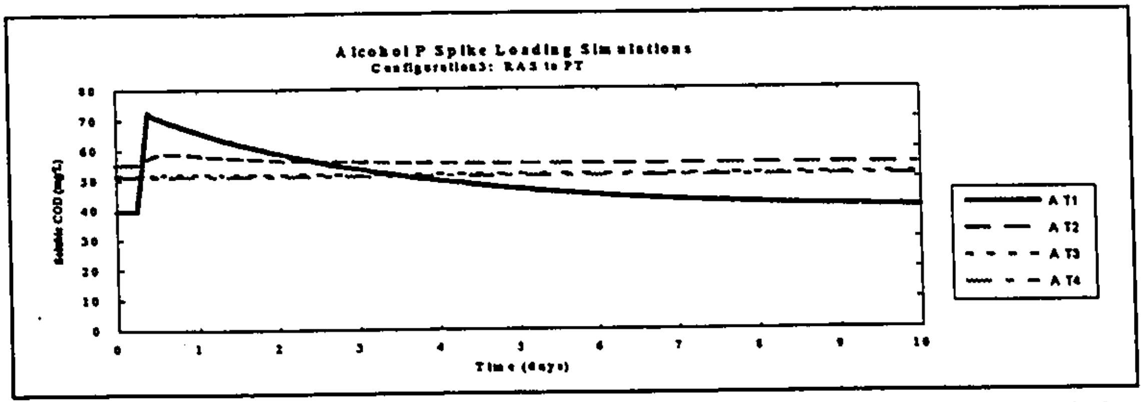

Figure 7.10a: Configuration 3: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in effluent soluble COD (mg/L) in each of the 4 aeration tanks in the system.

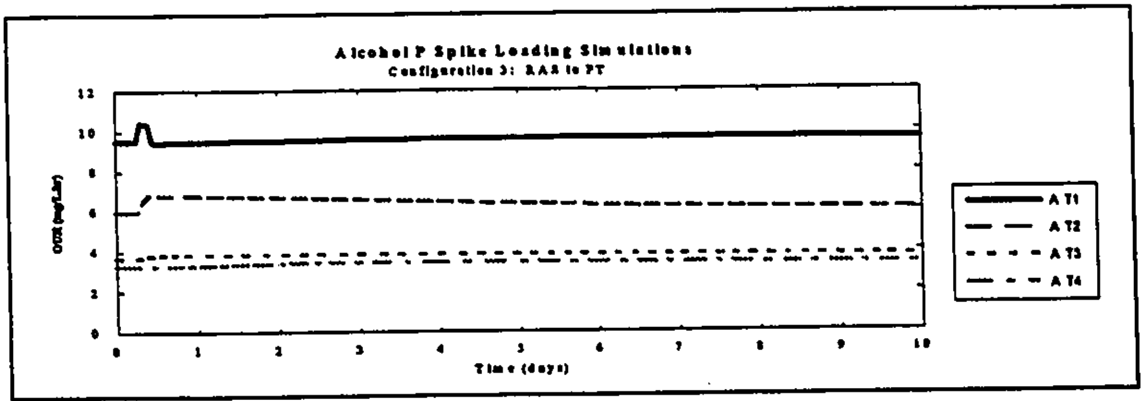

Figure 7.10b: Configuration 3: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in OUR (mg/L/hr) in each of the 4 aeration tanks in the system.

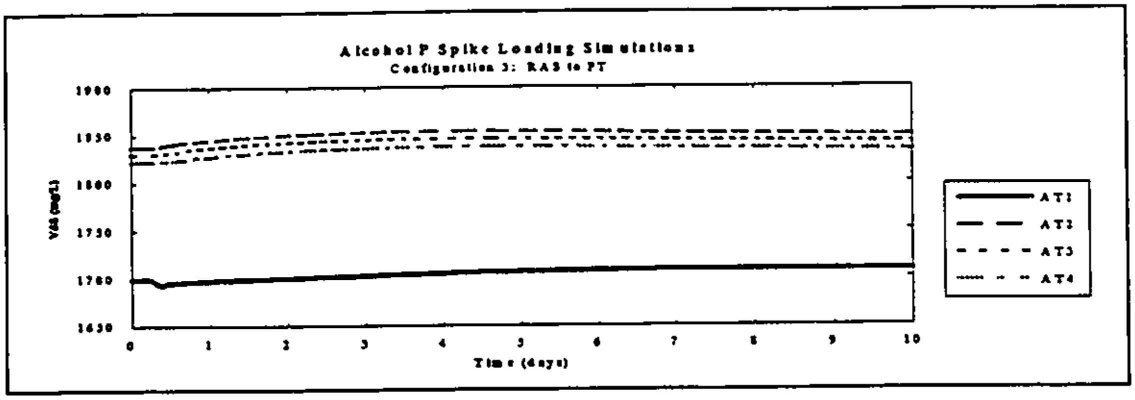

Figure 7.10c: Configuration 3: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in VSS (mg VSS/L) in each of the 4 aeration tanks in the system.

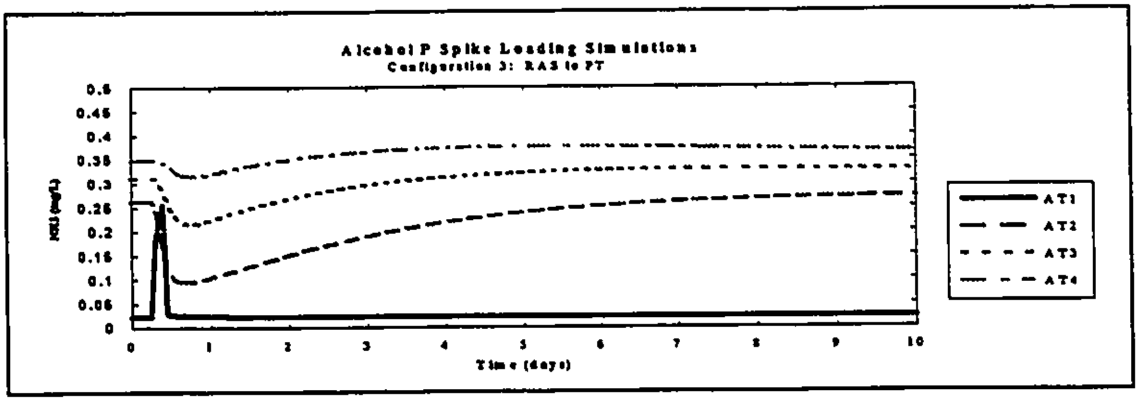

Figure 7.10d: Configuration 3: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in ammonia (mg N/L) in each of the 4 aeration tanks in the system.

7.5.4 Response of Configuration 4 to an Alcohol Spike

This operating mode also sends RAS back to the pretreatment tank (PT) to convert PT into an aeration basin. The PT flow is directed to AT1 where it mixes with the remaining influent streams and RAS recycle. In terms of treatment capacity, it is very similar to configuration 2 with all feed going into AT1. As a result, the model responses of the system were very similar to the system response discussed in that section (7.5.2) and are illustrated in Figure 7.11(a) to (d).

The effluent soluble concentration increased to about 75 mg COD/L which was higher than in Configuration 2 where all feed was directed to AT1, but where the pretreatment tank did not contain biomass. This behaviour again was related to the nutrient limiting conditions which prevented all the COD from being removed. With biomass going into PT there was an increased level of degradation of VOC compounds initially which further contributed to the nutrient deficiency. Therefore, it took longer to degrade the additional COD from the spike loading of alcohol. This resulted in a final effluent alcohol COD concentration which was slightly higher than the level simulated in Configuration 2.

The shock load also served to increase the VOC emissions from the whole system by 5 kg COD per day due to the nutrient limiting conditions. Other than these minor differences, the response of both configuration 2 and 4 were similar and indicate that such configurations are unable to attenuate a shock loading of the alcohol. Again, the importance of the long hydraulic retention time for certain influent streams in AT1 is supported.

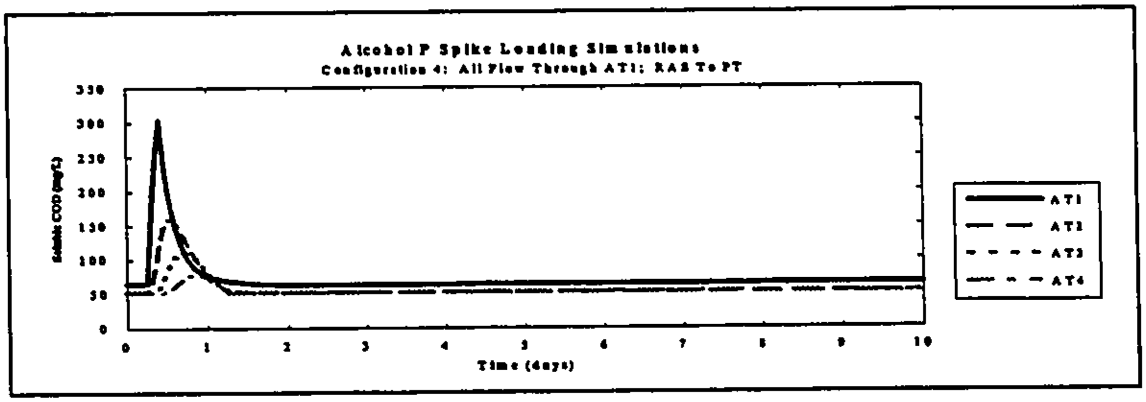

Figure 7.11a: Configuration 4: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in effluent soluble COD (mg/L) in each of the 4 aeration tanks in the system.

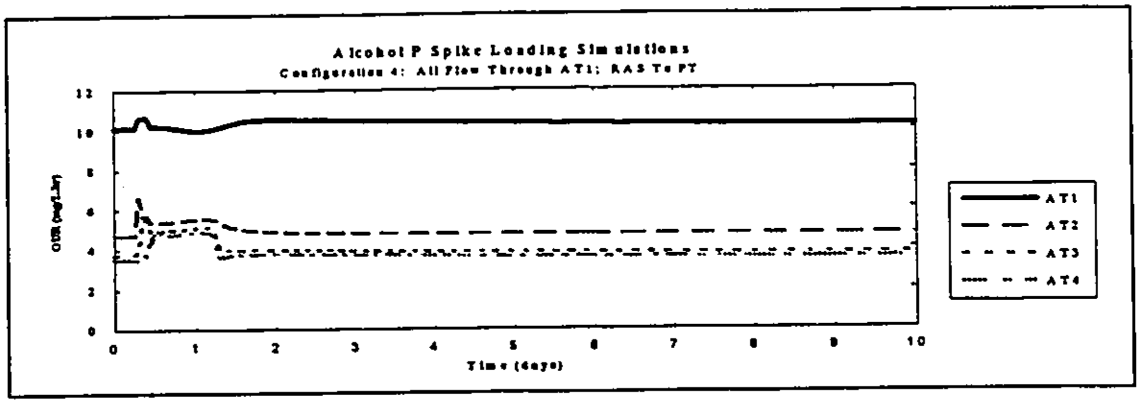

Figure 7.11b: Configuration 4: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in OUR (mg/L/hr) in each of the 4 aeration tanks in the system.

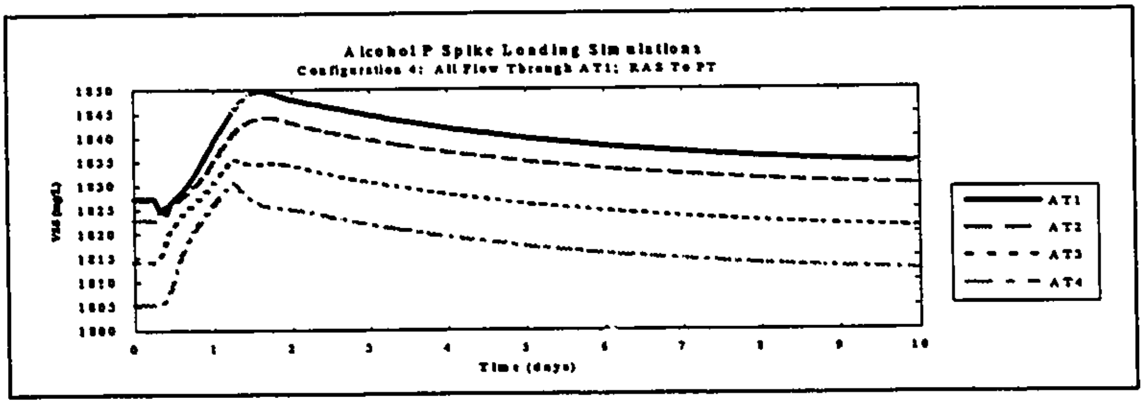

Figure 7.11c: Configuration 4: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in VSS (mg VSS/L) in each of the 4 aeration tanks in the system.

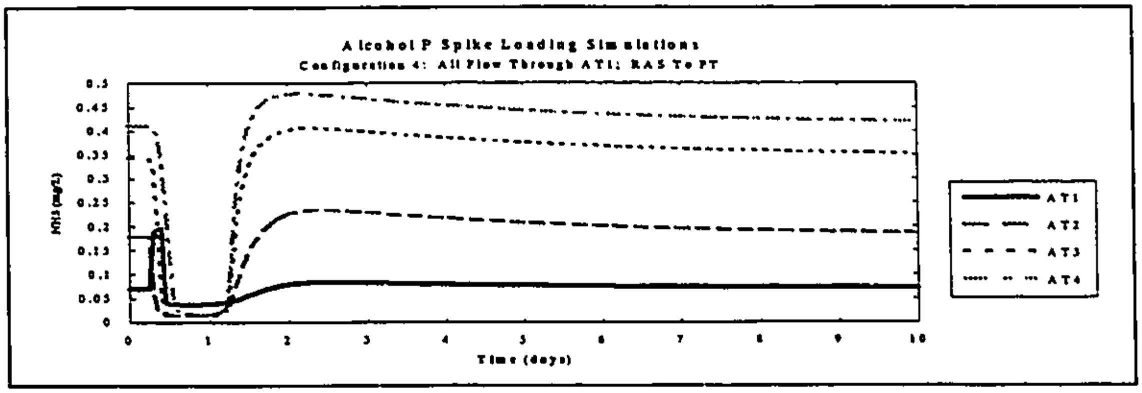

Figure 7.11d: Configuration 4: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in ammonia (mg N/L) in each of the 4 aeration tanks in the system.

7.5.5 Response of Configuration 5 to an Alcohol Spike

This configuration involved operating the activated sludge system as two sets of two tanks in series. Results of the simulations are presented in Figure 7.12(a) to (d). As described earlier, this system also reduced the total HRT of the influent streams. Therefore, it is not surprising that this mode of operation was not able to attenuate the shock loading of the alcohol compound.

The soluble COD concentration from AT1 and AT3 increased to 170 mg/L during the spike loading before gradually returning to original levels. The final effluent concentration from AT2 and AT4 increased by approximately 10 mg/L. Similarly, the VSS and OUR in the all of the tanks increased initially as the additional substrate was utilized, and then returned to pre-spike levels. The ammonia levels also reflected the increased substrate and decreased rapidly to nutrient limiting growth levels during the initial spike. Therefore, like the other operating alternatives which reduced the HRT of the model components which are treated in AT1, problems arose when a shock loading of a compound such as the alcohol was discharged to the activated sludge system.

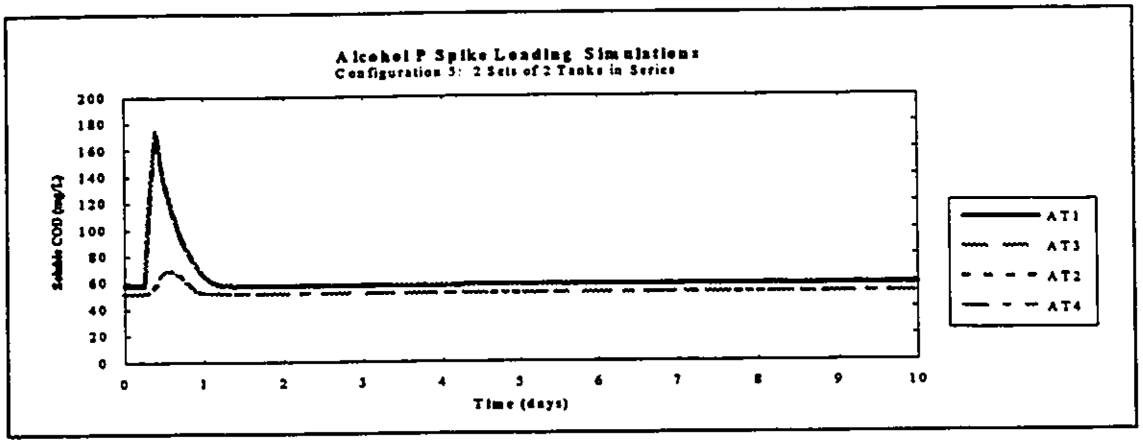

Figure 7.12a: Configuration 5: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in effluent soluble COD (mg/L) in each of the four aeration tanks in the system.

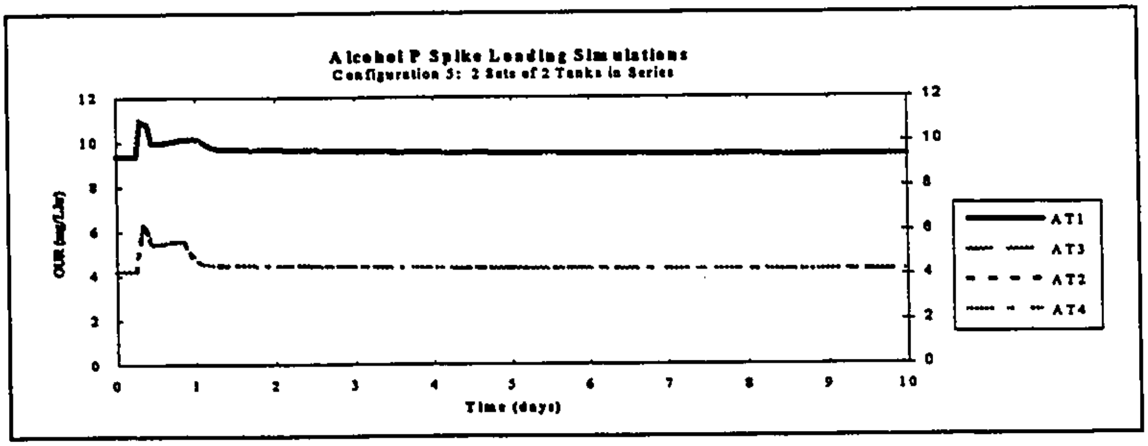

Figure 7.12b: Configuration 5: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in OUR (mg/L/hr) in each of the four aeration tanks in the system.

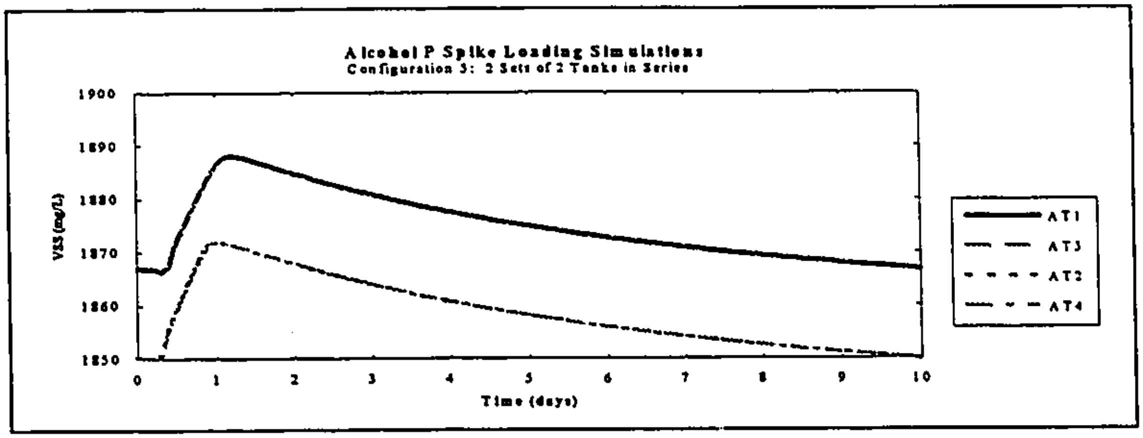

Figure 7.12c: Configuration 5: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in VSS (mg VSS/L) in each of the four aeration tanks in the system.

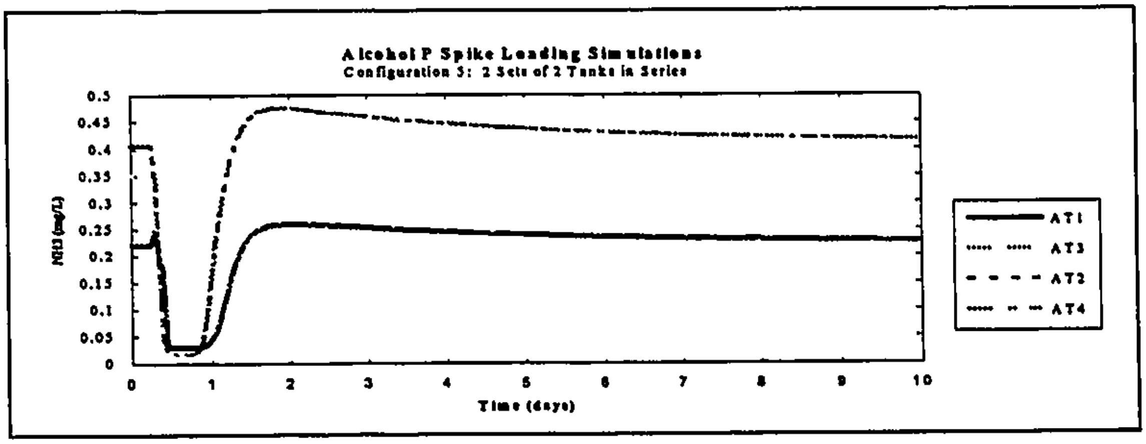

Figure 7.12d: Configuration 5: The response of the petrochemical activated sludge system during a spike loading of alcohol P. The graph illustrates the change in ammonia (mg N/L) in each of the four aeration tanks in the system.

7.5.6 Summary of System Response to a Shock Loading of Alcohol

The above discussion on the response of this activated sludge system indicates that a long hydraulic retention time is required to degrade adequately shock loadings of alcohol P spikes. Any of the configurations which reduced the HRT in the first aeration basin were not able to attenuate the shock loading and impacted the quality of the final effluent stream in terms of soluble COD. The observations presented above also illustrate the impact of nutrient deficiencies on an activated sludge system and how these hinder the effective treatment of the wastewater, especially under transient spike loadings. The model also predicted an impact on the VOC emissions due to the nutrient deficiencies. By modelling the different configurations presented above, suggested modes of operating the system to maintain effluent quality can be determined. For the case of attenuating a shock loading the present configuration was appropriate. If VOC emissions were also a concern then the advantage of redirecting the RAS to the pretreatment tank provided an alternative solution.

7.6 APPLICATION OF MODELS FOR OPTIMIZING SYSTEM PERFORMANCE

The model predictions presented above for the various operating scenarios served to illustrate the ability of an activated sludge model to monitor all the interactive processes occurring in the system. In each of the different configurations, many processes were impacted by changes in the influent and operating conditions. The simulation model provided a tool to evaluate the potential impact of these changes and to identify operating modes which minimized the overall impact. By evaluating different scenarios suggestions on which alternative maximizes the effluent quality can be determined. A mathematical model cannot necessarily mimic every possible response which occurs in a full-scale activated sludge system, but it provides a starting point for altering the system while minimizing the potential for system upset. The model allows the user to focus on viable alternatives and disregard possibilities which likely are detrimental to the successful operation of the system.

The example discussed above for the petrochemical activated sludge system indicated that a long HRT was required for adequate treatment of certain influent streams. Using these modelling tools, operations staff then have an understanding of the limitations of the plant and the types of operating scenarios to avoid. Model simulations suggested alternatives which may provide better treatment of the wastewater which could be tested on the full-scale system. Once the configuration is applied to the actual operating system changes have to be implemented to fine tune system operation, but the general operating mode can be established from model simulations. Therefore, the model of the activated sludge system serves as an effective guide to system performance, but practical knowledge of the operation of these systems must always be considered when analysing any modelling simulation.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 OVERVIEW

The objective of this study was to develop comprehensive mechanistic dynamic models for simulating the behaviour of activated sludge plants treating petroleum and petrochemical refinery wastewaters. To date, comprehensive modelling of activated sludge systems has concentrated on the treatment of municipal wastewaters (e.g. the IAWPRC ASM1 model). A review of the literature confirmed that an analogous model was not available for predicting system behaviour of petroleum-based activated sludge plants. Due to significant differences in the characteristics of the municipal and petroleum-based wastewaters, the IAWPRC ASM1 model cannot be used directly for predicting the behaviour of these industrial systems. However, development of the municipal activated sludge treatment models did provide guidance on developing equivalent models for the treatment of petroleum and petrochemical refinery wastewaters.

Based on the experience gained in developing the IAWPRC model, an approach was identified for developing the models for activated sludge systems treating petroleum and petrochemical refinery wastewaters:

- Identification of the components and processes important to system behaviour. In accomplishing this task, decisions are made on the structure and complexity of the model.

- Collection of data on known system response. This stage of model development usually involves conducting an experimental programme to collect response data on systems operated under closely controlled conditions. These data usually are necessary for model development to supplement full-scale plant operating data.

- Formulation of a system of mathematical expressions to represent the processes occurring in the activated sludge system. This involves determining stoichiometric expressions to identify the mass balance relationships and kinetic expressions to determine the rate-concentration dependence. These equations are combined with the process configuration to simulate system behaviour.

- Calibration/verification of the model to determine the stoichiometric and kinetic constants in the model equations.

Having identified an overall approach, this methodology was applied to the development of two activated sludge models treating two different types of petroleum-based wastewater:

(1) Imperial Oil Petroleum Refinery, Nanticoke, Ontario,
(2) Petrochemical Refinery, Sarnia, Ontario.

The specific approach used to develop the model for each of these systems was slightly different. Operation of the laboratory scale system treating the wastewater from the Imperial Oil petroleum refinery had provided an extensive database for model development (Baker, 1993). Since these systems could be closely monitored, the key relationships which influenced system behaviour could be determined and quantified. Therefore, this system was used to assist in the initial formulation of the model structure for both systems. The database collected during the operation of this bench scale system also was utilized to calibrate the model to the behaviour of this system. Initial model development of an activated sludge system treating petroleum refinery wastewaters, therefore, was a process which required an extensive experimental program.

This stage of the research established a general model structure for activated sludge systems treating other petroleum-based wastewaters. The next stage in the project was to apply the model structure to another wastewater generated from processing crude oil and its derivatives at a petrochemical refinery. The aim of this portion of the model development process was to establish that extensive experimentation was not necessary to develop an activated sludge model for systems treating similar types of industrial wastewater.

To develop the model for this petrochemical system, selection of model components was based on long term operating data at the plant and the need to track certain components in these wastewaters as a result of regulatory requirements. Establishing the experimental database for model development involved performing several aerobic batch tests rather than operating a continuous-flow system. Using the batch test data along with data on full-scale operation of the plant, the petrochemical model was formulated, and then calibrated and verified.

Adaptation of the petroleum refinery activated sludge model involved consideration of both model components and processes. The model components needed to be modified to reflect the characteristics of the petrochemical wastewater. Once the components were determined, the corresponding processes removing each contaminant from the wastewater needed to be established. For the petrochemical application in this study, the processes determined in the petroleum refinery model were adequate with two exceptions:

- In a petroleum refinery application reduced sulphur compounds were assumed to be removed via biological sulphur oxidation. In contrast, in the petrochemical system removal of reduced sulphur species (a meta-bisulphite compound added upstream of the activated sludge plant) was assumed to occur via a chemical oxidation. As a result, a chemical oxidation process had to be added for the petrochemical model. In terms of a general model structure it seems appropriate to include both removal processes for modelling petroleum-based wastewaters.

- The second modification involved including a second hydrolysis reaction in the petrochemical system. Due to the presence of a particular aliphatic amine in this wastewater, an hydrolysis reaction which converted the compound into mixed COD and ammonia was included in the model to describe this process.

After implementing these two minor modifications, the structure developed for the petroleum refinery system adequately described the petrochemical system. The key to the successful application of the model structure developed for the petroleum refinery model was that the removal processes in the petrochemical system were comparable to those already formulated in this model. Although the specific model components in each system were different, the nature of the different compounds or groups of compounds was similar, and therefore, were removed from the system in a similar fashion. Development of a model to predict the behaviour of the activated sludge system at the petrochemical facility illustrated these points. It also confirmed that limited experimentation provided adequate data for calibration of the model.

Several comments should be noted, however, when considering the development and application of these activated sludge models. In any modelling tool, the mathematical equations are representations of process behaviour. To develop a model which is of reasonable complexity, simplifying assumptions about system behaviour often must be made. Therefore, modelling efforts are aimed at identifying the key elements which influence system response so that trends in behaviour can be established. The models developed in this study identified the major removal processes occurring in these systems, but will continue to be refined as new experience is gained.

The determination of model coefficients also requires assumptions. Associated with the calibration of a model is a certain degree of uncertainty since the procedure is designed to determine a single set of values capable of predicting system response under different operating conditions. This process inherently involves compromise.

When using these modelling tools, experience with the behaviour of these systems should always be considered. The models do provide valuable information on the type of strategies to apply when operating these systems and indicate potential problems which may arise when the system is operated in a certain fashion. This can assist in minimizing any harmful effect a change in operating parameters could have on the ability of the activated sludge plant to effectively treat the refinery wastewater. In other words, these models provide excellent guidance on the nature of the response to expect rather than absolute predictions. Application of the models to the optimization of the activated sludge system operating at the petroleum refinery site illustrated the power of the models to predict system performance under various operating modes, but also addressed some of the limitations of such models.

8.2 APPLICATION OF THE ACTIVATED SLUDGE SYSTEM MODEL STRUCTURE TO OTHER PETROLEUM-BASED WASTEWATERS

The procedure used to develop the activated sludge model specific to the petrochemical refinery illustrates the ability to adapt the model structure developed for the petroleum refinery application (Chapter 3) to the petrochemical application. This was accomplished with minimal experimentation which alleviated the problems of conducting the time consuming experimentation associated with developing the initial model structure. The result was a time-efficient procedure capable of developing a calibrated model of an activated sludge system treating a petrochemical wastewater. Illustrating the successful use of this method to calibrate the petrochemical model confirmed that a simplified means to calibrate the models of any further application of the petroleum based model is available. Such a method reduces the effort required to calibrate a model to the particular system of concern and provide a model which can be used to predict effectively the system response.

The process used to develop a model of a petroleum or petrochemical activated sludge system model by adapting the petroleum refinery model structure can be summarized briefly as follows. The key step in the procedure is confirming the main components of interest in the wastewater. This can be accomplished by experimentally measuring certain parameters, and by using monitoring data which has been collected on a particular system. If the facility is new, the wastewater characteristics from a similar facility may be utilized. The removal processes associated with each of these compounds or groups of compounds then must be determined. Experience gained in developing the model structure for treating the petroleum/petrochemical wastewaters provides guidance on the types of processes to expect with certain types of compounds. The structure also provides the mathematical representations required to describe these different removal processes. With the compounds and removal processes established, aerobic batch experiments assist in determining the kinetics of the different removal processes. These tests generate the required data to evaluate the kinetic coefficients in the model structure for the activated sludge system of interest. Once the model has been calibrated and verified, the model can be used as a tool to assist in process design or optimization.

8.3 RESEARCH CONTRIBUTION

This research project provides an improved understanding of the behaviour of activated sludge systems treating wastewaters generated at petroleum and petrochemical refineries. It is contended that the research:

- Consolidates current knowledge on petroleum refinery and petrochemical refinery activated sludge systems.
- Provides better understanding of the behaviour of these systems and dispels certain myths regarding the expected response to influent loadings.
- Identifies important removal processes in petroleum based activated sludge systems.
- Provides a model framework for application to wastewater treatment systems treating wastewaters generated from processing of crude oil and its derivatives.
- Provides an effective tool to understand system behaviour.
- Assists designers of new systems and assists engineers and operators in effectively operating systems.

8.3.1 Differences between activated sludge treatment of municipal wastewaters and industrial petroleum based wastewaters

An important aspect of model development for activated sludge systems treating the petroleum-based wastewaters was identifying the differences between these wastewaters and municipal wastewaters. These differences were such that the municipal activated sludge model could not be applied directly to the prediction of system response of a system treating petroleum based wastewaters. The following points highlight the key differences between the two types of system.

- Stripping of volatile organic compounds plays an important role in the removal of organic material and as a result, has a significant impact on solids production and oxygen consumed in the aeration tank of an industrial system. In municipal wastewaters the concentration of VOC's generally is very small, and therefore, the impact on solids production and oxygen consumption is small. Hence, stripping of VOC's has not been a concern in municipal models developed for design and optimization purposes.

- Inhibition kinetics must be included in an industrial system due to the potential for discharges of inhibitory compounds such as phenolics.

- Sulphur compounds in petroleum-based wastewaters may contribute significantly to oxygen demand in these systems. This is not considered in municipal models.

- The yield of organisms from a petroleum-based wastewater is lower than in a municipal system. A possible explanation for this phenomenon was presented.

- Hydrocarbons significantly influence the behaviour of these systems. For example, high concentrations of these compounds influence settling properties of the sludge (not investigated in this study), and adsorbed hydrocarbons can result in overestimating the decay rate of organisms in batch aerobic digestion tests. Also adsorbed COD tends to be utilized slowly impacting the dynamic response of the system. Each of these observations is important to the behaviour of the petroleum-based systems, and therefore, accurate monitoring of the oil and grease concentrations is important for predicting system response. Necessarily, this component must be included in the model.

- The large portion of the organic material in an industrial wastewater is soluble compared to a municipal wastewater. Therefore, the hydrolysis/solubilization processes are not as important as in municipal systems.

- In models for municipal systems, it has been found adequate to divide the COD components into soluble and particulate forms. In the industrial systems, however, it was found that system behaviour could be influenced specifically by one or two particular compounds. For example, groups of compounds such as hydrocarbons and phenolics must be tracked in these systems to mimic system response properly. Therefore, more specific information on the fractions of various compounds present in these industrial systems is important and must be reflected in the models.

These points illustrate the major differences between the two types of wastewater. As a result, the models of the activated sludge systems treating these petroleum/petrochemical wastewaters are different to reflect the components and processes characteristic of each system. This research has identified these differences.

8.4 RECOMMENDATIONS FOR FURTHER STUDY

The results presented in this study provide a basis on which to build further studies and increase the understanding of the behaviour of petroleum based biological systems. Studies in the following areas would provide valuable insight into the behaviour of these systems:

- Response of the petroleum and petrochemical refinery activated sludge systems under shock loadings such as spikes of concentrated wastewater entering the plant.

- Consideration of the fate of specific contaminants within the wastewater. [This experimental study only provides information in terms of bulk parameters and groups of compounds].

- Determination of more detailed information on the characteristics of growth and decay of the microorganisms within these systems i.e. yield of organisms on hydrocarbons and related organic compounds, the rate of decay, and the impact of adsorbed compounds.

- Temperature effects on the operation of the systems.

- Study influence of pH on the operation of the systems.

8.5 SUMMARY

In summary, this study has developed two activated sludge system models for the treatment of petroleum refinery and petrochemical refinery wastewaters. The models were developed and calibrated based on the wastewaters treated at two actual refineries. While developing these two models, a process was identified for the development of analogous models for activated sludge systems treating other petroleum-based wastewaters. Using the model structure identified in this study as a basis, an efficient method for developing these models based on a limited experimental programme was established.

The use of these models was illustrated by simulating the response of the petrochemical activated sludge system under different operating scenarios. This process indicated that these models are effective tools for assisting in decision-making processes and provide guidance on the optimum way to operate a particular facility to minimize system upset. Optimization of existing systems and design of new systems are key motivating factors for having developed models of these activated sludge systems.

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APPENDIX 1 : MISA MONITORING GUIDELINES FOR THE PETROLEUM REFINERIES IN ONTARIO

TABLE A1.1:ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS FOR EFFLUENT LIMITS (MOE, 1988)

#	ANALYTICAL TEST GROUP NAME	PARAMETERS
1	Chemical Oxygen Demand	Chemical oxygen demand (COD)
2	Total cyanide	Total cyanide
3	Hydrogen ion (pH)	Hydrogen ion (pH)
4a	Nitrogen	Ammonia plus ammonium Total Kjeldhal Nitrogen
4b	Nitrogen	Nitrate + Nitrite
5a	Organic carbon	Dissolved organix carbon (DOC)
5b	Organic carbon	Total organic carbon (TOC)
6	Total phosphorus	Total phosphorus
7	Specific conductance	Specific conductance
8	Suspended solids	Total suspended solids (TSS) Volatile suspended solids (VSS)
9	Total metals	Aluminum Beryllium Cadmium Cobalt Copper Lead Molybdenum Nickel Silver Thallium Vanadium Zinc
10	Hydrides	Antimony Arsenic Selenium
11	chromium (hexavalent)	chromium (hexavalent) (Note 1)
12	Mercury	Mercury
13	Total alkyl lead	Tetra-alkyl lead (Note 2) Tri-alkyl lead (Note 2)
14	Phenolics (4AAP)	Phenolics (4AAP)
15	Sulphide	Sulphide
16	Volatiles, Halogenated	1,1,2,2-tetrachloroethane 1,1,2-Trichloroethane 1,1-Dichloroethane

TABLE A1.1 cont'd: ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS FOR EFFLUENT LIMITS (MOE,1988)

#	ANALYTICAL TEST GROUP-NAME	PARAMETERS
16	Volatiles, Halogenated	1,1-Dichloroethylene
		1,2-Dichlorobenzene
		1,2-Dichloroethane
		1,2-Dichloropropane
		1,3-Dichlorobenzene
		1,4-Dichlorobenzene
		Bromoform
		Bromomethane
		Carbon Tetrachloride
		Chlorobenzene
		Chloroform
		Chloromethane
		Cis-1,3-Dichloropropylene
		Dibromochloromethane
		Ethylene dibromide
		Methylene chloride
		Tetrachloroethylene
		Trans-1,2-Dichloroethylene
		Trans-1,3-Dichloropropylene
		Trichloroethylene
		Trichlorofluoromethane
		Trichlorofluormethane
		Vinyl chloride (Chloroethylene)
17	Volatiles, Non-halogenated	Benzene
		Ethylbenzene
		Styrene
		Toluene
		o-Xylene
		m-Xylene and p-Xylene (Note 3)
18	Volatiles, Water Soluble	Acrolein
		Acrylonitrile
19	Extractables, Base Neutral	Acenaphthene
		5-nitro Acenaphthene
		Acenaphthylene
		Anthracene
		Benz(a)anthracene
		Benzo(a)pyrene
		Benzo(b)fluoranthene

TABLE A1.1 cont'd: ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS FOR EFFLUENT LIMITS (MOE, 1988)

#	ANALYTICAL TEST GROUP-NAME	PARAMETERS
19	Extractables, Base Neutral	Benzo(g,h,i)perylene
		Benzo(k)fluoranthene
		Camphene
		1-Chloronaphthalene
		2-Chloronaphthalene
		Chrysene
		Dibenz(a,h)anthracene
		Fluoranthene
		Fluorene
		Indeno(1,2,3-cd)pyrene
		Indole
		1-Methylnaphthalene
		2-Methylnaphthalene
		Naphthalene
		Perylene
		Phenanthrene
		Pyrene
		Benzylbutylphthalate
		Bis(2-ethylhexly)phthalate
		Di-n-butylphthalate
		4-Bromophenyl phenyl ether
		4-Chlorophenyl phenyl ether
		Bis (2-chloroisopropyl) ether
		Bis (2-chloroethyl) ether
		2,4-dinitrotoluene
		2,6-dinitrotoluene
		Bis(2-chloroethoxy)methane
		Diphenylamine (Note 4)
		N-Nitrodiphenylamine (Note 4)
		N-Nitrosodi-n-propylamine
20	Extractables, Acid (Phenolics)	2,3,4,5-Tetrachlorophenol
		2,3,4,6-Tetrachlorophenol
		2,3,5,6-Tetrachlorophenol
		2,3,4-Triachlorophenol
		2,3,5-Triachlorophenol
		2,4,5-Triachlorophenol
		2,4,6-Triachlorophenol
		2,4-Dimethylphenol

TABLE A1.1 cont'd: ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS FOR EFFLUENT LIMITS (MOE, 1988)

#	ANALYTICAL TEST GROUP-NAME	PARAMETERS
20	Extractables, Acid (Phenolics)	2,4-Dinitrophenol 2,4-Dichlorophenol 2,6-Dichlorophenol 4,6-Dinitro-o-cresol 2-Chlorophenol 4-chloro-3-methylphenol 4-Nitrophenol m-cresol o-cresol p-cresol Pentachlorophenol Phenol
21	Extractables, Phenoxy Acid Herbicides	
22	Extractables, Organochlorine Pesticides	
23	Extractables, Neutral-Chlorinated	1,2,3,4-Tetrachlorobenzene 1,2,3,5-Tetrachlorobenzene 1,2,4,5-Tetrachlorobenzene 1,2,3-Trichlorobenzene 1,2,4-Trichlorobenzene 2,4,5-Trichlorobenzene Hexachlorobenzene Hexachlorocyclopentadiene Hexachloroethane Octachlorostyrene Pentachlorobenzene
24	Chlorinated Dibenzo-p-dioxins and Dibenzofurans	2,3,7,8-Tetrachlorodibenzo-p-dioxin Octachlorodibenzo-p-dioxin Octachlorodibenzofuran Total heptachlorinated dibenzo-p-dioxins Total heptachlorinated dibenzofurans Total hexachlorinated dibenzo-p-dioxins

TABLE A1.1 cont'd: ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS FOR EFFLUENT LIMITS (MOE, 1988)

#	ANALYTICAL TEST GROUP-NAME	PARAMETERS
24	Chlorinated Dibenzo-p-dioxins and Dibenzofurans	Total hexachlorinated dibenzofurans Total pentachlorinated dibenzo-p-dioxins Total pentachlorinated dibenzofurans Total tetrachlorinated dibenzo-p-dioxins Total tetrachlorinated dibenzofurans
25	Solvent extractables	Oil and grease
26	Fatty and Resin Acids	
27	Polychlorinated Biphenyls (PCBs) (Total)	PCBs (Total)

Note 1: Analyse for hexavalent chromium only if total chromium is greater than 1.0 mg/L.

Note 2: Analyse for alkyl leads only if total lead is greater than 1.0 mg/L.

Note 3: m-Xylene and p-Xylene often co-elute in the analysis. A single combined result may be reported as m-xylene.

Note 4: Diphenlyamine & N-Nitrosodiphenylene often co-elute in the Gas Chromatography/Mass Spectrometry (GC/MS) analysis. A single combined result may be reported as Diphenylamine.

APPENDIX 2 : EXPERIMENTAL DATA FOR DETERMINATION OF ORGANISM DECAY RATE CONSTANT

The following two tables tabulate the experimental results and the calculations on the data required to determine the organism decay rate constants on the activated sludge treating petroleum refinery wastewater. Two batch tests were conducted to determine the decay rate constant for a system operating at a 10 day SRT and a system operating at a 20 day SRT. The plot for determining the decay rate constant for the 20 day system was illustrated in the main text. The plot for the 10 day system is illustrated below in Figure A2.1. The tabulated results of raw data are reported in Table A2.1 and A2.2.

During the initial stages of the test, the decay rate appeared to be greater than during later stages. It was hypothesized that adsorbed hydrocarbons remaining on the sludge was being consumed during this period. Once this absorbed COD was utilized, the actual decay rate of the organisms could be determined. Therefore, determination of the decay rate of the organisms had to account for this phenomenon. To do this, measurements of OUR on the first day of the batch test were assumed to be influenced by the degradation of hydrocarbon i.e. the OUR readings were greater than those required for endogenous respiration due to the consumption of oxygen for degradation processes. The decay rate of the sludge was calculated using those points after this period of time. This resulted in decay rates similar to those associated with decay of organisms in municipal systems.

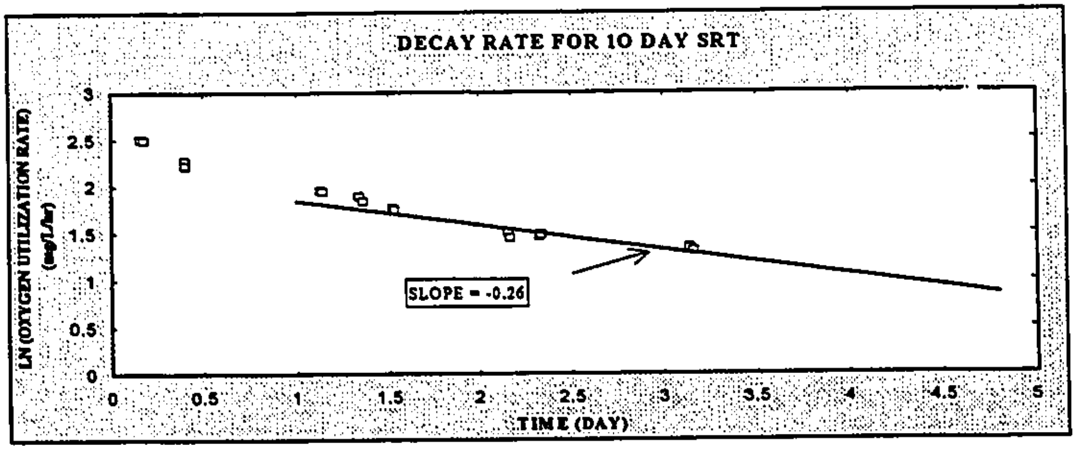

Figure A2.1: The organism decay rate for an activated sludge removed from a system treating petroleum refinery wastewater is illustrated. The rate was calculated to be 0.26 day^{-1}.

Table A2.1: Experimental Results and Calculations of Batch Organism Decay Rate Constant Determination on a System Operated at a 10 Day SRT.

TIME (day)	OUR (mg/l/hr)	LOG(OUR)	LN (OUR)	TREND
0.16	12.2	1.088	2.505	2.365
0.18	12.1	1.084	2.497	2.357
0.4	9.7	0.987	2.272	2.270
0.4	9.2	0.964	2.219	2.270
1.13	7.0	0.847	1.950	1.981
1.14	7.0	0.845	1.946	1.977
1.34	6.6	0.820	1.887	1.898
1.36	6.3	0.799	1.841	1.890
1.52	5.8	0.766	1.765	1.827
1.53	5.8	0.760	1.751	1.823
2.16	4.5	0.653	1.504	1.574
2.17	4.3	0.628	1.447	1.570
2.33	4.3	0.635	1.463	1.506
2.34	4.4	0.643	1.482	1.502
3.14	3.8	0.582	1.340	1.186
3.16	3.7	0.568	1.308	1.178

* The organism decay rate constant was determined by calculating the slope of the Trend data. For the 10 Day SRT the organism decay rate was calculated as -0.26 day^{-1} assuming the first day and a half of the test was influenced by degradation of hydrocarbons i.e. the first eight data points were not included in this calculation.

Table A2.2: Experimental Results and Calculations of Batch Organism Decay Rate Constant Determination on a System Operated at a 20 Day SRT.

TIME (day)	OUR (mg/l/hr)	LOG (OUR)	LN (OUR)	TREND
0.00	12.1	1.083	2.493	2.559
0.04	14.0	1.146	2.639	2.542
0.08	14.5	1.161	2.674	2.525
0.13	14.8	1.170	2.695	2.508
0.88	9.8	0.991	2.282	2.203
1.06	9.9	0.996	2.293	2.126
1.23	5.3	0.724	1.668	2.058
1.81	4.9	0.690	1.589	1.821
2.35	3.8	0.580	1.335	1.600
2.92	3.9	0.591	1.361	1.371
3.35	4.4	0.643	1.482	1.193
3.92	1.9	0.279	0.642	0.964
4.92	2.4	0.380	0.875	0.557

* The organism decay rate constant was determined by calculating the slope of a semi -log plot of the data. For the 20 Day SRT the organism decay rate was calculated as -0.25 day^{-1} assuming the first six points in the set were influenced by degradation of hydrocarbons.

APPENDIX 3 : DEVELOPMENT OF EQUATIONS USED TO DETERMINE THE ENDOGENEOUS RESPIRATION OF ACTIVATED SLUDGE

In a biological system microorganisms are known to die and decay, but exactly how the process proceeds is not explicitly known. As a result there are two approaches which have been developed to describe the process of organism decay in a biological wastewater treatment system:

(1) Endogeneous Respiration Approach,
(2) Death-Regeneration Approach.

The first hypothesis is the endogeneous decay theory and operates on the premise that organisms feed on other microorganisms in order to maintain their basic energy requirements when there is no other biodegradable substrate available. As a result a certain mass of viable organisms disappears in the system as it is utilized by the remaining organisms. Similar to growth on biodegradable substrate, this process consumes oxygen. The process also generates an unbiodegradable fraction which accumulates in the reactor as endogeneous residue.

The second hypothesis is the death-regeneration process which suggests that a percentage of viable organisms are continually dying and lyse biodegradable substrate into the system. A fraction of these dead organisms cannot be degraded and as a result contributes an unbiodegradable fraction to the activated sludge system. The degradable substrate contributes to the other biodegradable COD in the wastewater and undergoes the same steps of adsorption, storage, and abstraction when bcing utilized for synthesis of new cell material. Oxygen is consumed in the synthesis process.

Both these approaches produce similar estimates for the parameters describing the decay processes which occur within an aerobic activated sludge system. Problems arise, however, with the endogeneous respiration theory in anoxic and contact stabilization systems. As a result the death-decay theory has become more accepted since it is capable of explaining the phenomena which occur in all the biological systems. Further detail on the justification of the death-regeneration approach is outlined in Dold, Ekama, & Marais (1980).

The following equation development relates the equations which apply to each of the endogenous decay theories.

Endogenous Respiration Formulation:

Let the *net* endogeneous decay rate constant per day for heterotrophic organisms be b and the concentrations of active organisms be X_a. Therefore, the rate of active organism loss is represented by the following equation:

$$\frac{dX_{al}}{dt} = -b * X_a \qquad (A3.1)$$

where Xal = active organisms lost due to endogenous respiration.

The fraction of viable organisms that disappears, but is unbiodegradable and remains in the wastewater as endogenous residue is represented by f. The rate that the endogenous residue, Xe, is generated is represented by the following:

$$\frac{dXe}{dt} = f * b * Xa \qquad (A3.2)$$

The oxygen consumed, O_e, in endogenous respiration due to the net loss of viable organisms is represented by:

$$O_e = P(1-f) * b * X_a \qquad (A3.3)$$

where P = the COD/VSS ratio of the organisms.

Death- Regeneration Approach:

For this approach it is necessary to define the *actual* death rate constant of active organisms as b' per day and the *actual* unbiodegradable fraction as f'. Therefore, the active mass lost, X'_{al}, due to the die-off of organisms is represented by:

$$\frac{dX'_{al}}{dt} = - b' * X_a \qquad \text{(A3.4)}$$

The mass of biodegradabe substrate, S'xal, released into the system is:

$$\frac{dS'xal}{dt} = P\,(1 - f') * b' * Xa \qquad \text{(A3.5)}$$

The mass of organisms, X'ag, synthesized from the COD released into the system is represented by:

$$\frac{dX'ag}{dt} = Yh * P\,(1 - f') * b' * Xa \qquad \text{(A3.6)}$$

where Y_h = the yield of the heterotrophic organism on the substrate.

The oxygen consumed during the synthesis of the lysed substrate is represented by the following equation developed from the above relationships:

$$O'_e = (1 - P * Y_h) * P * (1 - f) * b' * X_a \qquad \text{(A3.7)}$$

The accumulation of unbiodegradable cell material, X'_e, due to the death process is given by:

$$\frac{dX'e}{dt} = f' * b' * Xa \qquad \text{(A3.8)}$$

The importance of outlining both approaches was due to the fact that under steady state conditions both hypotheses produce the same results. This enables relationships to be developed between the net and actual endogenous fractions and the net and actual decay rate constants. This is critical since the net decay rate is the decay rate which can be easily measured on an activated sludge system while the actual decay rate is the value which must be input into an activated sludge model. The following two relationships must hold true based on the equations indicated above :

$$f * b = f' * b' \qquad \text{(A3.9)}$$

and,

$$-b = -b' + Yh * P\,(1-f') * b' \qquad \text{(A3.10).}$$

Solving for f' and b', the following two equations result:

$$f' = f * \frac{(1 - Y_h P)}{(1 - Y_h P f)} \qquad \text{(A3.11)}$$

$$b' = \frac{(1 - Y_h P f) * b}{(1 - Y_h P)} \qquad \text{(A3.12)}$$

These equations govern the decay processes in the activated sludge process. The net decay rate, b, was measured experimentally and can be utilized directly in Equation A3.12.

APPENDIX 4: DATA COLLECTED DURING DAILY MONITORING OF THE ACTIVATED SLUDGE SYSTEM OPERATING AT THE PETROCHEMICAL FACILITY

During the operation of the activated sludge system treating wastewaters generated on- and off-site of the petrochemical facility at Sarnia, Ontario there are many parameters monitored on a regular basis. There are certain parameters which must be monitored daily to abide by Ministry of the Environment Regulations for controlling effluent quality discharge. Other parameters are monitored less frequently. During model development, this database on system performance was a valuable source of information. It was used in various stages of model formulation and calibration.

The data was collected and applied in two different ways:

- Daily parameters were collated to determine the average long term operating conditions of the system. This information was used to determine flows and loadings to the system, and to establish the components of interest which should be included in the model.
- Parameters measured on the system on the days that batch tests were conducted with various influent streams were tabulated to provide an indication of the specific concentrations of certain compounds in a given influent stream at the time of the test. This information was valuable during the calibration of the petrochemical activated sludge model.

The long term average values for the characteristics of the different influent streams are listed in the Tables A4.1 and A4.2 below. These include the average flowrates of the influent streams as well as the concentrations of the components associated with the influent.

Tables A4.3 to A4.5 tabulate the loadings of different contaminants to the aeration tanks. These assisted in assessing the importance of different streams.

For the days that the batch tests were conducted, the daily monitored parameters measured by the plant staff were collated. These values are tabulated below in Table A4.6.

Table A4.1: Average daily flowrates of the influent streams. Streams 1,2, and 3 are based on on-line measurements, while the remaining streams are based on typical values reported by plant staff.

STREAM	FLOW AVERAGE ($m^3/d \times 10^{-3}$)	MAXIMUM FLOW ($m^3/d \times 10^{-3}$)
Stream 1	4.24	6.16
Stream 2	12.6	18.5
Stream 3	0.775	1.98
Stream 4	0.002	0.002
Stream 5	0.5	0.5
Stream 6	few gallons	
Total	18.1	27.2

Table A4.2: Quality of the different influent streams.

	DOC (mg/L)		Phenolics (mg/L)		NH_3-N (mg/L)		Suspended Solids (mg/L)	
Stream	Ave.	Max.	Ave.	Max.	Ave.	Max.	Ave.	Max.
Stream 1	31.4	950	0.07	1.23	3.86	64	20	416
Stream 2	47.1	281	0.4	3.0	1.6	25	119	536
Stream 3	440	5720	0.067	1.2	3.5	110	99	2383
Stream 4	81000	-	81000	-	-	-	-	-
Stream 5	884	6700	8.73	852	3.1	110	-	-
Stream 6	-	-	-	-	-	-	-	-

Table A4.3: Loading of DOC to the aeration tanks in the petrochemical activated sludge system.

Stream	Average (kg/d)	% Total Plant Load	Maximum (kg/d)
Stream 1	135	8.2	226
Stream 2	589	35.9	2450
Stream 3	313	19.1	6190
Stream 4	162	9.9	-
Stream 5	442	26.9	3350
Stream 6	-	-	-
Total Plant Loading	1641	100	

Table A4.4: Loading of Ammonia (NH_3-N) to the aeration tanks in the petrochemical activated sludge system.

Stream	Average (kg/d)	% Total Plant Load	Maximum (kg/d)
Stream 1	16.4	40.9	226
Stream 2	19.8	49.4	286
Stream 3	2.3	5.7	27.5
Stream 4	-	-	-
Stream 5	1.6	4.0	55.0
Stream 6	-	-	-
Total Plant Loading	40.1	100	

Table A4.5: Loading of Phenolics to the aeration tanks in the petrochemical activated sludge system.

Stream	Average (kg/d)	% Total Plant Load	Maximum (kg/d)
Stream 1	0.3	3.0	5.2
Stream 2	5.2	0.2	42.4
Stream 3	0.05	0.0	1.0
Stream 4	162	94.3	-
Stream 5	4.3	2.5	426
Stream 6	-	-	-
Total Plant Loading	172	100	

Table A4.6: Parameters monitored daily on the petrochemical activated sludge system. The days listed in the table below are those on which batch tests were run.

Stream	Parameter	08/02	09/02	23/02	24/02	25/02	26/02	15/06	16/06
Stream 1	DOC	118	96	142	56	38	35	19	25
	Alcohol	2.3	8.1	28	19.4	15	5.5	2.1	3.2
	Aliphatic Amine		203.1	4.2	5.4	6.4	0.888		0.889
	Phenolics	0.3	0.15	0.45	0.09	1.26	0.09	0.048	0.045
	NH_3	5.8	3	64	11.8	11.4	4	1.2	1
Stream 2	DOC	41	31	69	36	26	29	65	74
	Alcohol		3.7						
	Aliphatic Amine								
	Phenolics	1.8	0.9	0.45	0.36	0.03	0.99	0.81	0.03
	VOC	47.7	44.8	106.3	113	63.6	50	100.7	77
	NH_3	2	1.8	2	0.6	1.6	1.6	3.6	3.8
Stream 3	DOC	351	390	616	579	646	572	183	143
	Alcohol	187.5	138.1	321.2	1118	815	460	20	47
	Aliphatic Amine			0.7	3.9	9	6.6		
	Phenolics	0.03	0.036	0.09	0.069	0.045	0.054	0.06	0.051
	NH_3	13.2	16.6	20	42	50	38	16	11.6
Stream 5	DOC	750	920	437	300	269	239	117	110
	Alcohol	558	726.9	206.4	194	115	101	59	64
	Aliphatic Amine	0.8		16.8	44.7	79.2	84	9.4	8.2
	Phenolics	1.29	0.78	75.6	22	249	18	0.6	0.03
	NH_3	6	7	44	5.6	8	8	6	5
Effluent	TOC	12	12	16	13	12	10	14	25
	NH_3	0.2	0.2	2.6	3.6	0.6	0.8	0.2	0.1

These tables of information complete the data which was required from the full-scale petrochemical activated sludge system in order to calibrate the model. This information was used in conjunction with a specifically designed experimental programme to attain all the data required for model development.

APPENDIX 5: RESULTS OF THE GRAB SAMPLES MEASURED ON THE INFLUENT STREAMS AND SLUDGE REMOVED FROM THE AERATION TANKS

A key stage in the development of the activated sludge model for treating petrochemical wastewaters is identification of the compounds that are treated in the system and the characteristics of the biomass treating the influent contaminants. This enables selection of the appropriate compounds to include in the model and to assist in determining model parameters. The parameters required for model development and calibration were identified in Chapter 6.

In order to obtain all the necessary information grab samples were measured at various points during the experimental program. Initially, grab samples were taken in August, 1992 to obtain preliminary estimates of the type and quantity of compounds present in the different streams. These samples were used to confirm the compounds which were to be included in the formulated model. More comprehensive data was collected on the influent streams and activated sludge during February, 1993, and June, 1993. This data was used in the calibration stage of model development. The results of the grab samples measured during each of these time periods are tabulated in the following tables. Table A5-1 lists the grab samples taken on each influent stream that the facility treats for all the testing periods. Table A5-2 tabulates the characteristics of the sludge sampled from AT1 and AT2, while Table A5-3 summarizes the results of the grab samples on sludge from AT4.

Table A5-1: This table lists the experimental results measured on the grab samples of the different influent streams to the petrochemical activated sludge plant. Determining the characteristics of the different influent streams was an integral part of model development.

PARAMETER		Unfilt. COD (mg/L)	Filt. COD (mg/L)	TOC (mg C/L)	TOC/ COD	Unfilt. TKN (mg N/L)	Filt. TKN (mg N/L)	NH3 (mg N/L)	NO3 (mg N/L)	SO4- (mgS04/L)
STREAM AND DATE OF SAMPLING										
Stream 1	08/02/93	227	167	48	0.287	3.4	2.85	0.45	0.5	
	22/02/93	477	219	57.41	0.262	6.3	5.8	0.84	0.87	169.6
	23/02/93	496	157.3	27.06	0.172	8.7	2.75	0.9	0.36	124
	24/02/93	251	206	25.55	0.124	6.33	5.7	4.19	2.39	28.04
	25/02/93	179.7	174	22.55	0.126	3.63	3.5	2.35	0.55	30.95
	26/02/93	207.6	175.3	24.82	0.142	2.6	2.3	0.6	0.73	28.55
	16/06/93	474	435.2			6.9	6.3			
Stream 2	20/08/92	174.0	59.0	28.6	0.485	4.5	3.85	0.95	5.248	60.08
	23/02/93	166.0	103.5	36.39	0.352	6.4	6.4	1.56	0.85	14.63
	24/02/93	129.0	101.1	31.16	0.308	5.3	5.2	0.72	2.31	93.66
	25/02/93	133	109.6	31	0.282	3.6	3.65	1.66	4.88	117.5
	26/02/93	231	177	50.63	0.286	3.4	3.1	1.55	2.72	114.7
Stream 6	16/06/93	2076.9	1957.5			104.2	93.3		0.53	
Stream 3	20/08/92	1696.7	1629.0	287.1	0.169	3.3	2.87	2.96	5.306	7036
	23/02/93	5995.0	5739.0	574.5	0.1	39.35	39.15	33.68	1.56	8975
	24/02/93	2023.0	1830.7	442.1	0.241	37.5	36.8	34.83	2.81	9330
	25/02/93	3504.0	3184.7	689	0.216	48.1	47.5	38.4	0.76	10170
	26/02/93	3273.0	3069.3	639	0.208	40.85	42.35	33.11	1.22	10000
	15/06/93	690.0	637.2			14.75	14.2		0.24	
Stream 4 Supernatant	08/02/93	182160	155200	25108	0.238	423	403.7	29.04	-0.05	172.6
	23/02/93	138000	136400	12060	0.088	450	90	9.8	4.8	295
	25/02/93	138000	132800	32060	0.241	512.5	490	17.2	16.6	655.6
	15/06/92	190000	192200			560	510		8.4	
Stream 5	08/02/93	3399	2322	630	0.271	10.25	13.2	5.35	0.12	5383
	23/02/93	1101	1100	261.1	0.237	17.15	15.25	3.88	0.58	1207.5
	26/02/93	918.3	881.7	178.1	0.202	261	109	7.38	4.56	1170
EFFLUENT	20/08/92	270.4	113.6	25.4	0.224	0.19	0.25	0.05	2.78	695
	23/02/93	81.6	68.5	12.97	0.189	6.19	5.93	4.69	2.33	562.5
	24/02/93	56.0	59.7	11.99	0.201	1.69	1.45	1.83	5.06	576
	25/02/93	65.9	55.2	16.5	0.299	1.37	1.34	0.58	2.68	572.5
	26/02/93	94.9	61.1	12.48	0.204	3.4	0.72	0.71	3.66	496.3
	15/06/93		95.5				1.35			
	16/06/93		121.8				1.06			

NOTE: Shaded values indicate suspect data point.

Table A5-2: The results of the measurements conducted on the sludge samples from AT1 and AT2 are reported in the table below. These experimental results enabled the characteristics of the sludge in the system to be determined.

CHARACTERIZATION OF SLUDGE FROM AT1 AND AT2

DATE	TSS (mg TSS)	VSS (mg VSS)	VSS/TSS	UNFILT. COD mg COD/L	FILT. COD mg COD/L	UNFILT. TKN mg N/L	FILT. TKN mg N/L	COD/VSS	TKN/VSS
AT1 20/08/92	2799	1662	0.59	3190	117.3	30.0	0.4	1.85	
AT2 20/08/92	3123	1811	0.58	3557	74.9	58.0	0.4	1.92	

Table A5-3: The results of the measurements conducted on the sludge samples from AT4 are reported in the table below. These experimental results enabled the characteristics of the sludge in the system to be determined.

CHARACTERIZATION OF SLUDGE FROM AT4

DATE	TSS (mg TSS)	VSS (mg VSS)	VSS/TSS	UNFILT. COD mg COD/L	FILT. COD mg COD/L	UNFILT. TKN mg N/L	FILT. TKN mg N/L	COD/VSS	TKN/VSS
9/2/93	3047	1833	0.60	3248	33.6	120.8	2.5	1.74	0.06
23/02/93	2801	1756	0.63	2630	87.7	140.0	5.9	1.44	0.08
24/02/93	2602	1623	0.62	2565	153.9	122.5	1.1	1.54	0.07
25/02/93	2834	1724	0.62	2465	71.5	165.0	1.8	1.35	0.1
26/02/93	2502	1511	0.60	2600	58.1	126.3	1.3	1.72	0.08

APPENDIX 6: EXPERIMENTAL RESULTS OF THE BATCH TESTS PERFORMED ON EACH OF THE INFLUENT STREAMS TO THE PETROCHEMICAL ACTIVATED SLUDGE PLANT

In order to calibrate the activated sludge model of the petrochemical plant specially designed experiments needed to be conducted. The experiments needed to provide information on the kinetics of the various processes occurring within the system. The relevant information was obtained by conducting a series of batch experiments with the different streams. Batch tests were performed during two different time periods to obtain data on the behaviour of the system under varying influent conditions. This enabled the model to be calibrated using one set of data, and then verified using the second set of data.

The batch tests involved mixing return activated sludge (RAS) with one of the influent streams to the petrochemical facility. The ratio of the volume of RAS to the volume of influent stream was calculated so that the mass of organic compound to be removed could be done so in two to three hours. Having established a suitable ratio, the influent sample was added to the volume of RAS. The mixture was continuously aerated and maintained in a constant water bath at 25°C. Initial samples were taken when the RAS and the influent sample were first mixed, and then at regular intervals until the test was completed. The mixture was monitored for OUR, COD, and TKN over the duration of the test. The end of the test was indicated when the OUR reached endogenous levels. This testing procedure was repeated for each of the influent streams in February. Another set of batch tests were conducted in June. The measurements determined during these experiments are tabulated below for each batch test.

The following table presents the results of the batch test conducted on Stream 1 on February 24, 1993. It indicates the volumes of influent and RAS used in the test. The characteristics of the influent and RAS are also indicated. The RAS was taken from the petrochemical activated sludge system operating at a sludge age of 35 days.

Table A6.1: Results from Stream 1 batch test on February 24, 1993.

INITIAL CHARACTERISTICS	
VOLUME OF INFLUENT (mL)	900
Initial Filtered COD (mg/L)	101.0
Initial Filtered TKN (mg N/L)	5.3
VOLUME OF RAS (mL)	125
Filtered COD of RAS (mg/L)	59.7
VSS OF RAS (mg/L)	4112
Endogenous OUR of RAS (mg/L/hr)	8.3

MONITORED PARAMETERS					
TIME (min)	***OUR (mg/L/hr)***	***TIME (min)***	***COD (mg/L)***	***TKN (mg N/L)***	***NITRATE (mg N/L)***
0	16	0	123.6	4.98	
5	16	10	118.8	7.88	
7	8.5	20	111.6	8.1	
12	8.5	30	106.8	8.81	
16	8.5	40	110.0	10.13	
21	8.0	65	102.0	8.89	
26	8.0	90	82.8	9.15	
31	7.5	145	110.0	8.56	
36	7.5				
44	6.5				
50	6.5				

The following table presents the results of the batch test conducted on Stream 2 on February 25, 1993. It indicates the volumes of influent and RAS used in the test. The characteristics of the influent and RAS are also indicated. The RAS was taken from the treatment system operating at a sludge age of 35 days.

Table A6.2: Results from Stream 2 batch test on February 25, 1993.

INITIAL CHARACTERISTICS	
VOLUME OF INFLUENT (mL)	850
Initial Filtered COD (mg/L)	174
Initial Filtered TKN (mg N/L)	3.5
VOLUME OF RAS (mL)	125
Filtered COD of RAS (mg/L)	55.0
VSS OF RAS (mg/L)	3953.3
Endogenous OUR of RAS (mg/L/hr)	7.75

MONITORED PARAMETERS					
TIME (min)	***OUR (mg/L/hr)***	***TIME (min)***	***COD (mg/L)***	***TKN (mg N/L)***	***NITRATE (mg N/L)***
0	25	0	154.8	3.05	
5	25	12	113.3	3.32	
8	15	20	100.0	3.58	
12	15	30	115.2		
15	11.5	45	114.4	5.10	
24	11	67	110.0	4.79	
29	11	85	93.2	3.68	
36	10.3	100	89.6	3.49	
40	10.3	115	104.8	3.29	
52	8.5				
60	8.5				
75	5.5				
87	6.5				
90	6.5				
105	5				
108	5				
120	4.2				
124	4.2				
180	2				
189	2				

The following table presents the results of the batch test conducted on Stream 3 on February 24, 1993. It indicates the volumes of influent and RAS used in the test. The characteristics of the influent and RAS are also indicated. The RAS was taken from the petrochemical activated sludge system operating at a sludge age of 35 days.

Table A6.3: Results from Stream 3 batch test on February 24, 1993.

INITIAL CHARACTERISTICS	
VOLUME OF INFLUENT (mL)	100
Initial Filtered COD (mg/L)	1830.0
Initial Filtered TKN (mg N/L)	36.8
VOLUME OF RAS (mL)	700
Filtered COD of RAS (mg/L)	59.7
VSS OF RAS (mg/L)	2902.7
Endogenous OUR of RAS (mg/L/hr)	10.0

MONITORED PARAMETERS

TIME (min)	***OUR (mg/L/hr)***	***TIME (min)***	***COD (mg/L)***	***TKN (mg N/L)***	***NITRATE (mg N/L)***
0	62	0	244.6	4.87	
14	33.8	10	252.8	4.91	
17	33.8	20	220.8	4.71	
22	33.6	30	184.0	4.16	
26	33.6	45	172.8	3.78	
31	33.0	60	176.0	3.57	
35	33.0	170	97.6	1.51	
55	32.5	200	97.6	1.18	
61	32.5	230	93.2	1.65	
75	32.5				
80	32.5				
113	34.0				
118	34.0				
131	33.2				
159	32.5				
180	9.5				
188	9.5				
195	8.5				
200	8.5				
230	9.0				

The following table presents the results of the batch test conducted on Stream on February 25, 1993. The sludge was from the petrochemical system operating at a sludge age of 35 days.

Table A6.4: Results from Stream 4 batch test on February 25, 1993.

INITIAL CHARACTERISTICS	
VOLUME OF INFLUENT (mL)	5
Initial Filtered COD (mg/L)	132800
Initial Filtered TKN (mg N/L)	98.0
VOLUME OF RAS (mL)	940
Filtered COD of RAS (mg/L)	71.5
VSS OF RAS (mg/L)	3911.0
Endogenous OUR of RAS (mg/L/hr)	7.5

MONITORED PARAMETERS

TIME (min)	***OUR (mg/L/hr)***	***TIME (min)***	***COD (mg/L)***	***TKN (mg N/L)***	***NITRATE (mg N/L)***
0	90.0	0	757.2	2.2	
3	90.0	10	747.0	5.0	
16	70.0	21	745.5	4.3	
20	70.0	30	724.0	3.55	
26	64.0	48	700.5	3.85	
30	64.0	69	698.5	3.45	
42	20.0	105	676.5	3.35	
48	20.0	150	602.0	2.95	
58	20.0	210	574.0	3.05	
63	18.5	280	636.0	3.0	
67	18.5	1000	66.4	2.76	
79	20.0				
85	20.0				
93	19.0				
115	19.0				
130	18.5				
134	18.5				
150	19.0				
180	19.0				
210	19.5				
245	19.5				
270	22.5				
285	22.0				
1000	7.0				

The following table presents the results of the batch test conducted on Stream on February 26, 1993. It indicates the volumes of influent and RAS used in the test. The characteristics of the influent and RAS are also indicated. The RAS was taken from the petrochemical activated sludge system operating at a sludge age of 35 days.

Table A6.5: Results from Stream 5 batch test on February 26, 1993.

INITIAL CHARACTERISTICS	
VOLUME OF INFLUENT (mL)	100
Initial Filtered COD (mg/L)	881.7
Initial Filtered TKN (mg N/L)	109.0
VOLUME OF RAS (mL)	940
Filtered COD of RAS (mg/L)	61.0
VSS OF RAS (mg/L)	2952.8
Endogenous OUR of RAS (mg/L/hr)	5.0

MONITORED PARAMETERS

TIME (min)	***OUR (mg/L/hr)***	***TIME (min)***	***COD (mg/L)***	***TKN (mg N/L)***	***NITRATE (mg N/L)***
2	38.0	0	145.5	11.6	
5	38.0	20	156.0	8.1	
11	41.5	35	106.5	7.0	
15	41.5	50		6.49	
20	37.5	95	82.5	6.23	
22	37.5	120	73.2		
25	17.0	130	83.6		
27	17.0				
30	18.7				
35	18.7				
40	22.5				
44	22.5				
70	23.0				
89	9.0				
93	9.0				
120	7.5				
127	7.5				
136	7.5				

The following table presents the results of the batch test conducted on Stream 2 on June 16, 1993. It indicates the volumes of influent and RAS used in the test. The characteristics of the influent and RAS are also indicated. The RAS was taken from the petrochemical activated sludge system operating at a sludge age of 35 days.

Table A6.6: Results from Stream 2 batch test on June 16, 1993.

INITIAL CHARACTERISTICS	
VOLUME OF INFLUENT (mL)	850
Initial Filtered COD (mg/L)	435.2
Initial Filtered TKN (mg N/L)	6.3
VOLUME OF RAS (mL)	150
Filtered COD of RAS (mg/L)	119.2
VSS OF RAS (mg/L)	3706.4
Endogenous OUR of RAS (mg/L/hr)	5.5

MONITORED PARAMETERS

TIME (min)	***OUR (mg/L/hr)***	***TIME (min)***	***COD (mg/L)***	***TKN (mg N/L)***	***NITRATE (mg N/L)***
0	21	0	387.6		
5	21	11	336.6	4.23	-0.1
11	6	35	281.2	4.1	-0.1
15	3.2	45	176	4.85	0.13
25	4.7	67	154	5.07	-0.1
35	6	85	163.6	5.12	
45	4.8	130	129.6	4.55	-0.12
56	5				
67	4.2				
80	3.3				
98	4				
110	3				
125	2.8				

The following table presents the results of the batch test conducted on Stream 3 on June 15, 1993. It indicates the volumes of influent and RAS used in the test. The characteristics of the influent and RAS are also indicated. The RAS was taken from the petrochemical activated sludge system operating at a sludge age of 35 days.

Table A6.7: Results from Stream 3 batch test on June 15, 1993.

INITIAL CHARACTERISTICS	
VOLUME OF INFLUENT (mL)	100
Initial Filtered COD (mg/L)	637.3
Initial Filtered TKN (mg N/L)	14.75
VOLUME OF RAS (mL)	900
Filtered COD of RAS (mg/L)	97.6
VSS OF RAS (mg/L)	3544
Endogenous OUR of RAS (mg/L/hr)	3.2

MONITORED PARAMETERS

TIME (min)	***OUR (mg/L/hr)***	***TIME (min)***	***COD (mg/L)***	***TKN (mg N/L)***	***NITRATE (mg N/L)***
0	25.2	0	151.6		
5	25.2	10	109.2	1.67	4.88
10	11.3	25	104.0	1.75	4.71
25	11.7	45	92.8	1.27	5.05
45	6.5	65	98.8	1.45	3.97
55	6.0	80	94.8	1.01	
65	5.5				
80	4.6				
90	3.3				
110	3				
125	2.8				

The following table presents the results of the batch test conducted on Stream 4 on June 15, 1993. It indicates the volumes of influent and RAS used in the test. The characteristics of the influent and RAS are also indicated. The RAS was taken from the petrochemical activated sludge system operating at a sludge age of 35 days.

Table A6.8: Results from Stream 4 batch test on June 15, 1993.

INITIAL CHARACTERISTICS	
VOLUME OF INFLUENT (mL)	1
Initial Filtered COD (mg/L)	197800
Initial Filtered TKN (mg N/L)	510
VOLUME OF RAS (mL)	1000
Filtered COD of RAS (mg/L)	103.2
VSS OF RAS (mg/L)	3760.0
Endogenous OUR of RAS (mg/L/hr)	3.7

MONITORED PARAMETERS

TIME (min)	***OUR (mg/L/hr)***	***TIME (min)***	***COD (mg/L)***	***TKN (mg N/L)***	***NITRATE (mg N/L)***
0	47.5	0	301.0	0.98	4.88
10	31.0	10	295.5	1.21	
12	9.0	20	251.0	1.21	
20	11.0	81	227.0	1.98	
33	13.0	130	169.5		
44	14.7				
60	19.0				
81	23.0				
95	35.5				
117	61.0				
130	88.5				
135	3.3				
140	7.3				

The following table presents the results of the batch test conducted on Stream on June 16, 1993. It indicates the volumes of influent and RAS used in the test. The characteristics of the influent and RAS are also indicated. The RAS was taken from the petrochemical activated sludge system operating at a sludge age of 35 days.

Table A6.9: Results from Stream 6 batch test on June 16, 1993.

INITIAL CHARACTERISTICS	
VOLUME OF INFLUENT (mL)	85
Initial Filtered COD (mg/L)	1957.5
Initial Filtered TKN (mg N/L)	93.3
VOLUME OF RAS (mL)	900
Filtered COD of RAS (mg/L)	122.4
VSS OF RAS (mg/L)	3774.6
Endogenous OUR of RAS (mg/L/hr)	4.5

MONITORED PARAMETERS

TIME (min)	***OUR (mg/L/hr)***	***TIME (min)***	***COD (mg/L)***	***TKN (mg N/L)***	***NITRATE (mg N/L)***
0	67.0	0	276.5		
5	67.0	5	354.4	26.35	4.86
10	44.5	20	315.2	22.35	5.24
20	28.0	35	306.4	22.08	5.98
35	25.0	55	188.0	22.58	
42	18.5	75	189.3	21.43	6.05
55	15.5	100	169.2		
62	16.0	150	186.0		
75	16.0	180	157.4	17.24	9.54
90	14.0	220	177.6	15.67	
112	14.0				
120	17.0				
140	19.0				
167	12.0				
180	11.0				
200	7.5				
220	10.0				

Along with these batch tests with the influent wastewaters, there were also batch tests performed on the activated sludge in order to determine the decay rate of the organisms. The raw data collected in these tests are presented below.

Table A6.10: Results of an organism decay rate test conducted starting on February 22, 1993 on activated sludge from the petrochemical facility.

TIME [day]	*OUR [mg/L/hr]*	*LN (OUR) [mg/L/hr]*
0	13.6	2.61
0.73	9.0	2.2
0.93	5.5	1.7
1.71	5.3	1.67
1.98	5.0	1.61
2.92	5.0	1.61
3.15	4.0	1.39
3.68	3.5	1.25
3.75	3.8	1.34

Table A6.11: Results of an organism decay rate test conducted starting on February 26, 1993 on activated sludge from the petrochemical facility.

TIME [day]	*OUR [mg/L/hr]*	*LN (OUR) [mg/L/hr]*
0	8.1	2.09
0.97	5.5	1.7
1.85	4.5	1.50
2.9	6.8	1.92
3.92	3.7	1.31
4.74	2.5	0.92

APPENDIX 7: PROCEDURES FOR DETERMINATION OF THE VOLATILIZATION RATE CONSTANT, K_V

Many studies have been conducted on the volatilization and stripping of volatile organic compounds from activated sludge systems (Hseih *et al.*, 1994; Melcer *et al.*, 1993; Munz & Roberts, 1989; Matter-Muller *et al.*, 1981; Roberts *et al.*, 1984). Volatilization generally occurs from the surface of quiescent basins such as the clarifiers, whereas in aerated basins the stripping mechanism accounts for the majority of the losses of volatile organic compounds (Melcer *et al.*, 1993). The information collected in these studies was utilized to model the stripping processes occurring in the petroleum/petrochemical activated sludge systems. Since the influent wastewater is directed to aerated tanks in both systems under consideration in this study, stripping rather than volatilization is assumed to be the main removal mechanism of the volatile organic compounds. Biodegradation may also contribute to the VOC removal, but this is not relevant to this particular discussion.

The most common form of modelling the removal of volatile organic compounds from a system is a first order relationship with respect to the concentration of VOC in the wastewater. This is represented by the following equation :

$$r_v = K_V C \qquad \text{(A7.1)}$$

where r_v = rate of stripping from the system,
K_V = volatilization constant, and
C = concentration of the volatile organic compound.

This was the form of the equation used in the activated sludge models of the petroleum refinery and petrochemical refinery activated sludge plants. However, an effective means of estimating the volatilization constant is important for predicting the behaviour of the VOC's in the system. For the petroleum refinery wastewaters, the volatilization rate was determined experimentally as 60 day^{-1}, by monitoring the rate of decline in COD while a sample of influent wastewater was being aerated. A series of tests was performed on the petroleum refinery wastewater to estimate this value. The sample of wastewater was aerated at a similar rate to that used in the laboratory activated sludge system, and the

COD measured at 10 to 15 minutes time intervals over several hours. This provided a reasonable estimate of the stripping of compounds from this system, since the system was being operated in the laboratory.

For the case of the petrochemical system, it was more critical that the characteristics of the actual aeration system be taken into account since calibration of the model involved use of full-scale data. Therefore, a slightly different approach was utilized to determine the volatilization rate of this system. The work of other researchers studying this specific problem was used to provide the appropriate estimates. This work was used in conjunction with a VOC study conducted at the petrochemical wastewater treatment facility.

The rate of stripping of volatile organic compounds in activated sludge systems with subsurface aeration can be modelled by the following equation presented in Matter-Muller *et al.* (1981):

$$r_v = \frac{Q_a H (1-e^{-F})}{V} C \qquad \text{(A7.2)}$$

where Q_a = air flow rate through the tank,
V = volume of the wastewater,
H = Henry's Law Coefficient, and
F = $K_La\, V / H\, Q_a$.

In the F term, the term K_La is referred to as the overall mass transfer rate constant and has units of time. According to the two film theory for overall mass transfer from the gas to liquid phases, the overall mass transfer rate constant can be determined from the combined resistances of transfer across the liquid phase and across the gas phase. This is represented by the following equation:

$$\frac{1}{K_La} = \frac{1}{k_La} + \frac{1}{k_Ga\, H} \qquad \text{(A7.3)}$$

Initial studies in this area assumed liquid film transfer was the controlling resistance for VOC removal (Matter-Muller *et al.*, 1981; Roberts *et al.*, 1984). This simplified the above equation so that the overall mass transfer coefficient equalled the liquid mass transfer coefficient. It has become evident in further studies that for certain VOC's the gas film resistance cannot be ignored (Munz & Roberts, 1989). Gas film resistance is important for volatile compounds with low values for the Henry's Law coefficient. In order to simplify the relationship in Equation A7.3, Munz and Roberts (1989) recommended using a ratio of the gas film mass transfer rate coefficient ($k_G a$) to the liquid film transfer rate coefficient ($k_L a$) of 40. Using this ratio in Equation A7.3 provides the following relationship :

$$K_L a = \frac{40\, H\, k_L a}{40\, H + 1} \qquad \text{(A7.4)}$$

In more recent studies (Hseih, 1994) the gas phase and liquid phase mass transfer coefficients were determined separately for various VOC's. This is a more accurate approach for estimating mass transfer coefficients, but beyond the scope of this particular study. It is an important approach, however, to consider in future works.

The relationship in Equation A7.4 for determining $K_L a$ can be used to calculate an estimated value for the overall mass transfer rate coefficient which can be used to calculate F. Once F is determined the volatilization rate, K_V, can be represented by :

$$K_V = \frac{Q_a\, H\, (1 - e^{-F})}{V} \qquad \text{(A7.5)}$$

This rate constant is used to model the stripping of volatile organic compounds at the petrochemical treatment plant using the first order rate equation indicated in Equation A7.1.

In order to estimate the mass transfer rate coefficients, $k_L a$, for a certain VOC, it is common practice to determine initially the $k_L a$ for oxygen. The transfer of oxygen can be estimated easily using the characteristics of the aeration equipment. The mass transfer rate constant of oxygen then is related to the mass transfer rate constant for the VOC by a proportionality factor, ψ, where

$$\psi = \frac{k_L a}{k_L a_{O2}} \tag{A7.6}$$

Studies have indicated that for most volatile organic compounds ψ ranges from 0.5 to 0.7 (Matter-Muller *et al.*, 1981). For purposes of the study of the petrochemical treatment system a value of 0.6 was utilized. [Note: The more recent work of Hseih (1994) indicated that this approach may have to be ammended for VOC's with low values for Henry's Law coefficients, but for this study the assumption of a constant value was suffcient.]

Using the following values in the above relationships a range of values for the volatilization constant, K_V, was determined:

Q_a = 15500 m^3/d
V = 3206 m^3
H = 0.033 and 0.170 (range established in the VOC study)
$k_L a_{O2}$ = 11 d^{-1}
ψ = 0.6
$k_L a$ = 6.6 d^{-1}

For H = 0.033,

$K_L a = 3.76$,
$\therefore\ F = 23.5$
$\therefore\ K_V = 0.16\ d^{-1}$

For H = 0.170,

$K_L a = 5.75$,
$\therefore\ F = 7.0$,
$\therefore\ K_V = 0.82\ d^{-1}$

Therefore, for the petrochemical activated sludge plant the range for K_V has been estimated as 0.16 to 0.82 d^{-1}. For purposes of model simulation a value of 0.4 d^{-1} was used simulate the response of the petrochemical system to the influent VOC concentration.