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Dynamic Models and Expert Systems for the Activated Sludge Process

A dissertation submitted in partial satisfaction of the
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by

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DEDICATION

To my wife Shan Liu and daughter Jessica (Jing-yue)

To my parents and parents-in-law

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ABSTRACT OF THE DISSERTATION

Dynamic Models and Expert Systems
for the Activated Sludge Process
by
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Professor Michael K. Stenstrom, Co-Chair
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The objective of this research was to develop dynamic models and expert systems to assist the design, optimization, operation, and control of the activated sludge process. The research effort focuses on two types of activated sludge processes - the high-purity oxygen activated sludge and petroleum refinery activated sludge.

The new high-purity oxygen activated sludge process model developed in this research, HIPURE2, is the first such model that uses the popular Activated Sludge Model No. 1, which is the activated sludge model developed by the International Association on Water Quality Task Group on Mathematical Modeling for Design and Operation of Biological Wastewater Treatment. HIPURE2 fits the data from a pilot plant and a full-scale plant very well using a single set of stoichiometric and kinetic coefficients. The comparison of HIPURE2 with a previous model, HIPURE, reveals that both of them are capable of describing the oxygen utilization patterns realistically though oxygen uptake rates are modeled very differently in these two models. A model calibration algorithm was developed and evaluated. The algorithm was capable of estimating model parameters reliably and accurately. Algorithm evaluation provided valuable information on the influences of a number of factors on model calibration.

An activated sludge model was developed for a petroleum refinery activated sludge process performs nitrification as well as model carbon oxidation. The model predicts effluent COD, ammonia, nitrite, nitrate, sulfide, and sulfate concentrations as well as oxygen uptake rate, air flow rate (aeration), and sodium hydroxide dosage (pH control).

An expert system was developed to improve the operation and control of an activated sludge wastewater treatment process in an integrated petroleum refinery. The expert system emphasizes the integration and interactions among process schematics, data management, report generation, data trending, and process diagnosis. The expert system indicates the location of a detected process failure through alarms. The expert system allows directly entry of monitoring data into a spreadsheet like template with checking for implausible values, data management and trending with a user friendly interface. The knowledge base is generic and structured which enables easy modification and expansion.

The concept of integrating process model and expert system was developed for the effluent treatment plant in the model refinery. It is illustrated that integrated expert system is a powerful tool to improve operation and control. It is shown that an integrated expert system can help find operation problems, diagnose causes, and provide both qualitative and quantitative control advice to the operators. Process efficiency and reliability can be enhanced substantially.

1. INTRODUCTION

The activated sludge process was invented in England in 1912 by Ardern and Lockett (Ardern and Lockett, 1914) and was so named because it involved the production of an activated mass of microorganisms capable of stabilizing a waste aerobically. The activated sludge process is now the most widely used biological wastewater treatment method for treating both domestic and industrial wastewaters. It is used throughout the world and remains the most popular treatment process available, with the majority of new treatment plants of the activated sludge type. Activated sludge systems comprise about 9000 US., 501 U.K., and over 600 France wastewater treatment plants (Healey, 1989; Pujol, *et al.*, 1991). Many different versions of the original process are in use today, such as conventional (plug-flow), complete-mixed, extended aeration, pure oxygen, sequencing batch reactor, contact stabilization, oxidation ditch, deep tank (90 ft) and deep shaft (Metcalf and Eddy, Inc., 1991).

Many problems associated with the activated sludge process remain unsolved despite the fact that the activated sludge process has become the most widely used biological wastewater treatment system and has been the subject of much research since the early 1910s. For example, the dynamic behavior of the activated sludge process under transient conditions is still not clearly understood. Inadequate knowledge of activated sludge dynamic behavior has led the design engineer to oversize the treatment process in order to accommodate the uncertainties involved. That is, due to the lack of knowledge of activated sludge process dynamics, the current design doctrine is to oversize the process. This results in greater capital cost investment and creates a greater burden on society. As depicted in Figure 1.1 the biological system is among most poorly understood systems in modern world (Karplus, 1976) despite the fact that the activated sludge process has been the subject of many investigations. The process is complicated by the presence of mixed populations of organisms, varying physical and chemical characteristics of the organic load, and the time-varying nature of the influent flow and substrate concentration.

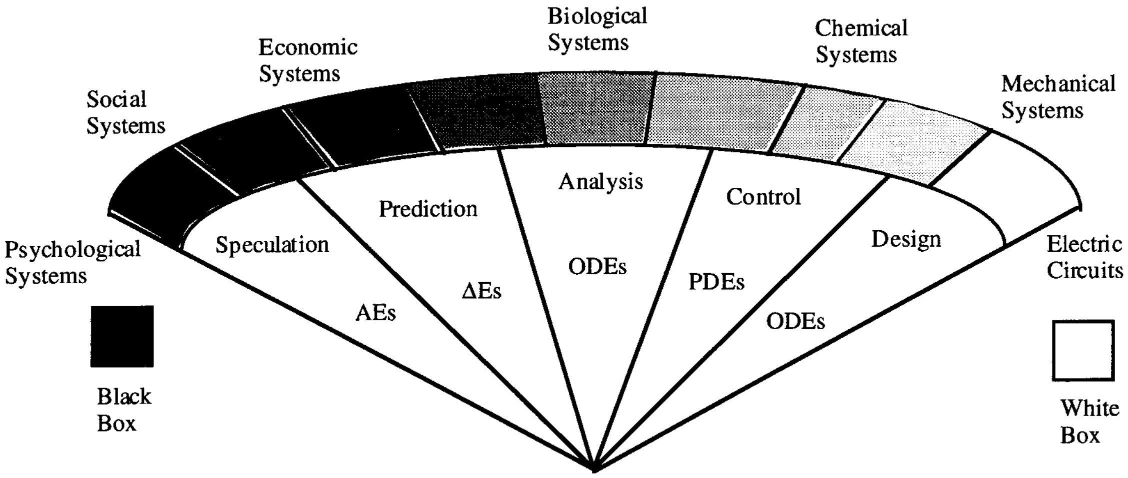


Figure 1.1 Karplus's Rainbow (Karplus 1976)

The complexity of the activated sludge process poses a major challenge to the operation and control of the treatment system. A survey conducted by US. EPA in 1979 found that 30 to 50 percent of the treatment plants failed to satisfy their NPDES (National Pollutant Discharge Elimination System) discharge limitations and four of the top five reasons cited were attributed to poor operation practices (Hegg *et al.*, 1979). There has been no significant improvement since that survey.

This dissertation explores the utilization of dynamic models and expert systems to help solve important problems associated with the design, optimization, operation, and control of activated sludge wastewater treatment plants. More specifically, this research focuses on the development of dynamic models and expert systems for two kinds of activated sludge processes - the high-purity oxygen activated sludge process and the petroleum refinery activated sludge process.

1.1 Activated Sludge Modeling

Process modeling represents an excellent way of investigating activated sludge process dynamics. Process modeling and computer simulation have proven to be extremely successful engineering tools for the design and optimization of wastewater treatment processes. The use of simulation has expanded rapidly during the past two decades because of the availability of large, high-speed computers. The recent trend toward personal computing allows for the expanded availability of individual computer workstations and further boosts the applications of computers in wastewater engineering.

There are many incentives for doing process modeling in wastewater engineering. Firstly, it is economically desirable. For design purposes, it is usually cheaper to use simulation techniques incorporating fundamental laboratory data into the mathematical model than it is to build numerous different sized pilot plants (exhaustive experimental approach). Secondly, it is a convenient way to investigate the effects of system parameters and process disturbances upon operation. It is usually a lot easier to develop alternative operating approaches and evaluate these alternatives via a mathematical model than by experimental methods. In order to verify the simulation results some experiments are usually performed, but only the really critical ones are necessary. Thirdly, simulation is a reasonable way of extrapolating performance and scaling up processes. By incorporating fundamental mechanisms into process simulations, system performance can be predicted in new and different operating regions. Finally, it helps to understand the behavior and mechanisms of the process. By understanding the rigors of mathematical modeling the engineer learns much about the process that is being simulated. In order to obtain a successful simulation, the significant process mechanisms must be quantitatively described. By solving the model, useful relation between process variables are revealed and can be easily observed (Ramirez, 1989).

The benefits of process modeling and simulation are also obvious in terms of the many purposes that it can serve. For the researcher, modeling serves as a conceptual framework upon which to build and test hypotheses, thereby extending knowledge. For the designer, modeling allows the exploration of the impact of a wide range of system variables, thereby greatly increasing his/her experiential space regarding a proposed process. Furthermore, when employed within the appropriate framework, modeling permits the development of near optimal design in which the desired process objectives are obtained at minimal cost. For the operator, modeling allows the development of control strategies by facilitating the investigation of treatment system performance. For the regulator, modeling allows judgments to be made about the impact of new effluent requirements on treatment system design and cost. Finally, for the engineering educator, modeling provides a tool with which students can explore new ideas, thereby enriching their education by engaging them actively in the learning process (Grady, 1989).

Significant progress has been achieved in activated sludge process modeling in the past four decades, particularly the past two decades. Mathematical models have been widely used as valuable tools in the design and operation of activated sludge wastewater treatment plants worldwide. Most conventional activated sludge models treat substrate and biomass as homogenous substances and their kinetic expressions are based on zero-order, first-order, or Monod (or Michaelis-Menton) kinetics. The development of structured activated sludge models began when the deficiencies of conventional activated sludge models were revealed. Many structured activated sludge models have been developed since early seventies. Among them the IAWQ (formerly IAWPRC) Activated Sludge Model No. 1 has become the most widely accepted and used activated sludge model throughout the world. A detailed review of activated sludge models is presented in Chapter 2.

In this study, dynamic models of two types of activated sludge processes were investigated - the high-purity oxygen activated sludge process and the petroleum refinery activated sludge process. Two full-scale activated sludge wastewater treatment plants were selected as models for this investigation - Sacramento Regional Wastewater Treatment Plant (SRWTP) and Chevron El Segundo Refinery Effluent Treatment Plant (ETP). SRWTP uses the high-purity oxygen activated sludge as a secondary treatment technique. Influent is primarily domestic wastewater except in the canning season when a significant portion of the influent is the canning wastewater. Chevron El Segundo ETP uses a completely-mixed, single-sludge carbon-oxidation and nitrification activated sludge process for the secondary treatment of the combined petroleum refinery process wastewater.

The IAWQ Activated Sludge Model No. 1 was modified for the high-purity oxygen activated sludge process. The modified Activatged Sludge Model No. 1 was used to develop a new mathematical model for the high-purity oxygen activated sludge process. A new activated sludge model was formulated for the petroleum refinery activated sludge process following the modeling principles embedded in the development of the IAWQ Activated Sludge Model No. 1 and a process simulation program was implemented using the activated sludge model.

1.2 Expert Systems

Despite tremendous successes achieved in activated sludge modeling, there are still a number of phenomena which are poorly understood and no sound mathematical models have been developed to describe them. Examples include sludge bulking, foaming, etc. Considerable progress has been made towards understanding these phenomena; our state-of-the-art knowledge, nevertheless, is incomplete and qualitative in nature for the most part so far. It is these poorly understood phenomena that contribute to many operation and control challenges in activated sludge wastewater treatment plants.

One of the biggest challenges faced by activated sludge wastewater treatment plants arises from their operation and control problems. For a high-purity oxygen activated sludge plant with its sophisticated reactor system and a petroleum refinery with its complex mixture of wastes, the challenge is that much greater.

Process upsets, transients, such as intermittent and shock loadings, sludge bulking, etc., are intrinsic parts of activated sludge process operations. In practice, operators rely heavily on their operating experience to properly operate and trouble shoot their activated sludge processes. Experienced operators are limited, and their experience is highly personal. When an experienced operator leaves, his experience leaves with him. In addition, the operational objective is always to keep the process as normal as possible. New operators do not have the luxury of experiencing a wide variety of process behavior in a short time and therefore need a long time to acquire their own experience.

In recent years, research in the field of Artificial Intelligence (AI) has had many important successes. Among the most significant of these has been the development of powerful computer systems known as "expert" or "knowledge-base" systems. These computer systems are designed to represent and apply factual knowledge of specific areas of expertise to solve problems. The potential power of expert systems which can replicate expensive or rare human knowledge has led to a worldwide effort to extend and apply this technology.

Although it is difficult to develop an expert system, there are many important reasons why expert systems are desirable. First, human experts, especially the most experienced ones, are very scarce, and hence very expensive. Expert systems, by contrast, are relatively inexpensive. They are costly to develop but cheap to operate. Second, it is easy to transfer or reproduce expert systems. However, transferring knowledge from one human expert to another is a laborious, lengthy, and expensive process. Third, expert systems give more consistent, reproducible results than does human expertise. A human expert may make different decisions in identical situations because of emotional factors. For example, a human expert may forget to use an important rule in a crisis situation because of time pressures or stress. An expert system is not susceptible to these distractions. Fourth, but by no means the last, expert systems allow automation of many tasks that could not be effectively handled by human experts (Yang, 1990).

The goal of the expert system development is to develop a user-friendly heuristic-based expert system for the refinery activated sludge wastewater treatment plant, an expert system which will do the following:

- manage monitoring data, including data entry, report generation, and trending;
- alert the operator to departures from the normal operating range;
- provide diagnoses and qualitative/semi-quantitative suggestions to the operator for steps to improve a deteriorating situation; and
- help in the training of newer, less-experienced operators.

To summarize, the objective of this investigation is to develop process models and expert systems for two types of activated sludge processes - the high-purity oxygen activated sludge process and the petroleum refinery activated sludge process. More specifically, the sub-objectives are:

1. Modify the IAWQ Activated Sludge Model No. 1 and use it to develop a new mathematical model for the high-purity oxygen activated sludge process (HPO-ASP) treating municipal wastewaters;
2. Development and evaluation of a model calibration algorithm for the high-purity oxygen activated sludge process;
3. Verify the new HPO-ASP model using both pilot and full-scale treatment plant data;
4. Develop an activated sludge model for the petroleum refinery activated sludge process performing single-sludge carbon oxidation and nitrification;
5. Develop a process simulation program for the petroleum refinery activated sludge process based on the refinery activated sludge model developed;
6. Develop an expert system for the effluent treatment plant (ETP) of a west coast integrated petroleum refinery to help resolve operation and control problems that a mathematical model can not handle;

7. Develop and illustrate the concept, program architecture, and benefits of integrated expert system.

2. LITERATURE REVIEW

2.1 Activated Sludge Fundamentals

The activated sludge process consists of two units - the aeration tank (or basin) and the secondary clarifier (sedimentation tank) (Figure 2.1). From the bottom of the secondary clarifier, settled and concentrated sludge is returned back to the aeration tank to maintain the mixed liquor suspended solids (MLSS) at desirable level. Excess sludge produced each day is wasted from the return sludge line and discharged, frequently, to a sludge thickener to keep the system operating at an controlled sludge age (mean cell retention time, MCRT or sludge retention time, SRT).

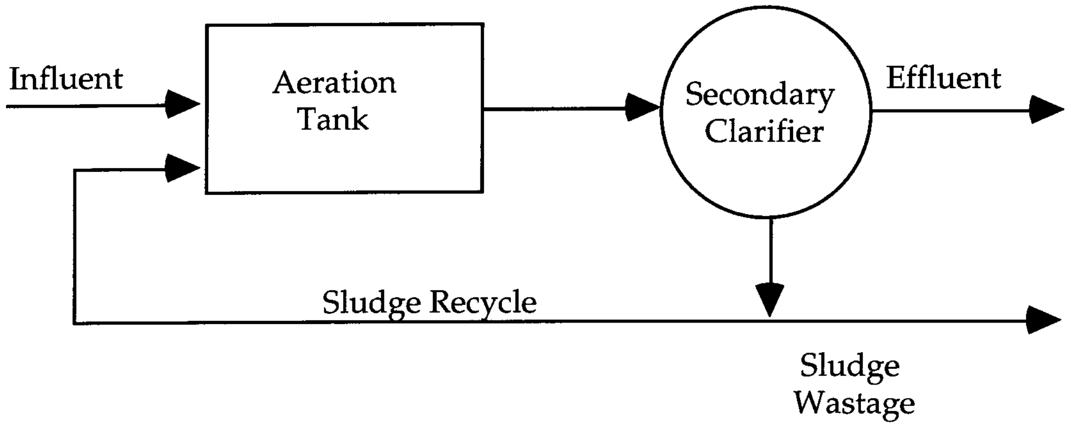


Figure 2.1 Flow diagram of the activated sludge process

The activated sludge process is the most widely used secondary treatment process for treating both municipal and industrial wastewaters. The units of an activated sludge wastewater treatment plant consist of the following - bar screen, grit chamber, primary clarifier, aeration tank, secondary clarifier, chlorination chamber, sludge thickener, sludge

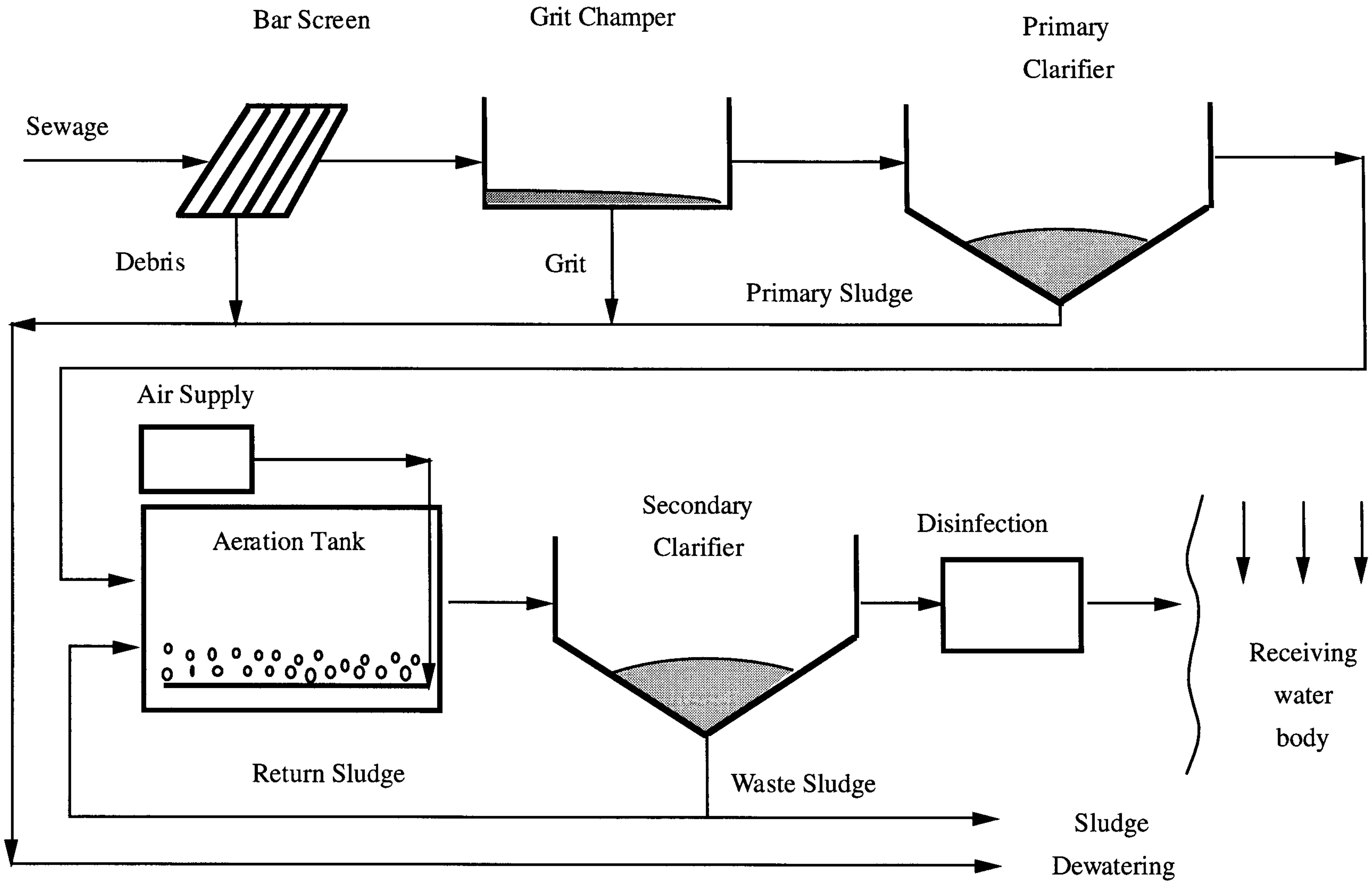


Figure 2.2 Typical flow diagram of a municipal Activated Sludge Wastewater Treatment Plant

digester, etc. (Figure 2.2). The scope of this investigation is limited to the activated sludge process only. It is beyond the purpose of this dissertation to investigate every unit process of a whole activated sludge treatment plant, although the operation and control of units such as dissolved air flotation (DAF) was covered for a petroleum refinery effluent treatment plant (Chapter 7). Instead, efforts were exclusively devoted to the modeling of the activated sludge process, especially the aeration tank since it is the most important unit in activated sludge wastewater treatment plants.

It is worth pointing out that by focusing on the activated sludge process the author is by no means implying that other units are not important. Every unit contributes to the proper functioning of the treatment plant and failure of any unit could lead to the failure of the whole plant. It is thus of significant importance to develop a control strategy for the whole treatment plant. Wastewater treatment plant has been the subject of much research; steady-state and dynamic models and computer-compatible control strategies have been explored by various researchers for many years. The success of such models and controls strategies, nevertheless, largely depends on the performance of the activated sludge model for the reasons discussed in Chapter 1. Aeration system, for example, consumes a large percentage of total power consumption in an activated sludge wastewater treatment plant (up to 80% in certain cases). Control strategies that matches the oxygen dissolution with the oxygen uptake by biomass in aeration tank is highly desirable and expected to result in significant savings in electrical power expenditure. This, however, relies heavily on the ability of the activated sludge model to predict the dynamics of oxygen utilization. As it will be discussed later, the conventional activated sludge model failed to predict the lag and dampening of oxygen utilization in case of increased loadings. This demonstrates that activated sludge model is a limiting factor; our capability to control wastewater treatment plants is largely restricted by the availability of sound models. Therefore it makes sense that this research focuses on the development of dynamic models for the activated sludge process.

Within the activated sludge process, the biological reactor, aeration tank, plays a more important role and has been the focus of much research, which is also the focus of this investigation. The activated sludge process, however, can not perform well if the secondary clarifier does not function properly. The importance of the secondary clarifier is further discussed next.

Another distinction that needs to be made is between the activated sludge model and the activated sludge process model. It is important to understand the difference between them. An activated sludge model is a biokinetic model which describes the reaction mechanism and the stoichiometric and kinetic relations among different components/constituents/species in the biological reactor (the aeration tank). It answers questions like these: What biological processes are occurring (reaction pathways and/or mechanisms)? What components/species exist and are involved in the aeration tank (reactants, intermediates, and products, such as substrate, biomass, dissolved oxygen, etc.)? Stoichiometric relationships? Kinetic rate expressions? An activated sludge process model is a mathematical model of the activated sludge process. In general it consists of a number of differential and algebraic equations formulated based on fundamental scientific and engineering laws such as mass balance and energy balance. Activated sludge model, the biokinetic model, is only a sub-model which describes the reaction terms (source/sink) in the governing equations. Other factors that are usually considered in a process model include hydraulic flow regimes, e.g. plug-flow, completely mixed, or CSTR (completely stirred tank reactor) in series, tank configurations, inputs, controls, etc. The following example helps explain these statements. For an activated sludge process with a completely mixed aeration tank, which is approximated as an ideal CSTR here (Figure 2.3), the governing equations of the aeration tank are formulated as follows:

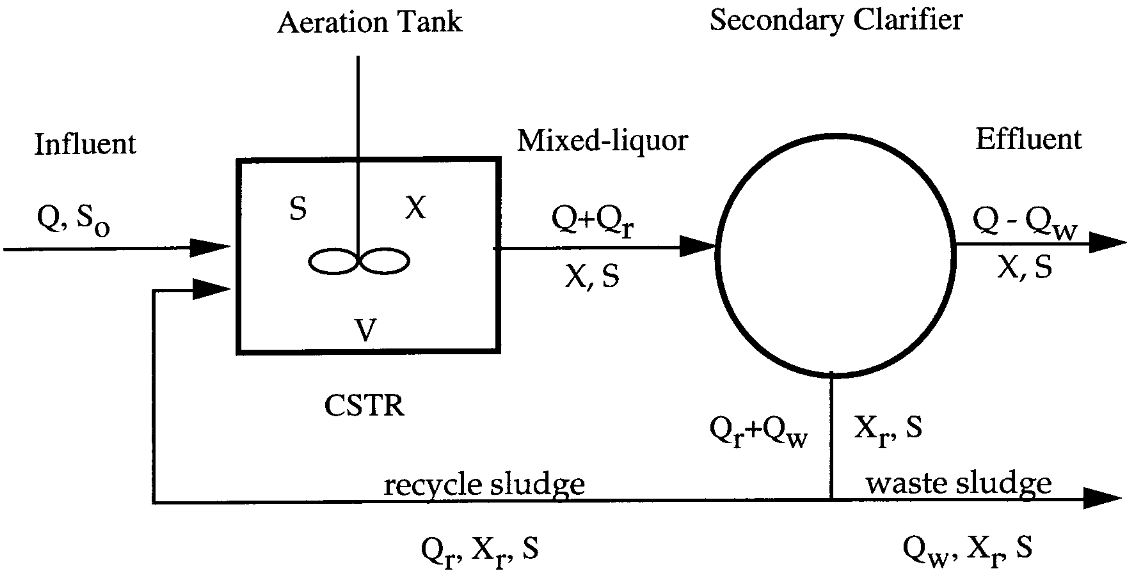


Figure 2.3 Mass balance of the activated sludge process

Mass Balance:

$$V\frac{dS}{dt} = QS_o + Q_rS - (Q+Q_r)S + r_{su}V \tag{2.1}$$

$$V\frac{dX}{dt} = QX_o + Q_rX_r - (Q+Q_r)X + r_{g'}V \tag{2.2}$$

$$V\frac{dS_{O_2}}{dt} = QS_{O_{2}o} + Q_rS_{O_{2}r} - (Q+Q_r)S_{O_2} + (OTR)V - (OUR)V \tag{2.3}$$

where

S - concentration of substrate [M(COD)L^{-3}]

X - concentration of biomass [M(COD)L^{-3}]

Q - flow rate [L^3T^{-1}]

o - as subscript, denotes influent

r - as subscript, denotes recycled sludge

w - as subscript, denotes wasted sludge

r_{su} = substrate utilization rate, [ML^{-3}T^{-1}]

r_g = rate of microorganism growth, [ML^{-3}T^{-1}]

$r_{g'}$ = net rate of microorganism growth, [ML^{-3}T^{-1}]

OUR = oxygen uptake rate, [ML^{-3}T^{-1}]

OTR = oxygen transfer rate, [M^{-3}T^{-1}]

dimensions:

M - mass

L - length

T - time

Note the implications of the following assumptions:

- Aeration tank is a CSTR. Therefore concentrations of S, X, and S_{O_2} are the same everywhere in the aeration tank and equal to that in the mixed liquor.
- Secondary clarifier does not affect soluble components. Therefore concentrations of S and S_{O_2} are the same at the following locations - mixed liquor, secondary effluent, return sludge, and wasted sludge. This, of course, is a much simplified picture.

In this aeration tank model, mass balance equations are written for three components: biomass X, substrate S, and dissolved oxygen S_{O_2}. The activated sludge model describes three of the four reaction terms in this model - r_{su}, $r_{g'}$, and OUR. It is clear that the activated sludge model is only part of the process model. The oxygen transfer rate (OTR) is the source term in the dissolved oxygen mass balance (Equation 2.3) and is described by a gas transfer equation which is apparently not part of the activated sludge model. The detailed discussion of OTR is reserved for Chapter 3, Section 3.1.2.1.3. In addition to oxygen dissolution, a process model may also include submodels that calculate the pH value in the aeration tank, estimates the stripping of carbon dioxide, etc. This will be shown in detail in Chapter 3, Section 3.1.2 when a new mathematical model is developed for the high-purity oxygen purity process. It is also evident that a clarifier model is needed to predict return sludge concentration X_r.

Aeration tank size and configuration represent other important aspects of activated sludge process models. Under steady-state conditions, the specific growth rate μ of biomass equals to the dilution rate D which is defined as the ratio of flow rate Q to tank volume V. This states that the specific growth rate is subject to hydraulic control. This is important since we can exert engineering control over the hydraulics of the system, i.e., $D = \mu = Q / V$. We can control the specific growth rate by changing the hydraulic flow to the reactor or change the size of the reactor (Rozich and Gaudy, 1992).

An activated sludge process model is not complete if a model of the secondary clarifier is not included. Secondary effluent quality and the performance of the aeration tank are strongly influenced by the performance of the secondary clarifier. The influence is two-fold: First, the clarification function of the clarifier dictates the quality of the effluent. If the clarifier fails to clarify the mixed liquor, the effluent quality standard cannot be met even if a perfect biodegradation is achieved in the aeration tank. One example of this type of process failure is sludge bulking, which does not adversely affect biodegradation but deteriorates the sludge settling characteristic to such an extent that the secondary clarifier is no longer able to produce clarified effluent. Secondly, the thickening function of the secondary clarifier determines the sludge concentration at the bottom of the clarifier. The sludge settled down to the bottom of the clarifier is thickened due to gravity. A normal range of mixed liquor suspended solids (MLSS) cannot be maintained if sludge is not thickened in the clarifier. The sludge blanket keeps rising and eventually sludge wash-out will occur. Poor sludge settling characteristics impair sludge thickening and thus the bottom sludge concentration becomes low. In order to handle the BOD load and sustain normal biodegradation, the MLSS value must be kept within a normal range, e.g. 1000 - 3000 mg/l. This means that sludge recycle must be increased to maintain the MLSS level. This further complicates the situation since increased sludge recycle constitutes a greater hydraulic load to the clarifier that further worsens the situation. The process operation thus falls into a vicious cycle. The interaction between aeration tank and clarifier is therefore of great importance (Mulbarger, *et al.* 1985).

In short, an activated sludge model is a biokinetic model that describes the stoichiometric and kinetic relations among different components/species. An activated sludge process model is a mathematical description of the process that use the activated sludge model as a sub-model and is formulated based on laws such as mass conservation.

The activated sludge model is the most important part of the activated sludge process model. The fact that the activated sludge model is only part of the activated sludge process model does not impede its importance. The activated sludge model depicts the fundamental reaction mechanisms of all kinds of activated sludge processes. It is independent of specific processes. An activated sludge process model might be viewed as the integration of a generic biokinetic model -activated sludge model- and the process-specific facets of an activated sludge process.

2.2 Activated Sludge Modeling Fundamentals

The fundamentals of activated sludge modeling is discussed is this section, which include the method of model representation and wastewater and biomass characterization.

2.2.1 Method of Model Representation

2.2.1.1 Format

One problem often associated with papers presenting models describing complex systems is that it is difficult to follow the development of the author's ideas. In particular, it is often difficult to trace all the interactions of the system components. The matrix format of model representation, as advocated by the IAWQ (formerly IAWPRC) Task Group on Mathematical Modeling for Design and Operation of Biological Wastewater Treatment, offers the best opportunity for overcoming this problem while conveying the maximum amount of information (Henze, *et al.*, 1987).

The details of representing activated sludge models in matrix format will be illustrated in the following sections when activated sludge models are reviewed.

2.2.1.2 Notation

Another problem frequently encountered in activated sludge modeling is related to the lack of an unified notation. Different authors often use very different notation to represent the same reaction components and their interactions. This makes models difficult to evaluate and compare and hinders the progress of activated sludge modeling.

In this dissertation, the notation recommended by a IAWQ Working Group (Grau, *et al.* 1982), *Notation For Use In The Description Of Wastewater Treatment Processes*, is followed wherever applicable. In the recommended notation, all soluble components/species are denoted as S and all particulate components/species are denoted as X, with symbolic subscripts further differentiating constituents and numerical subscripts indicating the location in the process. For example, S_{S_0} and X_{S_0} represent the soluble substrate (readily biodegradable) and particulate substrate (slowly biodegradable) in the influent. Previous activated sludge models reviewed in this chapter are converted into matrix format using the recommended notation. The conversion results in great ease in following and evaluating these activated sludge models.

2.2.2 Characterization of Wastewater and Biomass

Traditionally, organic matters in wastewater are characterized by collective parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC). Five-day BOD (BOD5) may be the most widely used parameter for characterizing wastewater in the past and is still widely used today, especially for regulatory purposes. BOD5, however, has been under intensive criticisms in the past two decades. The following limitations of the BOD test have been reported: (1) a high concentration of active, acclimated seed bacteria is required; (2) pretreatment is needed when dealing with toxic wastes, and the effects of nitrifying organisms must be reduced; (3) only the biodegradable organics are measured; (4) the test does not have stoichiometric validity after the soluble organic matter present in solution has been used; and (5) an arbitrary, long period of time is required to obtain results. Of the above, perhaps the most serious limitation is that the 5-day period may or may not correspond to the point where the soluble organic matter that is present has been used. The lack of stoichiometric validity at all times reduces the usefulness of the test results (Metcalf & Eddy, Inc. 1991). COD has been identified by many researchers to be a more appropriate parameter for representing the organic matters in wastewater (Gaudy and Gaudy, 1971). COD is preferred to other parameters such as BOD or TOC for a number of reasons: (1) COD is easier to measure. For a given wastewater sample, the measurement of COD takes about 3 hours (standard method; quick COD only takes about 1 hour), while the measurement of BOD_5 takes 5 days. (2) COD can be more accurately and precisely measured than BOD. COD measurement uses chemical oxidation. BOD measurement uses microbial inoculum (seeding). More attention and skill are required to successfully perform a BOD test. Gaudy and Gaudy (1971) should be credited for first proposing that COD be used in lieu of BOD in wastewater treatment for its merits mentioned above.

Research on the characterization of wastewater and biomass has been largely propelled by the advances in the modeling of biological wastewater treatment processes, especially the activated sludge process. As will be discussed next, organic matter and biomass are assumed to be homogenous substances in conventional activated sludge models, and are measured as BOD (more commonly as BOD_5) and VSS (volatile suspended solids). Conventional models, however, failed to accurately predict the dynamics of oxygen utilization as well as other key process responses. In structured activated sludge models, it is necessary to divide the organic matter into different fractions, such as biodegradable fraction and nonbiodegradable fraction. Biomass is also differentiated into fractions such as active mass and inert mass. As more biological reactions are identified and included into activated sludge models, more components/species are incorporated into models. This, in turn, prompts more experimental investigation to characterize wastewater and biomass. Experimental findings, on the other hand, also lead to modifications of models.

2.2.2.1 COD Fractions

Ekama, Dold and Marais (1986) proposed procedures for determining influent COD fractions and the maximum specific growth rate of heterotrophs in activated sludge systems. The influent COD of municipal wastewaters is categorized into four fractions: readily (soluble) and slowly (particulate) biodegradable, and soluble and particulate unbiodegradable within the framework of the IAWQ Activated Sludge Model No. 1. Some of the procedures are dependent on knowledge of the heterotrophic yield and endogenous mass loss rate constants. The so-called particulate organic matter spans a wide rage of particle size and can be further divided into colloidal (0.001-1μm), supracolloidal (1-100μm), and settleable (>100μm) (Levine, *et al.* 1991). It should be noted that the division of organic matter into soluble and particulate fractions is more operational than physical in activated sludge modeling. The division is not strictly based on physical measurements such as filtration; rather it is based on biological responses of the activated sludge, such as oxygen uptake. Some complex organic molecules are truly soluble in a physical sense but could be classified as particulate because they behave like particulate matter to microorganisms (Henze *et al.* 1987).

Sollfrank and Gujer (1991) investigated the characterization of domestic wastewater for mathematical modeling of the activated sludge process. Based on oxygen uptake measurements a procedure is introduced to characterize organic material in domestic wastewater in view of mathematical models for the activated sludge process. The methods allows the determination of stoichiometric as well as kinetic parameters necessary for the description of heterotrophic growth and hydrolysis of slowly biodegradable organic matter. From the information gained a kinetic model for the activated sludge process is formulated and experimentally verified under dynamic loading conditions.

Germirli, *et al.* (1991) conducted an assessment of the initial inert soluble COD in industrial wastewater. The commonly used COD parameter does not differentiate between inert and biodegradable organic matter in wastewaters. This differentiation is quite necessary and significant for industrial effluents with high organic content. In such strong wastes the soluble influent COD fraction may severely interfere with the treatability results or challenge the effluent limitation criteria adopted for different industrial categories. The methods suggested in the literature to identify this fraction are not designed to differentiate between soluble inert organic matter and soluble residual microbial products generated during the experiments. Germirli *et al.* (1991) proposes two different methods for the assessment of the initial soluble inert COD fraction and summarizes their comparative evaluation. The methods are tested for five different industrial wastes characterizing pulp and paper, meat processing, antibiotics, textile and dairy effluents with total soluble COD concentration ranging from 1000 to 9300 mg/l. The results indicate significant interference of soluble residual microbial products which may be identified and corrected for with the proposed methods.

Most recently, Mamais *et al.* (1993) developed a rapid physical-chemical method for the determination of readily biodegradable soluble COD in municipal wastewater. The method involves removal by flocculation and precipitation of colloidal matter that normally passes through 0.45 μm membrane filters. Results from four domestic wastewaters demonstrated that the physical-chemical method and the biological method gave virtually identical results. The physical-chemical method was used successfully to measure the quantity of truly soluble organic matter removed in the anaerobic zone of bench-scale enhanced biological phosphorus removal activated sludge systems.

2.2.2.2 Viability of Biomass

It is well known that only a fraction of the activated sludge, which is usually measured as volatile suspended solids (VSS), is viable; a significant fraction is inert mass which originates from the inert organic matter in the influent and the inert organics derived from decay. Another fraction of the MLVSS is the residue of particulate substrate which was initially entrapped into sludge flocs upon contact and subject to hydrolysis subsequently. Only the viable fraction, the active biomass, is responsible for metabolism of substrate. Weddle and Jenkins (1971) reported that conventional and low-rate activated sludges consist largely of nonviable solids. The viable aerobic heterotrophic microorganism content of such activated sludges is between 10 and 20 percent.

Conventional activated sludge models, which relate substrate (often in BOD5) and biomass (often in VSS) through Monod kinetics, suffer from the disadvantage that only the viable fraction of biomass is responsible for the kinetics. In structured activated sludge models, the viability of biomass is considered by dividing VSS into several fractions, e.g. active biomass, inert organic matter, entrapped substrate, etc. For example, if the IAWQ Activated Sludge Model No. 1 is applied to an activated sludge system performing carbon oxidation only, MLVSS and MLSS are expressed as:

$$MLVSS = (X_I + X_S + X_P + X_{BH}) / f_{COD/VSS} \tag{2.4}$$

$$MLSS = (X_I + X_S + X_P + X_{BH}) / f_{COD/VSS} + X_{nv} \tag{2.5}$$

where X_I, X_S, X_P, and X_{BH} are inert organic matter from influent, particulate substrate (slowly biodegradable substrate), inert organic matter arising from biomass decay, and active biomass (active heterotrophs) respectively. The unit for all of them is [M(COD)L^{-3}]. A conversion factor, $f_{COD/VSS}$, is applied to convert the unit of volatile fraction of MLSS, MLVSS, from COD to VSS. X_{nv} is the non-volatile (inorganic) faction of MLSS and its unit is mass per unit volume. $f_{COD/VSS}$ equals to 1.42 when volatile suspended solids (VSS) is approximated by the formula $C_5H_7O_2N$. Dold *et al.* (1980) and Dold and Marais (1986) suggested a value of 1.48 for $f_{COD/VSS}$, which they called f_{CV}.

It is known experimentally that the active fraction of biomass decreases when sludge age increases. This fact is reflected, at least in part, in structured activated sludge models by the increase of inert mass fraction in biomass with sludge age. In other words, the fraction of inert organic matter derived from biomass decay will increase with increasing sludge age. It is obvious that conventional activated sludge models do not possess such a capability.

A variety of techniques exist for determining the viability of biomass, such as direct counting of viable bacteria, measurement of adenosine triphosphate (ATP) generation, measurement of oxygen uptake rate, etc. (Weddle and Jenkins, 1971; Green and Shelef, 1981; Chung and Neethling, 1988; Jensen *et al.*, 1988; Jorgensen *et al.*, 1992).

Weddle and Jenkins (1971) found that the ATP content of activated sludge reflects its viable organism content and it appears that this cell constituent can be used as a rapid and convenient indicator of viable organisms in activated sludge because the ATP content/viable cell remains constant over a wide net growth rate range. Green and Shelef (1981), however, argued that the ratio is a constant only for the typical net growth ranges met in the activated sludge process. They found that the ratio is not a constant in batch and plug-flow reactors. Jensen *et al.* (1988) also reported that the biomass/ATP ratio changes significantly with different metabolic conditions.

Oxygen uptake rate (OUR) is another popular parameter for representing biomass viability. Weddle and Jenkins (1971) discovered that the ratio of OUR/viable cell is constant for the net growth rate range from 0.03 to 6 day^{-1}. OUR measurements have been widely used in substrate and biomass characterization and studies of activated sludge kinetics (Ekama *et al.* 1986; Sollfrank and Gujer, 1991).

Other biomass viability parameters include dehydrogenase enzyme activity (Weddle and Jenkins, 1971), optical density (OD) (Jensen *et al.* 1988, Jorgensen *et al.* 1992), and fluorescein diacetate (FDA) hydrolysis (Jensen *et al.* 1988, Jorgensen *et al.* 1992).

2.2.3 Reaction Mechanisms

Prominent reactions of the activated sludge process are reviewed in this section, which include substrate utilization and active biomass formation, substrate storage, hydrolysis, biomass decay, nutrient assimilation, etc.

2.2.3.1 Substrate

Substrate removal is defined as the process in which substrate is removed from water. The removal is attributed to substrate utilization and storage (biochemical) as well as entrapment (physical). For heterotrophs, substrate is carbonaceous organic matter. For autotrophs, substrate is inorganic matter, e.g. ammonia and nitrite for nitrifiers and sulfide and/or elemental sulfur for sulfur oxidizers (Table 3.5). Much research indicates that substrate, the biodegradable fraction of influent organic matter, is composed of both soluble and particulate organics. It has been found that particulate organic matter constitutes to over 60% of the total COD in certain raw sewage (Takahashi, *et al.*, 1969). The removal mechanisms of these two forms of substrate, nevertheless, are quite different.

Particulate substrate is rapidly removed from water phase upon contact with sludge flocs in the aeration tank. Many mechanisms contributes to the phenomenon, e.g. adsorption, colloidal deposition, and physical enmeshment or entrapment. It has been demonstrated that over 98% of colloidal and suspended matter is removed from the liquid phase upon contact with sludge in 8 to 15 minutes. This is instantaneous when one considers that the hydraulic detention time is in the magnitude of hours. Therefore the removal of particulate matter from the liquid phase has been treated as an instantaneous process in activated sludge modeling.

While most structured activated sludge models agree on the instantaneous removal of particulate substrate from liquid phase, they differ significantly on the subsequent reactions involving entrapped particulate substrate. After particulate substrate is entrapped into sludge flocs, it becomes part of sludge flocs and is subject to a series of subsequent reactions. Different approaches have been adopted to describe these reactions.

2.2.3.1.1 Utilization

Substrate utilization and cell growth are two facets of one biochemical process - metabolism (Equation 2.16). Other coupled reactions include oxygen uptake, carbon dioxide generation, etc. The soluble fraction of substrate consists of relatively simpler organic compounds and is amenable to direct metabolism. The following "pseudo-reaction" may be used to describe the reaction:

$$S + O_2 + (N,P, ...) + ... \xrightarrow{\text{microorganism}} X + CO_2 + H_2O + ... \qquad (2.6)$$

where S - substrate; O_2 - oxygen; X - cells; N, P - nutrients.

Equation (2.6) represents the overall reaction of substrate removal and biomass growth. It shows the reactants and end products of the reaction but reveals no information on the route and possible intermediates of the reaction. The real reaction pathway consists of complicated chain reactions (Bailey and Ollis, 1986) and has not been fully understood. Equation (2.6) suffices for the purpose of activated sludge modeling since it is both impractical and unnecessary to include intermediate reaction steps into activated sludge models.

Monod kinetics is often used to describe the rates of substrate utilization and biomass growth of Equation (2.6). Caution should be exercised when using Monod type rate expressions. Only the metabolism of soluble substrate follows Monod kinetics; particulate substrate does not.

2.2.3.1.2 Storage

Substrate storage is perhaps the most important concept for the structured activated sludge models developed by the Andrews Group. The concept of substrate storage was first developed and applied by the Andrews Group (Blackwell 1971, Busy 1973, Busby and Andrews 1975, Stenstrom 1976, Clifft 1980, and Clifft and Andrews 1981). The concept was later adopted by the University of Cape Town (UCT) Group (Ekama and Marais 1979 and Dold *et al.* 1980). The concept is that substrate, soluble or particulate, can be stored by microorganisms and converted to stored mass which is part of MLVSS. It should be noted that substrate storage is more an engineering concept than a true microbial mechanism though its conceptualization was based on experimental findings in microbiology, e.g. formation of glycogen, poly-β-hydroxybutyrate (PBH), and phosphorus granules in microorganism cells. The IAWQ Task Group claimed that substrate storage lacks of generality as an activated sludge reaction mechanism; but no evidence was provided to back up the statement.

In the Clifft and Andrews Activated Sludge Model (Clifft and Andrews, 1981) soluble substrate can either be metabolized directly by heterotrophs or stored as stored mass in sludge flocs. In the IAWQ Activated Sludge Model No. 1 soluble substrate is metabolized; there is no other pathway. In the Clifft and Andrews Activated Sludge Model, entrapped particulate substrate is called stored substrate. Stored substrate is then converted into stored mass and the conversion was termed 'hydrolysis' by Clifft and Andrews (1981). It is obvious that 'hydrolysis' denotes a different reaction in Clifft and Andrews (1981) than it does in Henze *et al.* (1987). To avoid confusion, the reaction is simply called conversion of stored substrate to stored mass in this investigation. Stored mass is a concept that do not exist in the IAWQ Activated Sludge Model No. 1.

There is no indication that the controversy over substrate storage will end soon. Reaction mechanisms incorporated in structured activated sludge models were formulated based on the best available knowledge in microbiology but it is not appropriate to consider them as true mechanisms in the microbial sense. It is more appropriate to regard them as engineering concepts based on microbiology and biochemistry. After all, the purpose of activated sludge modeling is to help solve engineering problems. Much research is needed before the controversy over substrate storage can be resolved.

It is interesting that recent research of the UCT Group on nitrification denitrification biological excess phosphorous removal systems indicates that the substrate storage approach, as implemented in Dold *et al.* (1980), is superior to the IAWQ Task Group's approach for the description of particulate substrate removal (Wentzel, *et al.* 1992). This is almost the only report that is in favor of the substrate storage concept in the past five years.

2.2.3.1.3 Entrapment

It is well documented in the literature that particulate substrate, as well as other particulate organic matter, is rapidly removed from liquid when influent enters into the aeration tank. This rapid removal of particulate organic matter has been referred to as entrapment by many practitioners. A number of mechanisms contribute to the phenomenon, which include entrapment in flocs, sedimentation, sorption, etc. Bunch and Griffin (1987) found that colloidal fraction between 0.03 μm and 1.5 μm was removed within 5 minutes (Figure 2.4). This is instantaneous compared with the hydraulic detention time of the aeration tank (6-8 hours). Entrapment has been considered as an instantaneous step in structured activated sludge models and has not been explicitly modeled.

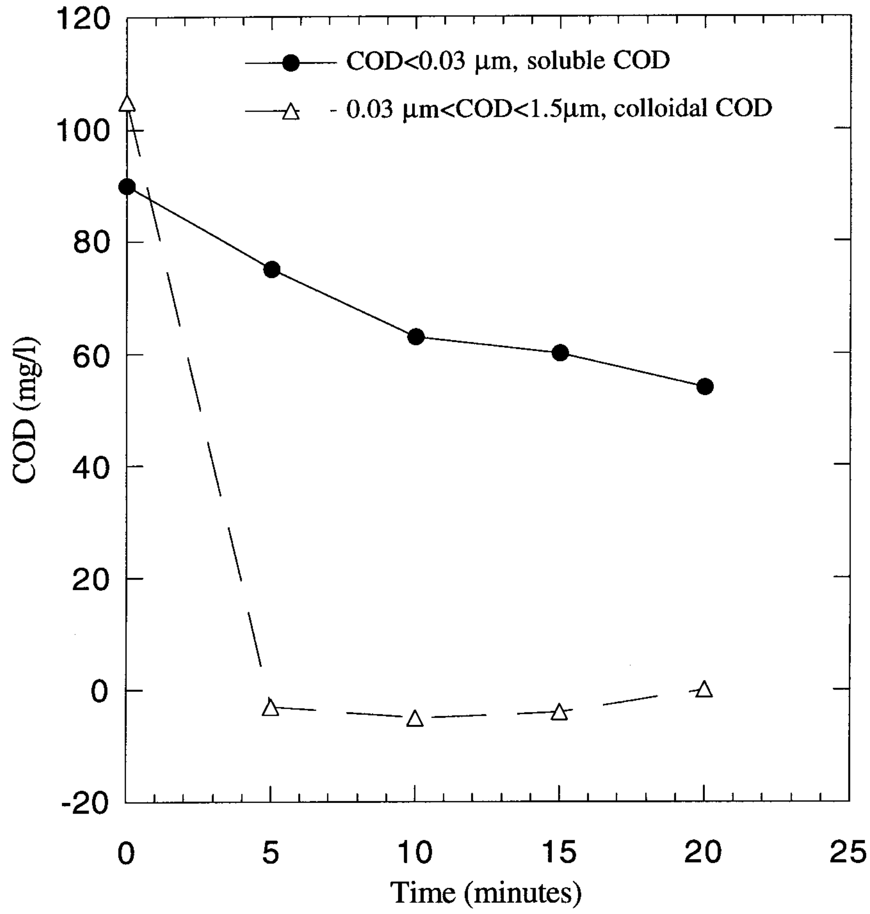


Figure 2.4 Rapid removal of colloidal and soluble substrate (Bunch and Griffin, 1987)

2.2.3.1.4 Hydrolysis

In the IAWQ Activated Sludge Model No. 1 hydrolysis is the reaction that converts slowly biodegradable substrate (particulate) into readily biodegradable substrate (soluble). Hydrolysis may be considered as the break-down of particulate, complex organic matter to soluble, often less complex, organic matters through the extracellular enzymatic activities of microorganisms. Hydrolysis is an important reaction in the activated sludge process. A significant fraction of the organic matter in domestic wastewater is in particulate form and will be partly hydrolyzed during its residence in the aeration tank. In general, microorganisms are not capable of metabolizing particulate substrate directly since in most cases substrate needs to diffuse through cell membranes into cells before it can be utilized to generate energy (anabolism) and synthesize new cells (catabolism). For domestic wastewater, representative complex compounds are carbohydrates (such as starch and cellulose), lipids, proteins, and nucleic acids, which need to be hydrolyzed into simpler compounds, such as glucose, short-chain fatty acids, and amino-acids, before they can be metabolized.

The IAWQ Activated Sludge Model No. 1 assumes that hydrolysis involves no utilization of electron acceptors but requires the presence of them. Furthermore, the rate of hydrolysis is considered to be lower under anoxic conditions (nitrate as electron acceptor) than under aerobic conditions (oxygen as electron acceptor) and apparently completely stopped under anaerobic conditions (neither oxygen nor nitrate are present) (Henze *et al.* 1987). Henze and Mladenovski (1991) found the hydrolysis rate of nitrogenous compounds is significantly affected by the electron donor available. The rate at 20 °C is high under aerobic conditions, medium under anaerobic conditions, and low under anoxic conditions. The medium hydrolysis rate under anaerobic conditions apparently conflicts with the zero rate extrapolation made by Henze *et al.* (1987). The finding, however, does not affect the IAWQ Activated Sludge Model No. 1 since it does not involve anaerobic conditions.

2.2.3.2 Biomass

2.2.3.2.1 Active Biomass Formation

The synthesis of active biomass (new cells) results from metabolism (utilization) of substrate (Equation 2.6). Since only soluble substrate can be readily metabolized, the formation of active mass is directly coupled to the utilization of soluble substrate. In the Clifft and Andrews Activated Sludge Model stored mass can also be metabolized as well as extracellular soluble substrate. Therefore active biomass is produced from the metabolism of both soluble substrate and stored mass.

2.2.3.2.2 Biomass Decay

It is well established that the observed yield from the growth of heterotrophic biomass decreases as the SRT (MCRT) of a reactor is increased. This phenomenon is thought to be due to many mechanisms, including predation, death, lysis, and endogenous metabolisms. Although it can be modeled in many ways, the most common technique under aerobic conditions is to incorporate all of the mechanisms into a single rate expression which is first order with respect the concentration of active biomass and to let each unit of biomass COD lost result in the utilization of an equivalent amount of oxygen (Grady and Lim, 1980). This approach is often referred to as endogenous respiration. The endogenous respiration approach was then modified to include the generation of inert organic matter by biomass decay (McKinney, 1963; Busby and Andrews, 1975). Under this approach, a fraction of the decayed mass is converted to inert mass while the rest of it is compeltely oxidized and results in the utilization of an equivalent amount of oxygen (Table 2.4 though Table 2.8).

Although the endogenous respiration approach has worked well for the modeling of aerobic systems performing carbon oxidation and nitrification many questions arise when the terminal electron acceptor is not oxygen, e.g. nitrate for denitrification. If endogenous respiration is still to be used to describe biomass decay, at least three rate expressions needs to be written for heterotrophs: decay under aerobic for heterotrophs (consumes oxygen), decay under anoxic conditions for heterotrophs capable of denitrifying (denitrifiers, consumes nitrate), and decay under anoxic conditions for heterotrophs incapable of denitrifying. A large number of switching functions are also needed to turn on and off a decay mechanism depending the type of electron acceptor (Henze, *et al.* 1987). It is obvious that such an approach is not attractive and not practically applicable.

An alternative approach is death-regeneration, which was first developed by Dold *et al.* (1980) and later adopted by Henze *et al.* (1987). Under the death-regeneration approach, decayed biomass is transformed to inert organic matter and slow biodegradable substrate. No loss of COD is involved in such a split and no electron acceptor is utilized. The rate of decay is independent of the type of electron acceptors and their concentration. The advantage of the death-regeneration approach is most obvious for single sludge carbon oxidation nitrification and denitrification activated sludge systems. For strictly aerobic systems the endogenous respiration approach suffices.

It should be noted that the death-regeneration approach is still valid under aerobic conditions. The decay coefficient, however, is different in both concept and magnitude from that used in endogenous respiration. As it will be shown later (Chapter 4 and Chapter 5) this can cause erroneous results if caution is not exercised.

2.2.3.3 O_2 Uptake and CO_2 Production

Oxygen uptake and carbon dioxide production are the accompanying reactions of substrate utilization/cell growth (Equation 2.6).

Oxygen is an essential nutrient for aerobic microorganisms. As an elemental constituent of water and of organic compounds, oxygen is a universal component of cells and is always provided in large amounts in the major nutrient, water. Many organisms, however, also require molecular oxygen (O_2). These are organisms that are dependent on aerobic respiration for the fulfillment of their energetic needs and for which molecular oxygen functions as a terminal oxidizing agent - electron acceptor (Stanier, *et al.*, 1986). The respiration of a molecule of glucose, for example, consumes 6 molecules of molecular oxygen, produces 6 molecule of carbon dioxide, and generates 38 ATPs (Bailey and Ollis, 1986).

In many cases, the value of OUR is obtained by taking a sample of mixed liquor, saturated with DO, and with a DO probe measuring the decrease in DO with time. The results are typically reported as mg O_2/L.min or mg O_2/L. h. Oxygen uptake rate is most valuable for plant operations when combined with volatile suspended solids (VSS) data. The combination of OUR with concentration of mixed liquor volatile suspended solids (MLVSS) yields a value termed 'specific oxygen uptake rate' (SOUR), or respiration rate. SOURs indicate the amount of oxygen used by microorganisms and are reported as mg O_2/gVSS.h (Metcalf and Eddy, Inc. 1991; Stenstrom, 1976).

The component parts of oxygen utilization by the cell include cell maintenance, respiratory oxidation for further growth (more biosynthesis), and oxidation of substrate into related metabolic end products. Oxygen utilization for growth is typically coupled directly to the amount of carbon-source substrate consumed (Bailey and Ollis, 1986).

The rate of oxygen uptake, OUR, can be taken as a measure of the biological activity. High OURs indicate high biochemical activity; low OURs indicate low biological activity (Metcalf and Eddy, Inc. 1991). For this reason the measurement of OUR has been widely used in substrate and biomass characterization (Dold *et al.*, 1986; Sollfrank and Gujer, 1991; Henze, 1992), stoichiometric and kinetic coefficient measurement (Kappeler and Gujer, 1992; Larrea, *et al.* 1992), and process control (Huang and Cheng, 1984; Stenstrom and Andrews, 1979). The expression of OUR has been formulated differently in different activated sludge models and has changed with the evolution of activated sludge models (Section 2.3.1.2).

The production of carbon dioxide has attracted little attention in activated sludge modeling except in the high-purity oxygen activated sludge process. The reason is that the amount of carbon dioxide generated by microorganisms is insignificant compared with the amount of air that flows through the liquid column in the air system. Furthermore the aeration tank is not covered and no carbon dioxide accumulation in liquid phase exists. Carbon dioxide production, however, is important for the high-purity oxygen activated sludge process because of the coverage of the aeration tank and the consumption of oxygen along the flow direction. The concentration of carbon dioxide increases from the first stage to the last stage of the aeration tank. The molar fraction of carbon dioxide in vent gas, for example, reaches about 12% in the model high-purity oxygen activated sludge process. Increase of carbon dioxide partial pressure significantly affects the ionic equilibria in liquid phase and drives the pH down.

The most common way of modeling carbon dioxide production is to link its rate of generation the oxygen uptake rate through the respiration quotient factor (RQ), which is often defined as mole of carbon dioxide generated per mole oxygen consumed. The concept of RQ has been most widely used in fermentation processes (Aiba and Furuse, 1990; Wang, *et al.*, 1977; Aiba *et al.*, 1976). For the activated sludge process, the application of RQ has been limited to pure oxygen systems (Mueller and Pannu, 1974).

2.2.3.4 Nutrient Assimilation

Nutrients, such as nitrogen and phosphorus, are essential for the healthy growth of microorganisms. Although nutrient is frequently defined as anything, such as oxygen, that microorganisms need for growth in microbiology, it frequently bears a more specific meaning in wastewater treatment - nitrogen and phosphorus. Domestic wastewaters contains a balanced diet and no nutrient supplement is necessary for treatment. Industrial wastewaters, on the other hand, frequently require nutrient supplementation when being treated. Depending on the nature of a industrial wastewater, nitrogen or phosphorus or both of them need to be supplemented. For example phosphorus supplement is necessary for the treatment of petroleum refinery wastewater (Chapter 4) and both nitrogen and phosphorus need to be supplemented for the treatment of pulp and paper wastewaters.

Modeling of the transformation and fate of nutrient components is limited to carbon oxidation and nitrification related reactions in this study. Reaction mechanisms are more complicated in nutrient removal systems (Wentzel *et al.* 1992) but they are not the subject of this investigation.

2.2.3.3.1 Nitrogen

Nitrogen is usually more abundant than phosphorus in sewage. In many cases only the transformation of nitrogenous matters in treatment systems is investigated and phosphorus species are ignored primarily because phosphorus species (such as ortho-phosphate) have lower concentrations and less adverse effects on receiving water bodies (ammonia exerts significant oxygen demand and stimulate eutrophication while phosphate only contributes to eutrophication). In this investigation the assimilation of nitrogen as a nutrient is investigated in both the high-purity oxygen activated sludge process (carbon oxidation only) and the single-sludge carbon oxidation nitrification system treating combined petroleum refinery wastewater.

Nitrogen in wastewater is characterized by the following parameters - inorganic nitrogen which includes ammonia, nitrite, and nitrate, and total Kjeldahl nitrogen (TKN) which includes ammonia nitrogen and organic nitrogen. Inorganic nitrogen is in soluble form but organic nitrogen could be in either soluble or particulate form. Only ammonia nitrogen can incorporated into new cells as nutrient; organic nitrogen needs to be ammonified before being assimilated.

When modeling the nitrogen-related processes in the carbon oxidation activated sludge process , one has to delineate the nitrogen species and the reactions in which they participate. Since nitrification does not occur in carbon-oxidation systems, nitrite and nitrate can be neglected. Ammonia is utilized as nutrient in the aerobic growth of heterotrophs and incorporated into new cells. Less clear is the transformation of the organic nitrogen species. First of all, organic nitrogen can be either soluble or particulate and their reaction mechanisms are different. Particulate organic nitrogen, which is associated with particulate organic matter, is believed to be entrapped into sludge flocs and subsequently hydrolyzed into soluble organic nitrogen, which is associated with soluble organic substrate. Soluble organic nitrogen, originating from influent or hydrolysis, is converted to ammonia through ammonification. Theoretically there could be inert organic nitrogen too - nitrogen in either soluble or particulate form but does not participate any reaction. If this were true, it would be conceivable that particulate inert organic nitrogen would contribute to the nitrogen content of MLSS and soluble inert organic nitrogen would become part of the effluent TKN. The importance of including such components into a activated sludge model, however, is doubtful. Firstly it is a reasonable assumption that organic nitrogen in domestic wastewater is biodegradable since its constituents are proteins-peptides-amino acids and nucleic acids (RNA and DNA). Secondly, its inclusion will certainly make a already complex activated sludge model even more complex. Thirdly, there is little nitrogen characterization information to support such division. Finally transformation of nitrogen species in the activated sludge process performing carbon oxidation is less important compared with carbonaceous metabolism. In short, if organic nitrogen is to be considered in an activated sludge model, it is reasonable to assume that it is biodegradable.

The transformation of organic nitrogen is still considerably complex even when inert organic nitrogen is excluded. It involves entrapment and hydrolysis of particulate organic nitrogen and ammonification of soluble organic nitrogen. Further simplification is possible and has been done in several investigations. Clifft and Andrews (1986) and Stenstrom, *et al.* (1989) assume that ammonia is the only important nitrogen component which is consumed as a nutrient by heterotrophs and regenerated into ammonia by biomass decay. This, of course, is a much simplified picture of nitrogen transformation for carbon oxidation activated sludge. It will be shown in Chapter 4 that such simplifications tend to under-predict effluent ammonia concentration, possibly because organic nitrogen in influent is not taken into account.

2.2.3.3.2 Phosphorus

Phosphorus is another important nutrient for activated sludge. Phosphorus deficiency may result in poor settling characteristics and a shift in the population to filamentous organisms. Classes of phosphorus-containing compounds of importance in aquatic systems include orthophosphate, polyphosphate, metaphosphate and organic phosphate (phospholipids, sugar phosphates, nucleotides, phosphoamides, etc.) (Snoeyink and Jenkins, 1980). Only orthophosphate can be readily utilized for cell synthesis. Polyphosphate, metaphosphate, and organic phosphate need to be transformed into orthophosphate before microorganisms can utilize them. Orthophosphate is included into the petroleum refinery model and its inclusion allows the prediction of phosphate supplement (Chapter 3).

2.2.3.3.3 C:N:P Ratio

There exists an optimum C:N:P ratio for activated sludge. The ratio differs from system to system, but C:N:P = 100:5:1 is a good estimate in general. Bates and Torabian (1981) investigated the effects of the COD:P ratio on laboratory activated sludge systems and concluded that the optimum COD:P ratio was 100:1, which was in good agreement with the traditional formula of C:N:P = 100:5:1.

2.3 Activated Sludge Models

Just as the activated sludge process has different modifications, e.g. conventional, extended aeration, oxygen, etc., activated sludge models takes a wide variety of forms. The following types of activated sludge models have been reported in the literature: time series (Novotny, *et al.*, 1991), statistical, stochastic (Debelak and Sims, 1981; Casares and Rodriguez, 1989), deterministic and mechanistic (Henze, *et al.* 1987), etc.

In this investigation only deterministic and mechanistic models are considered. Deterministic and mechanistic models are most useful to the researcher seeking to understand the events occurring in a system. Deterministic models incorporate direct links between inputs and outputs through rate equations that seek to mimic reaction mechanisms. Although statistical and other empirical models are able to fit real process responses well they are highly process specific and thus are not easily transportable to new situations.

2.3.1 Carbon Oxidation

Carbon oxidation, or carbonaceous BOD removal, is the process in which heterotrophs metabolize organic carbon, synthesize new cells, generate carbon dioxide, and release energy (ATPs), which is the most fundamental and important reaction in any activated sludge process. In addition to carbon oxidation, nitrification is another important process for this investigation. The high-purity oxygen activated sludge process performs carbon oxidation only. The petroleum refinery activated sludge process is a single-sludge carbon oxidation-nitrification process.

2.3.1.1 Conventional Models

The first group of activated sludge models is referred to as the conventional activated sludge model. By conventional, we mean that both substrate and biomass are considered to be homogeneous substances. Substrate is usually measured as BOD (more specifically, BOD5), and biomass is measured as volatile suspended solids (VSS). Many people contributed to the development, evolution, and maturity of the conventional activated sludge model. It is beyond our effort to credit each and every of them here. Monod, however, deserves special credit for first studying the growth of microorganisms in pure culture (Monod, 1942). The following kinetic expression, which was empirically derived by Monod to describe the substrate-limited growth of microorganisms, later became the foundation of activated sludge modeling.

$$\mu = \frac{\mu_m S}{K_S + S} \tag{2.7}$$

where μ - specific growth rate of biomass [T^{-1}] which is defined as the growth rate r_g divided by biomass concentration X (Equation 2.8); S - substrate concentration (M(COD)L^{-3}); μ_m - maximum specific growth rate [T^{-1}]; K_S - saturation coefficient [M(COD)L^{-3}].

The growth rate of microorganisms, r_g, is

$$r_g = \mu X = \frac{\mu_m S}{K_S + S} X \tag{2.8}$$

It should be noted that if $S >> K_s$, then $\mu = \frac{\mu_m S}{K_S + S} \approx \mu_m$. That is, the growth rate can be approximated as zero-order. If $S << K_s$, then $\mu = \frac{\mu_m S}{K_S + S} \approx \frac{\mu_m}{K_S} S$. That is, the growth rate can be approximated as 1st-order (Figure 2.5).

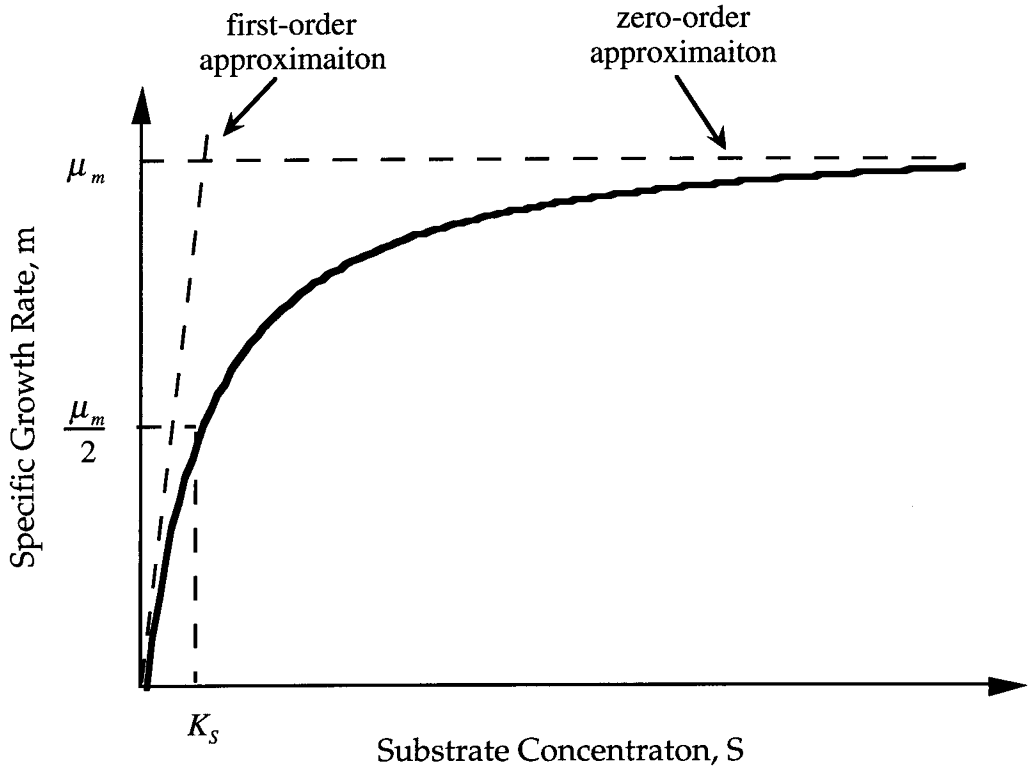


Figure 2.5 Substrate limited growth of a pure culture (Monod kinetics)

Equation (2.4) is identical in form to the kinetic rate expression developed by Michaelis and Menton in 1913 in their study of enzyme kinetics. The overall rate of biological reaction within a reactor is dependent on the catalytic activity of the enzymes in the prominent reaction. If it is assumed that enzyme-catalyzed reactions involve the reversible combination of an enzyme (E) and substrate (S) in the form of a complex (ES) with the irreversible decomposition of the complex to a product (P) and the free enzyme (E), the overall reaction can be written as

$$E + S \xleftrightarrow{k_1, k_{-1}} ES \xrightarrow{k_2} E + P \tag{2.9}$$

where k_1 and k_{-1} are the forward and backward reaction constants of the first reaction, respectively; k_2 represent the rate constant of the second reaction. The rate equation of [ES] is

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] \tag{2.10}$$

Assume that there is no accumulation of ES (pseudo steady state), thus

$$\frac{d[ES]}{dt} = 0$$

$$[ES] = \frac{k_1}{k_{-1}+k_2}[E][S] \overset{[E]_t=[E]+[ES]}{=} \frac{k_1}{k_{-1}+k_2}([E]_t - [ES])[S]$$

$$[ES] = \frac{1}{\frac{k_{-1}+k_2}{k_1}+[S]}[E]_t[S]$$

$$r_P = k_2[ES] = k_2\frac{1}{\frac{k_{-1}+k_2}{k_1}+[S]}[E]_t[S] \underset{k_m=\frac{k_{-1}+k_2}{k_1}}{\overset{V_{\max}=k_2[E]_t}{=}} \frac{V_{\max}[S]}{K_m+[S]} \tag{2.11}$$

The substrate utilization rate and biomass growth rate are related by Equation (2.12):

$$r_{su} = \frac{1}{Y}r_g = \frac{1}{Y}\frac{\mu_m S}{K_S+S}X \tag{2.12}$$

where Y = heterotrophic yield, $\frac{\text{Mass of Cells [M(VSS)]}}{\text{Mass of Substrate [M(COD)]}}$.

Growth, however, is only one facet of the biological process; decay is another important biological reaction in addition to substrate limited growth. Experimental evidence showed that the net biomass production is lower than that predicted by Monod kinetics which presumably assumes that the only biological reaction in the activated sludge process is the substrate limited growth of microorganisms. This phenomenon suggests that there exists other biological reactions that result in loss of biomass. Many different mechanisms have been found to be responsible for the decay of sludge, such as endogenous respiration, predation, lysis, etc. For the purpose of simplicity in engineering analysis, a general term decay is used to describe this phenomenon. A first order kinetic rate equation was found adequate to correctly describe biomass decay:

$$r_d = k_d X \tag{2.13}$$

where r_d - rate of biomass decay; k_d- decay coefficient.

Therefore, the net growth rate $r_{g'}$ is

$$r_{g'} = r_g - r_d = \frac{\mu_m S}{K_S + S} X - k_d X \tag{2.14}$$

Two processes consumes oxygen - aerobic growth of heterotrophs and endogenous respiration. The oxygen uptake rate is

$$OUR = \frac{1-Y}{Y} \mu_m \frac{S}{K_S + S} X - k_d X \tag{2.15}$$

The stoichiometric coefficient $\frac{1-Y}{Y}$ is derived from COD continuity. If the unit of biomass is M(COD)L^{-3}, then for the following reaction

(Y) Substrate + (x) O_2 + ... = (1) Biomass + CO_2 + ... (2.16)

the COD (or electron) conservation is

1 [M(COD)L^{-3}] (substrate) + x [M(-COD)L^{-3}] (Oxygen) = Y [M(COD)L^{-3}] (cell)

thus x = 1-Y.

Also note that, according to reaction law

$$\frac{-r_{su}}{Y} = \frac{-r_{O_2,g}}{1-Y} = \frac{r_g}{1} \tag{2.17}$$

where $r_{O_2,g}$ = oxygen consumption rate of growth, [M(-COD)L^{-3}T^{-1}]

Thus

$$r_{O_2,g} = -\frac{1-Y}{Y} r_g = -\frac{1-Y}{Y} \frac{\mu_m S}{K_S + S} \tag{2.18}$$

For sludge decay (endogenous respiration), if the unit of active mass is COD, the reaction is

(1) Active mass + (1) O_2 = (1) CO_2 + ... (2.19)

If the unit of active mass is [M(VSS)L^{-3}], a conversion factor of 1.42 COD/VSS should be applied.

Again according to reaction law

$$\frac{-r_d}{1} = \frac{-r_{O_2,d}}{1} \tag{2.20}$$

where $r_{O_2,d}$- oxygen consumption rate of decay, [M(-COD)$L^{-3}T^{-1}$]

Therefore $-r_d = -r_{O_2,d} = k_d X$ and

$$OUR = (-r_{O_2,g}) + (-r_{O_2,d}) = \frac{1-Y}{Y} \frac{\mu_m S}{K_S + S} X + k_d X \tag{2.21}$$

The flow diagram of the conventional activated sludge model is shown in Figure 2.6; the model is listed in Table 2.1 in matrix format.

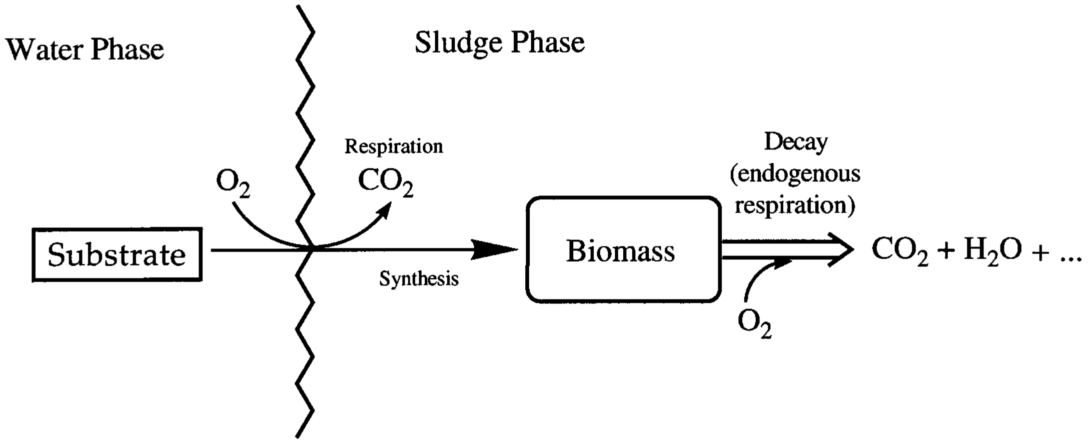


Figure 2.6 Flow diagram of the conventional activated sludge model

Table 2.1 Conventional/Unstructured Model (matrix format)

Component → i j ↓ Process	**1** X	**2** S	**3** S_{O_2}	Process Rate, ρ_j [M(COD)L^{-3}T^{-1}]
1 Growth	1	$-\frac{1}{Y}$	$-\frac{1-Y}{Y}$	$\mu_m\left(\frac{S}{K_S+S}\right)X$
2 Decay	- 1		- 1	k_dX
Observed Conversion Rate [M(COD) L^{-3} T^{-1}]	$r_i = \sum_j v_{ij}\rho_j$			
Stoichiometric Coefficient heterotrophic yield: Y	Biomass Concentrtion M[COD]L^{-3}	Substrate M[COD]L^{-3}	Dissolved Oxygen M[-COD]L^{-3}	*Kinetic Coefficients* maximum specific growth rate μ_m; half-velocity coefficient K_S sludge decay coefficient k_d

The advantage of representing the activated sludge model in matrix format can be vividly demonstrated by Table 2.1. All components are listed in the middle of the first row and the meanings of the component symbols are explained in the middle of the bottom row. The biological processes (mechanisms) are listed in the first column. The last column displays the kinetic rate expressions of all processes. The stoichiometric coefficient corresponding to a component and a process is shown in the cell formed by the column of the component and the row of the process. Stoichiometric and kinetic coefficients are explained in bottom right and left corners.

Additional advantage can be derived from expressing biomass in COD units. The microbial metabolism is a bacteria-mediated oxidation-reduction reaction in which electrons are transferred. Furthermore, an electron balance exits for respiration and growth/synthesis since electrons are neither destroyed nor generated. Oxygen is the most common electron acceptor in wastewater treatment. Thus it is natural to express substrate and biomass in terms of oxygen equivalent (OE) units, such as COD. The continuity of the model can be checked:

Continuity:

$$\upsilon_{1j} + \upsilon_{2j} + (-1)\upsilon_{3j} = 0$$

$$\upsilon_{1j} + \upsilon_{2j} + (-1)\upsilon_{3j} = 0$$

That is,

$$1 + (-\frac{1}{Y}) + (-1)(-\frac{1-Y}{Y}) = 0$$

$$(-1) + (-1)(-1) = 0$$

Note that the unit of dissolved oxygen is negative COD so (-1) is multiplied to the stoichiometric coefficients of S_{O_2}.

The observed conversion rate for the three components in Table 2.1 are:

$$r_1 = (1)\left(\frac{\mu_m S}{K_S + S} X\right) + (-1)(k_d X) = \frac{\mu_m S}{K_S + S} X - k_d X \tag{2.22}$$

$$r_2 = (-\frac{1}{Y})\left(\frac{\mu_m S}{K_S + S} X\right) = -\frac{1}{Y}\frac{\mu_m S}{K_S + S} X \tag{2.23}$$

$$r_3 = \left(-\frac{1-Y}{Y}\right)\left(\frac{\mu_m S}{K_S + S} X\right) + (-1)(k_d X) = -\frac{1-Y}{Y}\frac{\mu_m S}{K_S + S} X - k_d X \tag{2.24}$$

Note that (2.22), (2.23), and (2.24) are the same as (2.14), 2.12), and (2.15) respectively.

McCarty (1975) presented a method for developing a stoichiometric equation for bacteria-mediated reactions. That method was based on concepts of electron equivalent and electron balance which uses essentially the same approach as the one used here.

2.3.1.2 Structured Models

Despite the tremendous success of the conventional activated sludge model, its limitations were gradually revealed. Jacquart et al. (1972) and Marais and Ekama (1976) found that oxygen uptake rate of domestic wastewater had a lag and the conventional activated sludge model was unable to predict the lag. It was also found that the oxygen utilization in real activated sludge systems is much more dampened than that predicted by the conventional activated sludge model. Microbiological analysis of sludge flocs shows that active biomass is only a fraction of MLVSS. The fraction changes with sludge age and is 20-40% of MLVSS for typical sludge ages (3-12) days. There are other fractions in activated sludge flocs that are organic but not viable. In the conventional activated sludge model, X is ambiguously referred to as biomass; but it in fact stands for active biomass in the conventional activated sludge model since it is directly related to substrate utilization and heterotrophic growth. Many researchers found that Monod kinetics only applies to soluble substrate which can penetrate cell membrane and be readily utilized by microorganisms. Soluble substrate, however, is only a fraction of the total substrate. Particulate substrate constitutes up to 80% of the total in certain municipal wastewater (Takahashi, *et al.*, 1969). It is thus not rational to assume that the utilization of particulate substrate follows the Monod kinetics. It is more reasonable to postulate that a better prediction would be attained by dividing substrate into two fractions - soluble and particulate.

The limitations of the conventional activated sludge model serves as an impetus for the development of structured activated sludge models. Various attempts were made to develop structured models that provide better predictions than those of conventional activated sludge models.

In the following review of structured activated sludge models, emphasis is given the work of two research groups - John F. Andrews and his students at Clemson University, University of Houston, and Rice University and G. v. R. Marais and his colleagues and students at University of Cape Town, South Africa. The work of these two groups is focused on not only because it bears the most important structured activated sludge models but also because it represents sustained modeling efforts and gradual evolution of models.

2.3.1.2.1 Blackwell (1971)

Blackwell (1971) developed the first structured model of the Andrews Group by incorporating the concept of stored mass into the model (Figure 2.7).

It should be noted that in Blackwell's model substrate in liquid phase can be either directly metabolized to synthesize active mass or stored as stored mass first and then converted to active mass. The trigger for microorganisms to convert substrate to storage products was assumed to be an increase in substrate loading. Blackwell suggests that in the presence of an increasing food supply, the microorganisms take advantage of the situation by storing substrate which would ordinarily pass out of the system. As microorganisms adjust to higher substrate concentrations, it becomes more efficient to channel the substrate directly into synthesis pathways rather than to first synthesize storage products and then active mass. This dual mechanism for substrate removal was necessary in order to fit his experimental data (Blackwell, 1971).

Blackwell's model is reformulated following the principles proposed by two IAWQ task groups (Henze, *et al.*, 1987; Grau, *et al.*, 1982) and presented in matrix format in Table 2.2. It should be noted that biomass decay was not considered in Blackwell's model. Dissolved oxygen was not included as a component either. First-order kinetics was used to describe specific rates of growth on both substrate and stored mass. Y_c equals to one for the units used in Table 2.2. K_l is a switch function which switches on the conversion of stored mass to active mass exogenous substrate disappears. It should be noted that the rate expression of process 2, substrate storage, does not take into account the substrate concentration in liquid phase. ρ_2 was later modified by Busby and Andrews (1975) and Ekama and Marais (1979).

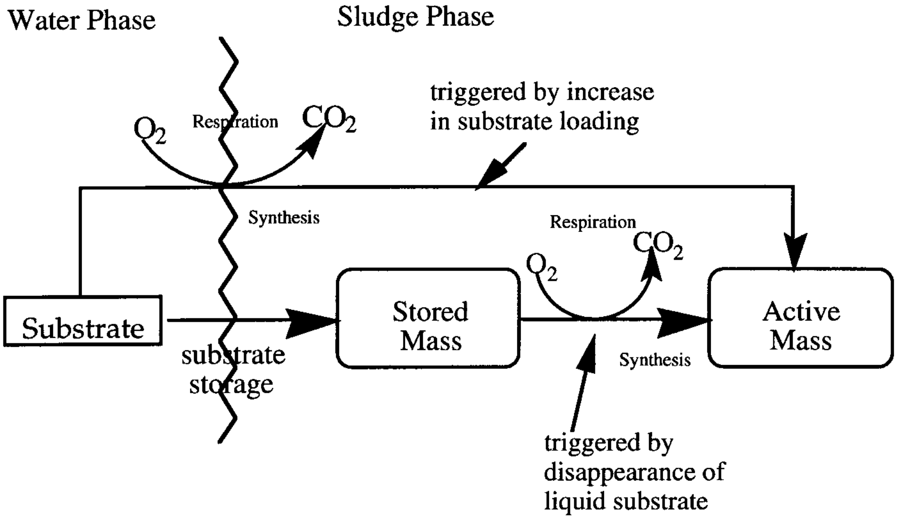


Figure 2.7 Blackwell's Structured Model

The dual mechanism of substrate removal establishes a built-in mechanism for competitive utilization of substrate. Switching between mechanisms depending on substrate loading seems unnecessary.

Table 2.2 Blackwell's Structured Activated Sludge Model in matrix form

Components →i j ↓Process	**1** S	**2** X_S	**3** X_a	Process Rate, ρ_j [ML^{-3}T^{-1}]
1 Direct Utilization of Substrate	$-\frac{1}{Y}$		1	$\hat{\mu}SX_a$
2 Substrate Storage	$-\frac{1}{Y_C}$	1		$R_T(\hat{f}_S - f_S)X_T$
3 Stored Mass to Active Mass		$-\frac{1}{Y_S}$	1	$K_1\hat{\mu}_C X_S X_a$
Observed Reaction Rate r_i [M(COD)L^{-3}T^{-1}]	$r_i = \sum_j v_{ij}\rho_j$			
Stoichiometric coefficients: Y, Y$_C$, Y$_S$ - yield coefficients of direct substrate utilization, substrate storage, and conversion of stored mass to active mass *Kinetic coefficients:* $\hat{\mu}$, $\hat{\mu}_C$ - maximum specific rates of growth on substrate and stored mass respectively [T^{-1}]	Substrate [M(COD)L^{-3}T^{-1}]	Stored Mass [M(COD)L^{-3}T^{-1}]	Active Mass [M(COD)L^{-3}T^{-1}]	R_T - proportionality constant [T^{-1}] $\hat{f}_S$ - maximum fraction of stored mass X_T=MLVSS $=X_a+X_S$ $f_S = \frac{X_S}{X_T}$

2.3.1.2.2 Jacquart *et al.* (1972)

Jacquart *et al.* (1972) is among the earliest research that divided the substrate into two fractions: soluble and particulate. In an effort to describe the obvious lag and dampening in oxygen uptake rate (see Figure 2.8), Jacquart *et al.* channeled the substrate into two pools which they called stored mass of soluble origin and stored mass of particulate origin respectively (Figure 2.9). The stored masses are then converted into active mass; the rates of conversion are expressed by Monod-type functions. Jacquart was able to fit the experimental data well by proposing the mechanisms depicted in Figure 2.9 though there was little experimental evidence from microbiology to support their assumptions.

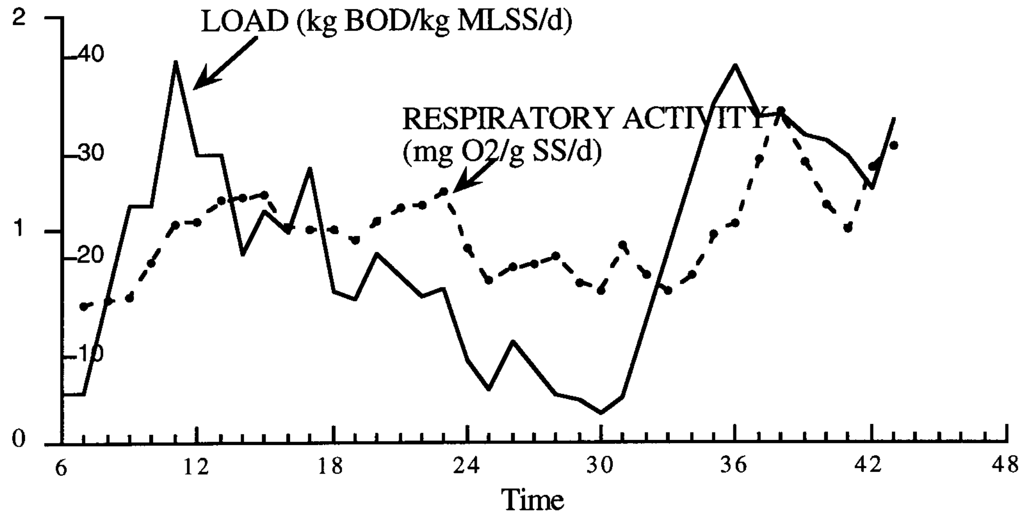


Figure 2.8 Lag and dampening of oxygen uptake (after Jacquart *et al.* 1972)

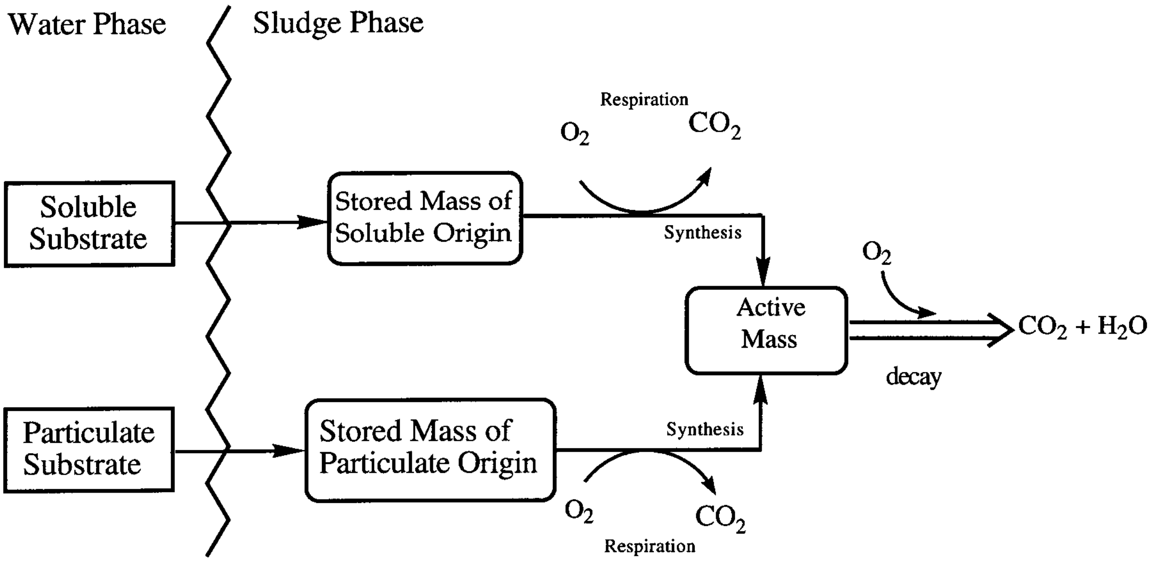


Figure 2.9 Flow Diagram of Jacquart *et al.*'s Structured Model

Jacquart *et al.*'s model is reformulated into matrix format and shown in Table 2.3. It should be noted that storage of particulate substrate is assumed to be instantaneous. As indicated next, this assumption is used in most structured activated sludge models

(Henze, *et al.*, 1987; Dold et al., 1980; Clifft 1980). The transport of particulate substrate from water phase to sludge phase has been found to be very fast both theoretically and experimentally and therefore has been treated as an instantaneous process in activated sludge modeling. The yields of processes 2 and 3, conversions of store mass of soluble and particulate origins to active mass, are assumed to be the same which are denoted as Y.

Table 2.3 Jacquart *et al.*'s structured activated sludge model in matrix form

Components → i j ↓ Process	**1** S_S	**2** $X_{stor,s}$	**3** $X_{stor,p}$	**4** X_{BH}	**5** S_{O_2}	Process Rate, ρ_j $[ML^{-3}T^{-1}]$
1 Soluble Substrate Storage	-1	1				$\hat{\mu}_{S,S_S}\left(\frac{S_S}{K_S+S_S}\right)X_{BH}$
2 Stored Mass (soluble origin) to Active Mass		$-\frac{1}{Y}$		1	$-\frac{1-Y}{Y}$	$p\left(\frac{X_{stor,s}}{K_{SS}+X_{stor,s}}\right)X_{BH}$
3 Stored Mass (particulate origin) to Active Mass			$-\frac{1}{Y}$	1	$-\frac{1-Y}{Y}$	$q\left(\frac{X_{stor,p}}{K_{SP}+X_{stor,p}}\right)X_{BH}$
4 Decay (endogenous respiration)				-1	-1	k_dX_a
Observed Reaction Rate $[ML^{-3}T^{-1}]$	$r_i=\sum_j v_{ij}\rho_j$					
Stoichiometric coefficients: heterotrophic yield Y	Soluble Substrate $[ML^{-3}T^{-1}]$	Stored mass of soluble orgin $[ML^{-3}T^{-1}]$	Stored Mass of Particulate Origin $[ML^{-3}T^{-1}]$	Active Mass $[ML^{-3}T^{-1}]$	Dissolved Oxygen $[M(-COD)L^{-3}T^{-1}]$	p, q - maximum growth rates of heterotrophs from stored mass of soluble and particulate origins respectively

2.3.1.2.3 Busby and Andrews (1975)

Not convinced that direct conversion of substrate to active mass is an important mechanism, Busby and Andrews (1975) assumed that all substrate is stored as stored mass before it is transformed into active mass. Unlike Jacquart *et al.* (1972), Busby and Andrews (1975) treats substrate as an homogenous substance; no distinction was made between soluble and particulate fractions of substrate (Figure 2.10). Sludge decay, however, is handled differently from Jacquart *et al.* (1972). Sludge decay is still modeled as endogenous respiration; but the products of decay are different. Jacquart *et al.* (1972) assumes complete oxidation - one unit of active mass COD imposes one unit of oxygen demand. The end products are carbon dioxide and water. Busby and Andrews (1975) assumed partial oxidation and the end products are carbon dioxide, water, and inert mass. The inclusion of inert mass is largely prompted by experimental findings that sludge decay generates inert mass and a large fraction of VSS is inert mass (McKinney, 1963). Busby's model is reformulated into matrix form and shown in Table 2.4. Note R_{XI}, specific active mass decay rate (T^{-1}), is more often referred to as decay coefficient (k_d).

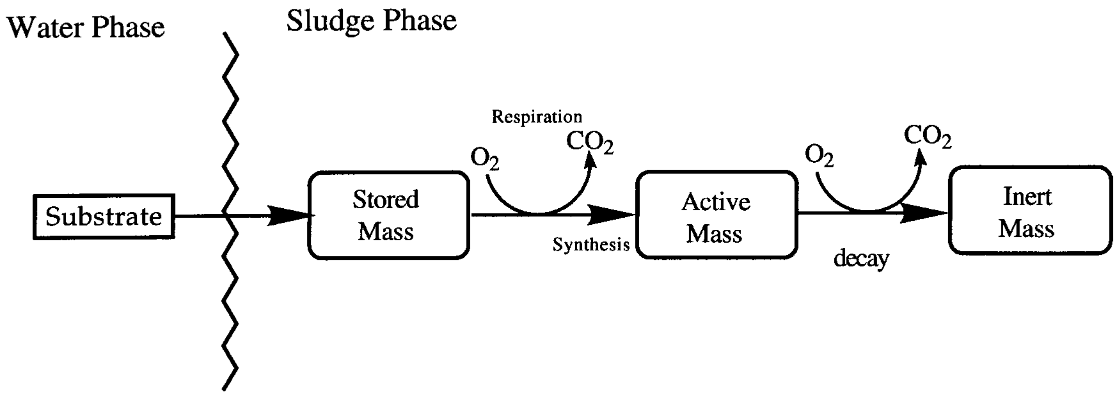


Figure 2.10 Flow diagram of the Busby and Andrews activated sludge model

Table 2.4 Busby's Structured Activated Sludge Model in matrix form

Components → i j ↓ Process	**1** S	**2** X_S	**3** X_a	**4** X_I	**5** S_{O_2}	Process Rate, ρ_j [ML-3T-1]
1 Substrate Storage	-1	1				$R_T X_T \left[\hat{f}_S \left(\frac{S}{K_S + S} \right) - f_S \right]$
2 Stored Mass to Active Mass		$-\frac{1}{Y_1}$	1		$-\frac{1-Y_1}{Y_1}$	$R_{XA} \left(\frac{X_S}{K_{XS} + X_S} \right) X_A$
3 Decay (Endogenous Respiration)			-1	Y_2	$-(1-Y_2)$	$R_{XI} X_A$
Observed Reaction Rate [ML-3T-1]	$r_i = \sum_j v_{ij} \rho_j$					
Stoichiometric coefficients: Y1 - yield coefficient, mass of active mass synthesized/mass of stored mass utilized Y2 - yield coefficient (mass of inert mass produced per unit mass of active mass decayed)	Substrate [ML-3T-1]	Stored Mass [ML-3T-1]	Active Mass [ML-3T-1]	Inert Mass [ML-3T-1]	Dissolved Oxygen [M(-COD)L-3T-1]	*Kinetic Coefficients:* R_T, $\hat{f}_S$, K_S, R_{XA}, K_{XS}, R_{XI} Other: X_T = MLVSS = $X_{stor} + X_a + X_I$ $f_S = \frac{X_S}{X_T}$

2.3.1.2.4 Stenstrom (1976)

While focusing on developing control strategies for activated sludge wastewater treatment plants, Stenstrom (1976) devoted considerable efforts to the modeling of the activated sludge process. Stenstrom (1976) found that Busby's model cannot be used for low sludge ages since the rate of formation of active mass approaches zero as the sludge age approaches washout and he attributed this deficiency to the rate expression of process 2, conversion of stored mass to active mass (see Table 2.4). Instead of using concentration of stored mass X_S in the rate expression, Stenstrom proposed the following modification to overcome the deficiency:

$$\rho_2 = R_{XA}\left(\frac{f_S}{K_{fs}+f_S}\right)X_A$$

where $f_S = \frac{X_S}{X_T}$.

This expression was empirically based. As it will be shown next, Dold *et al.* (1980) derived a similar rate expression by considering process 2 as a surface mediated reaction. Stenstrom's model is listed in Table 2.5.

Table 2.5 Stenstrom's Structured Activated Sludge Model in matrix format

Components → i j ↓ Process	**1** S	**2** X_S	**3** X_A	**4** X_I	**5** S_{O_2}	Process Rate, ρ_j [ML^{-3}T^{-1}]
1 Substrate Storage	-1	1				$R_T\left[\hat{f}_S\left(\frac{S}{K_S+S}\right)-f_S\right]X_T$
2 Stored Mass to Active Mass		$-\frac{1}{Y_1}$	1		$-\frac{1-Y_1}{Y_1}$	$R_{XA}\left(\frac{f_S}{K_{fs}+f_S}\right)X_A$
3 Decay (Endogenous Respiration)			-1	Y_2	$-(1-Y_2)$	$R_{XI}X_A$
Observed Reaction Rate [ML^{-3}T^{-1}]	$r_i = \sum_j \nu_{ij}\rho_j$					
Stoichiometric coefficients: yield coefficients: Y1, Y2	Substrate [ML^{-3}T^{-1}]	Store Mass [ML^{-3}T^{-1}]	Active Mass [ML^{-3}T^{-1}]	Inert Mass [ML^{-3}T^{-1}]	Dissolved Oxygen [M(-COD)L^{-3}T^{-1}]	*Kinetic Coefficients:* R_T, $\hat{f}_S$, K_S, R_{XA}, K_{fs}, R_{XI} Other: XT = MLVSS = $X_{stor}+X_a+X_I$ $f_S = \frac{X_S}{X_T}$

All the structured activated sludge models reviewed so far treat substrate as an homogeneous material except Jacquart *et al.* (1972). Stenstrom (1976) acknowledged that the separation of soluble and particulate substrates is a more fundamental approach but he thought the mathematical complexity introduced by these additional material balances would result in a prohibitively large model.

2.3.1.2.5 Marais and Ekama (1976)

In 1976, Marais and Ekama developed the first activated sludge model of the University of Cape Town (UCT) Group, South Africa. The activated sludge model of Marais and Ekama (1976) was a modification of the conventional activated sludge model of Lawrence and McCarty (1970) except that inert mass was assumed to be generated by sludge decay. Substrate was assumed to be a homogenous substance. Marais and Ekama (1976) also developed an explicit expression for oxygen uptake rate (OUR).

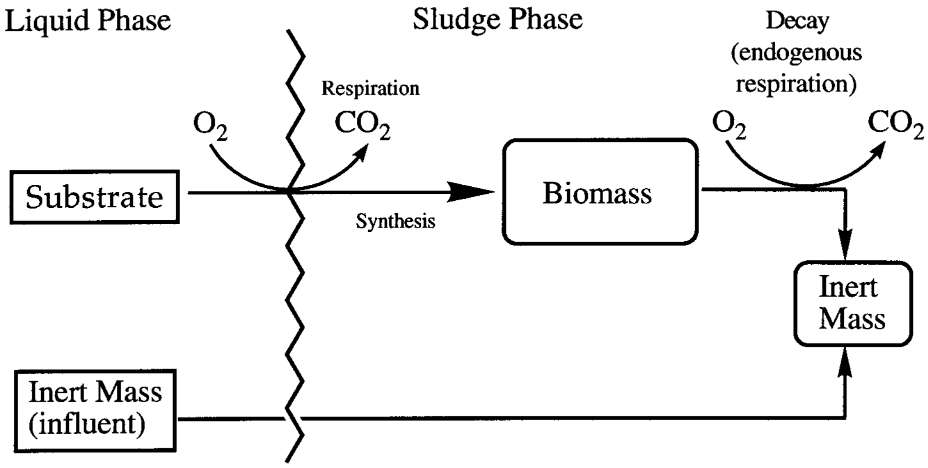


Figure 2.11 Flow diagram of Marais and Ekama (1976)

Marais and Ekama (1976) took into consideration the fact that a considerable fraction of organic matter is inert by dividing the total organic matter into two fractions - substrate and inert mass (particulate). The consideration of inert mass in wastewater and the generation of inert mass from sludge decay are the major features that qualify the model as a structured model. The flow diagram of the activated sludge model of Marais and Ekama (1976) is shown in Figure 2.11. The model is reformulated into matrix format and presented in Table 2.6.

Table 2.6 Activated sludge model of Marais and Ekama (1976)

Component → i j ↓ Process	**1** S	**2** X_e	**3** X_a	**4** S_{O_2}	Process Rate, ρ_j [ML^{-3}T^{-1}]
1 Aerobic Growth of Heterotrophs	-1		Y_h	$-(1-Y_h)$	$K_m\left(\frac{S}{K_S+S}\right)X_a$
2 Decay		f	-1	$-(1-f)$	$b_h X_a$
Observed Conversion Rate [M L^{-3} T^{-1}]	$r_i=\sum_j \nu_{ij}\rho_j$				
Stoichiometric coefficient: Y$_h$ - heterotrophic yield, mass of active mass produced per unit mass of substrate utilized, [M(COD)/M(COD) f - mass of inert organic matter produced per unit mass of active mass decayed, [M(COD)/M(COD)]	Substrate M[COD]L^{-3}	Inert Mass M[COD]L^{-3}	Active Mass M[COD]L^{-3}	Dissolved Oxygen M[-COD]L^{-3}	*Kinetic coefficients:* K$_m$ - maximum specific substrate utilization rate, d^{-1} K$_S$ - half-velocity coefficient, [M(COD)L^{-3}] b$_h$ - decay coefficient, d^{-1}

2.3.1.2.6 Ekama and Marais (1979)

Although the activated sludge model of Marais and Ekama (1976) performed well in predicting process behaviors under constant load and flow conditions, it was found impossible to correlate the predicted and observed oxygen uptake rates of a cyclically loaded completely mixed activated sludge process receiving domestic wastewater as influent. At the moment of feed termination a precipitous change in oxygen uptake rate was observed, thereafter the rate continued for 1.5 to 2 hours at a level of about 90 percent of that measured just before the feed was terminated; then followed by a period of approximately 5 hours during which the oxygen uptake rate gradually decreased until, fairly abruptly, the rate steadied at a value which could be associated with endogenous respiration.

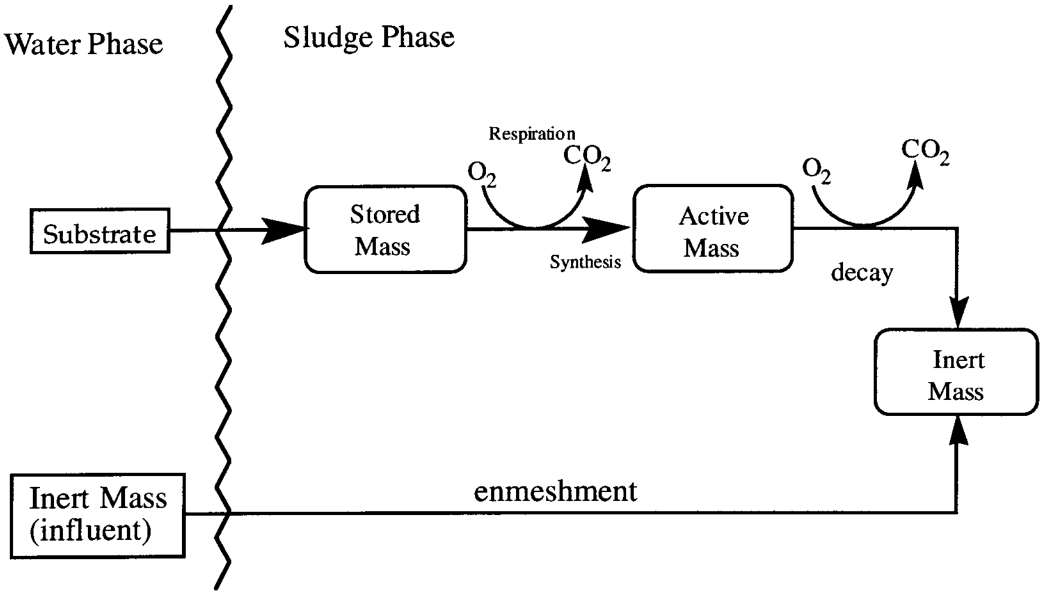


Figure 2.12 Activated Sludge Model Flow Diagram of Ekama and Marais (1979)

Ekama and Marais ascribed the difference between the observed and predicted response to the nature of the influent substrate: In domestic wastewater 60 to 70 percent of the COD is in a fine particulate form. The utilization of particulate substrate necessarily requires to be preceded by adsorption and storage on the organism, followed by extracellular enzymatic breakdown prior to transfer through the cell wall. Hence, they incorporated an adsorption mechanism to store the substrate onto the sludge. The adsorption mechanism they adopted was a modification of that developed by the Andrews Group (Blackwell, 1971, Busby, 1973, Busby and Andrews, 1975), with the modified formulation being:

$$\rho_1 = K_a S_b X_a \left(f_{ma} - \frac{X_S}{X_a} \right) \tag{2.25}$$

It should be noted that the above expression is similar to Blackwell's ρ_1 (Table 2.2) but differs in the following aspects: 1) Blackwell's rate expression did not take substrate concentration in water phase into account; Ekama and Marais did. 2) Blackwell (1971) evaluated the fraction of stored substrate upon MLVSS while Ekama and Marais calculated the fraction upon active mass. The activated sludge model of Ekama and Marais (1979) is similar to that of Busby and Andrews (1975) in the sense that both models took into consideration the substrate concentration in the water phase when

Table 2.7 Activated sludge model of Ekama and Marais (1979)

Components →i j ↓ Process	**1** S_b	**2** X_e	**3** X_S	**4** X_a	**5** S_{O_2}	Process Rate, ρ_j [ML^{-3}T^{-1}]
1 Substrate Storage	-1		1			$K_a S_b X_a \left(f_{ma} - \frac{X_S}{X_a} \right)$
2 Stored Mass to Active Mass			$-\frac{1}{Y_h}$	1	$-\frac{1-Y_h}{Y_h}$	$K_m \left(\frac{X_S}{K_S + X_S} \right) X_a$
3 Decay (Endogenous Respiration)		f		-1	$-(1-f)$	$b_h X_a$
Observed Reaction Rate [ML^{-3}T^{-1}]	$r_i = \sum_j \nu_{ij} \rho_j$					
Stoichiometric coefficients: heterotrophic yield Y	Substrate [ML^{-3}T^{-1}]	Inert Mass [ML^{-3}T^{-1}]	Stored Mass [ML^{-3}T^{-1}]	Active Mass [ML^{-3}T^{-1}]	Dissolved Oxygen [M(-COD)L^{-3}T^{-1}]	X_V = MLVSS

describing transformation of substrate to stored mass. The expressions, however, were different. Busby and Andrews (1975) incorporated a Monod type saturation function into the rate expression (see ρ_1 in Table 2.4). Ekama and Marais, however, found it adequate to formulate the expression by multiplying S to Blackwell's expression (Table 2.7).

The flow diagram of the activated sludge model of Ekama and Marais (1979) is depicted in Figure 2.12. The model is reformulated into matrix format and presented in Table 2.7.

2.3.1.2.7 Clifft and Andrews(1981)

Stimulated by previous experimental findings in microbiology and based on prior activated sludge modeling accomplishments, Clifft and Andrews (1981) proposed a general activated sludge model that is capable of predicting lag and dampening in oxygen utilization. Substrate is divided into two fractions - soluble and particulate. Soluble substrate is either directly metabolized or channeled to the pool of stored mass in sludge phase. Particulate substrate is entrapped into the sludge phase instantaneously upon contact with sludge flocs and forms the pool of stored particulate substrate which is subsequently converted (hydrolyzed) into stored mass. Stored mass is then transformed into active mass. Oxygen is consumed and inert mass is formed in sludge decay (Figure 2.13). The influences of previous models on Clifft's model can be clearly seen if one compares Figure 2.13 with Figure 2.7 through Figure 2.9.

Clifft's model was the last one from the Andrews Group. There have been many applications and minor modification of the model by other researchers; but no substantial change has been made.

Clifft's model is reformulated into matrix format and presented in Table 2.8. The influence of previous models on Clifft's model is clearly reflected if one considers the following facts: 1) In Blackwell's model, substrate can either be stored as stored mass or metabolized directly for synthesis. 2) In Jacquart *et al.*'s model, substrate is divided into soluble and particulate fractions. Clifft's model may be viewed as a natural extension of previous models from this perspective.

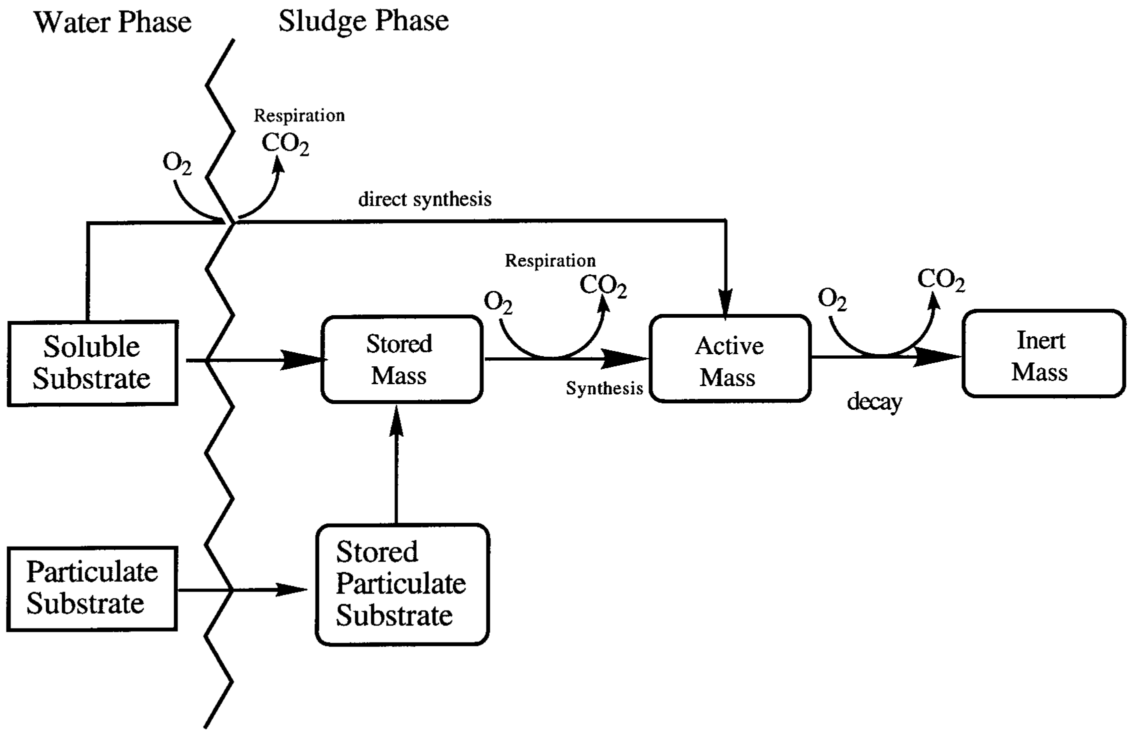


Figure 2.13 Flow diagram of the Clifft and Andrews Activated Sludge Model

Table 2.8 Clifft and Andrews Activated Sludge Model (Matrix Form)

Componet → i j ↓ Process	1 S_D	2 X_P	3 X_I	4 X_S	5 X_A	6 NH	7 S_O	Process Rate, ρ_j [ML^{-3}T^{-1}]
1 Soluble substrate to stored mass	-1			1				$K_T X_A S_D(\hat{f}_S - f_S)$
2 Soluble substrate to active mass	-1				Y_1	$-Y_{NS}$	$-(1-Y_1)$	$R_{SD} X_A S_D$
3 Stored substrate to stored mass		-1		1				$R_H\left(\frac{f_P}{K_{SP}+f_P}\right)X_A$
4 stored mass to active mass				$-\frac{1}{Y_1}$	1	$-Y_{NS}$	$-\frac{1-Y_1}{Y_1}$	$R_{XA} X_A f_S$
5 Decay of active mass			Y_2		-1	Y_{ND}	$-(1-Y_2)$	$K_D X_A$
Reaction Rate, r_i [ML^{-3}T^{-1}]	$r_i = \sum_j \nu_{ij}\rho_j$							
Stoichiometric parameters: Y_1 - yield, mass of active mass produced per unit mass of soluble substrate or stored mass utilized Y_2 - yield, mass of inert mass produced per unit mass of active mass decayed Y_{NS} - yield, mass of ammonia nitrogen utilized/mass of active mass synthesized Y_{ND} - yield, mass of ammonia nitrogen released/mass of active mass decayed	Soluble Substrate [M(COD)L^{-3}]	Particulate Substrate [M(COD)L^{-3}]	Inert Mass [M(COD)L^{-3}]	Stored Mass [M(COD)L^{-3}]	Active Mass [M(COD)L^{-3}]	Ammonia Nitrogen [M(NH$_3$-N)L^{-3}]	Dissolved Oxygen [M(-COD)L^{-3}]	*Kinetic parameters:* K_T - transport rate coefficient R_{SD} - direct growth rate R_H - hydrolysis rate coefficient R_{XA} - storage growth rate K_D - decay rate coefficient $\hat{f}_s$ - max. fraction of stored mass f_s - fraction of stored mass, $f_S = \frac{X_S}{X_S+X_A}$ f_P - fraction of stored particulate substrate, $f_P = \frac{X_P}{X_P+X_A}$

2.3.1.2.8 Dold, Ekama and Marais (1980)

Dold, Ekama, and Marais (1980) developed a structured activated sludge model at about the same time when Clifft's model was developed. The two models have many similarities, such as: 1) both models divide substrate into soluble and particulate; 2) both models used the concept of substrate storage developed by the Andrews Group. But Dold *et al.* (1980) differs the Clifft (1980) in the following aspects: Soluble substrate is metabolized directly; storage of soluble substrate is considered negligible. The handling of sludge decay was different from all previous model; a death-regeneration concept was adopted instead of endogenous respiration. Instead of consuming oxygen, sludge decay generates slowly biodegradable (particulate substrate) which is recycled back (Figure 2.14). Dold *et al.* demonstrated that with proper selection of coefficients the two approaches give identical results in aerobic systems. Additional advantages are derived in single sludge systems since the death-regeneration concept is applicable to aerobic, anoxic, and anaerobic zones.

As presented next, the IAWQ Activated Sludge Model No. 1 does not include the substrate storage as a possible mechanism. Is substrate storage an important mechanism? Is stored mass a real pool of mass within sludge flocs? There are no definitive conclusions yet. Dold *et al.* (1980) channeled particulate substrate in liquid phase to stored mass in sludge phase through substrate storage. This may be inappropriate since there has been much experimental evidence showing that this process is instantaneous; no kinetic expression is required. It is mainly because of this that the task group abandoned the substrate storage part of Dold *et al.*'s model upon which the IAWQ Activated Sludge Model No. 1 was based. Clifft and Andrews' way of handling particulate substrate storage is more rational at least from the theoretical point of view. The particulate substrate is entrapped into sludge phase instantaneously. The entrapped particulate substrate is then converted into stored mass. It is possible that Dold *et al.* combined these two steps into one; this, however, was never mentioned in Dold *et al.* (1980).

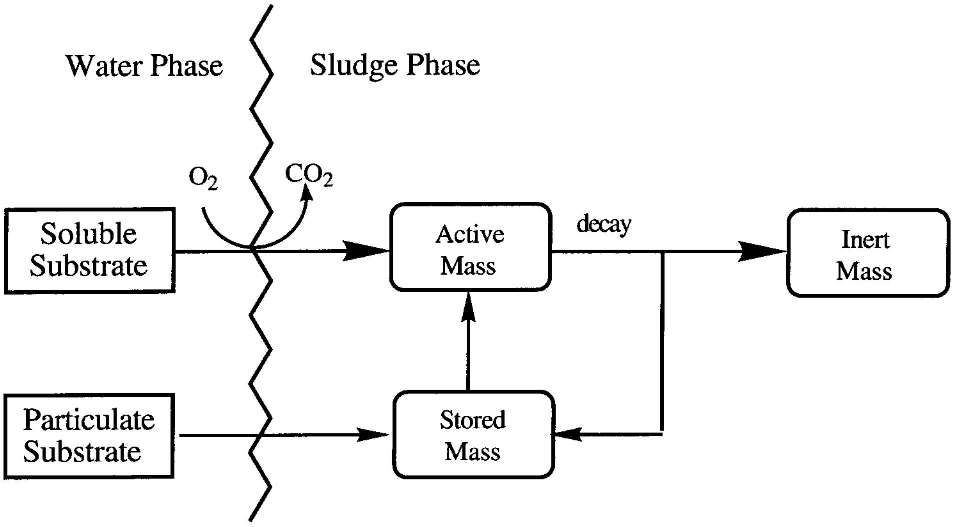


Figure 2.14 Activated Sludge Model Flow Diagram of Dold, Ekama, and Marais (1980)

The activated sludge model of Dold et al. (1990) has never been applied to the high-purity oxygen activated sludge process. It, nevertheless, has been widely used for modeling air activated sludge processes. It should be noted the Dold et al.'s model also includes the modeling of nitrification, which is not presented in Table 2.9.

Table 2.9 The Structured AS Model of Dold et al. (1980) (Matrix Form)

Component → i j ↓ Process	**1** $S_I(S_u)$	**2** $S_S(S_{bs})$	**3** $X_I(S_p)$	**4** $X_S(X_{bp})$	**5** $X_{stor}(X_S)$	**6** $X_{BH}(X_a)$	**7** S_O	Process Rate, ρ_j [$ML^{-3}T^{-1}$]
1 Aerobic growth of heterotrophs from soluble substrate		$-\frac{1}{Y_H}$				1	$-\frac{1-Y_H}{Y_H}$	$\hat{\mu}_H\left(\frac{S_S}{K_{SS}+S_S}\right)X_a$
2 Conversion of entrapped particulate substrate to stored mass				-1	1			$k_a X_S X_a\left(f_{S_m} - \frac{X_{stor}}{X_a}\right)$
3 Aerobic growth of heterotrophs from stored mass					$-\frac{1}{Y_H}$	1	$-\frac{1-Y_H}{Y_H}$	$K'_{mp}\left(\frac{X_{stor}}{K'_{sp}+X_{stor}}\right)X_a$
4 'Decay' of heterotrophs				f_p		-1	$-(1-f_p)$	$k_d X_a$
Reaction Rate, r_i [$ML^{-3}T^{-1}$]	$r_i = \sum_j v_{ij}\rho_j$							
Stoichimetric parameters: Heterotrophic yield: Y_H; Fraction of biomass yielding slowly biodegradable substrate: f_P	Soluble inert oganic matter [M(COD)L-3	Readily biodegradable substrate [M(COD)L-3	Particulate inert organic matter M(COD)L-3	Slowly biodegradable substrate M(COD)L-3	Stored mass M(COD)L-3	Active heterotrophic biomass M(COD)L-3	Dissolved Oxygen (gegative COD) M(COD)L-3	*Kinetic parameters:* Heterotrophic growth and decay: μ_H, K_{SS}, k_T, f_{sm}, $k_{em'}$, $k_{sp'}$, and k_d

2.3.1.2.9 Activated Sludge Model No. 1

Realizing the benefits to be derived from mathematical modeling, while recognizing the reluctance of many engineers to use it, the International Association on Water Quality (IAWQ; formerly IAWPRC) formed a task group in 1983 to promote the development of, and facilitate the application of, practical models to the design and operation of biological wastewater treatment systems. The goal was first to review existing models; and second to reach a consensus concerning the simplest one having the capability of realistic predictions of the performance of single sludge systems carrying out carbon oxidation, nitrification, and denitrification. The final report of the task group was published in 1987 and the activated sludge model developed by the task group was called Activated Sludge Model No. 1 (Henze, *et al.* 1987; Grady *et al.* 1986; Grady, 1989; Gujer and Henze, 1991). The formulation of Activated Sludge Model No. 1 was influenced by the work of many researchers, especially that of Dold *et al.* (1980) and Dold and Marais (1986). The flow diagram of Activated Sludge Model No. 1 is depicted in Figure 2.15 and the model is shown in Table 2.10 in matrix format.

Of the few changes the task group made to the carbon oxidation model of Dold *et al.* (1980), the most prominent was the elimination of the substrate storage concept which was originally developed and publicized by the Andrews Group and adopted by Ekama and Marais (1979) and Dold *et al.* (1980). While it is still controversial if the elimination was justified, the author thinks that a comparison of the IAWQ Activated Sludge Model No. 1 and the Clifft and Andrews Activated Sludge Model will provide interesting insights into the issue. The comparison is presented in Chapter 5.

It is should be noted that the activated sludge models reviewed in this chapter so far has been limited to carbon oxidation only. The IAWQ Activated Sludge Model No. 1, however, covers nitrification and denitrification as well as carbon oxidation. It is obvious that not all activated sludge systems are single sludge systems that carry out carbon oxidation, nitrification, and denitrification. For example, the high-purity oxygen activated sludge process investigated in this dissertation does not have nitrification and denitrification. Thus the IAWQ Activated Sludge Model No. 1 needs to be modified to match the reactions of the high-purity oxygen activated sludge process. Another example is the petroleum refinery activated sludge process in the model refinery which performs sulfur oxidation in addition to carbon oxidation and nitrification. Sulfur oxidation, of course, is not included in Activated Sludge Model No. 1. Therefore it is more important to understand the concepts and principles embedded into the development of Activated Sludge Model No. 1 and use them to modify the model and develop new models when necessary.

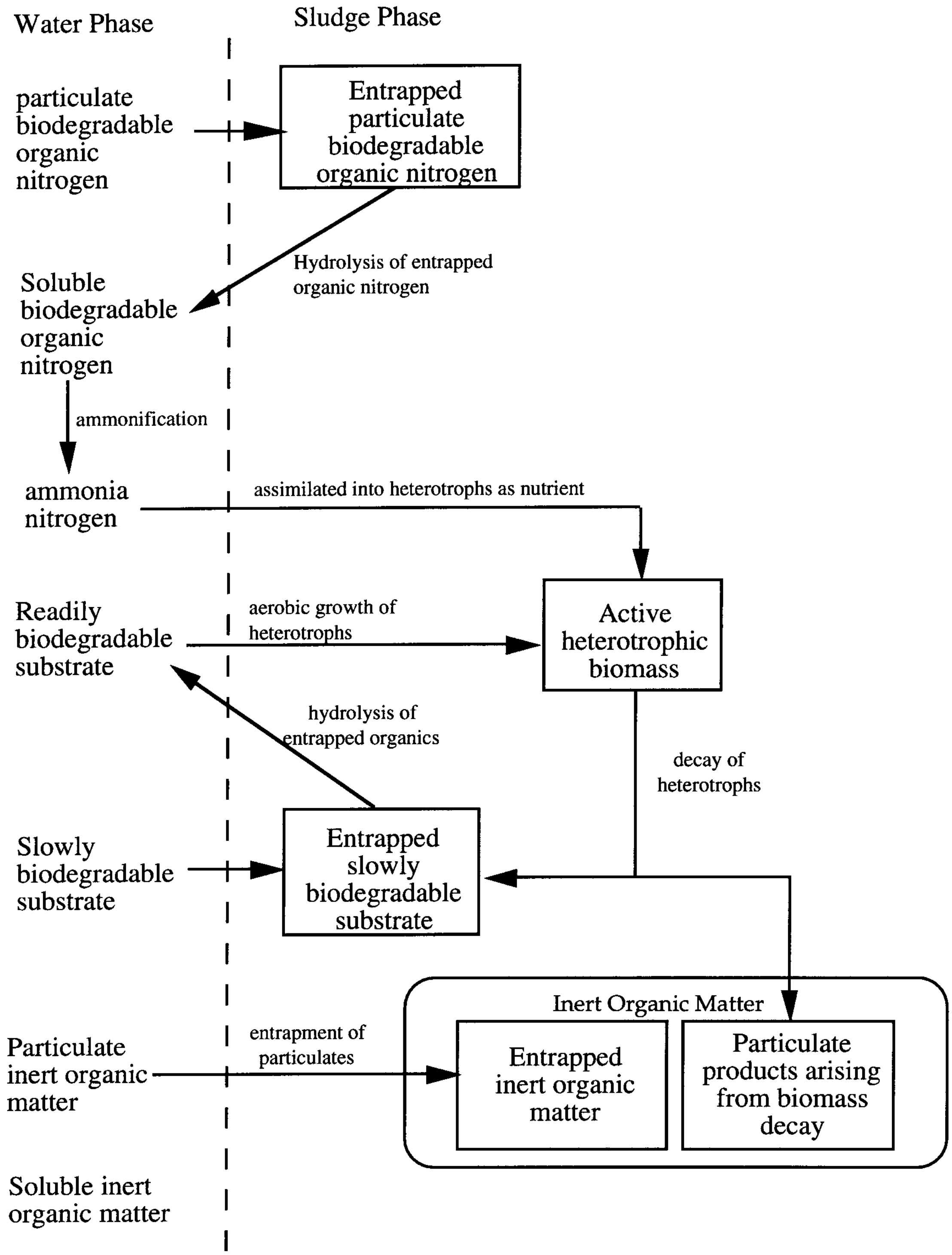


Figure 2.15 Flow Diagram of the IAWQ Activated Sludge Model No. 1

Table 2.10 The IAWQ Activated Sludge Model No. 1 (Part I)

Component → i j ↓ Process	1 S_I	2 S_S	3 X_I	4 X_S	5 X_{BH}	6 X_{BA}	7 X_P	8 S_O
1 Aerobic growth of heterotrophs		$-\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{Y_H}$
2 Anoxic growth of heterotrophs		$-\frac{1}{Y_H}$			1			
3 Aerobic growth of autotrophs						1		$-\frac{4.57-Y_A}{Y_A}$
4 'Decay' of heterotrophs				$1-f_p$	-1		f_p	
5 'Decay' of autotrophs				$1-f_p$		-1	f_p	
6 Ammonification of soluble organic nitrogen								
7 "Hydrolysis" of entrapped organics		1		-1				
8 "Hydrolysis" of entrapped organic nitrogen								
Observed Conversion Rate, r_i $[ML^{-3}T^{-1}]$	$r_i = \sum_j \nu_{ij}\rho_j$							
Stoichiometric parameters: Heterotrophic yield: Y_H Autotrophic yield: Y_A Fraction of biomass yielding slowly biodegradable substrate: f_P Mass N/mass COD in biomass: i_{XB} Mass N/mass COD in products from biomass decay: i_{XP}	Soluble inert organic matter $[M(COD)L^{-3}]$	Readily biodegradable substrate $[M(COD)L^{-3}]$	Particulate inert organic matter $[M(COD)L^{-3}]$	Slow biodegradable substrate $[M(COD)L^{-3}]$	Active heterotrophic biomass $[M(COD)L^{-3}]$	Active autotrophic biomass $[M(COD)L^{-3}]$	Particulate products arising from biomass decay $[M(COD)L^{-3}]$	Dissolved Oxygen (negtive COD) $[M(-COD)L^{-3}]$

Table 2.10 The IAWQ Activated Sludge Model No. 1 (Part II)

Component → i j ↓ Process	9 S_{NO}	10 S_{NH}	11 S_{ND}	12 X_{ND}	13 S_{ALK}
1 Aerobic growth of heterotrophs		$-i_{XB}$			$-\frac{i_{XB}}{14}$
2 Anoxic growth of heterotrophs	$-\frac{1-Y_H}{2.86Y_H}$	$-i_{XB}$			$\frac{1-Y_H}{14\cdot 2.86Y_H}-\frac{i_{XB}}{14}$
3 Aerobic growth of autotrophs	$\frac{1}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$			$-\frac{i_{XB}}{14}-\frac{1}{7Y_A}$
4 'Decay' of heterotrophs				$i_{XB}-f_P i_{XP}$	
5 'Decay' of autotrophs				$i_{XB}-f_P i_{XP}$	
6 Ammonification of soluble organic nitrogen		1	-1		$\frac{1}{14}$
7 "Hydrolysis" of entrapped organics					
8 "Hydrolysis" of entrapped organic nitrogen			1	-1	
Observed Conversion Rate, r_i $[ML^{-3}T^{-1}]$	$r_i=\sum_j \nu_{ij}\rho_j$				
Stoichiometric parameters: Heterotrophic yield: Y_H Autotrophic yield: Y_A Fraction of biomass yielding slowly biodegradable substrate: f_P Mass N/mass COD in biomass: i_{XB} Mass N/mass COD in products from biomass decay: i_{XP}	Nitrite and nitrate nitrogen $[M(N)L^{-3}]$	$NH_4^{+}+NH_3$ nitrogen $[M(N)L^{-3}]$	Soluble biodegradable organic nitrogen $[M(N)L^{-3}]$	Particulate biodegradable organic nitrogen $[M(N)L^{-3}]$	Alkalinity - molar units

Table 2.10 The IAWQ Activated Sludge Model No. 1 (Part III)

Component → i j ↓ Process	Process Rate, ρ_j $[ML^{-3}T^{-1}]$
1 Aerobic growth of heterotrophs	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{OH}+S_O}\right)X_{BH}$
2 Anoxic growth of heterotrophs	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\eta_a X_{BA}$
3 Aerobic growth of autotrophs	$\hat{\mu}_A\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_O}{K_{OA}+S_O}\right)X_{BA}$
4 'Decay' of heterotrophs	$b_H X_{BH}$
5 'Decay' of autotrophs	$b_A X_{BA}$
6 Ammonification of soluble organic nitrogen	$k_a S_{ND} X_{BH}$
7 "Hydrolysis" of entrapped organics	$k_h \frac{X_S / X_{BH}}{K_X+(X_S / X_{BH})}\left[\left(\frac{S_O}{K_{OH}+S_O}\right)+\eta_h\left(\frac{K_{OH}}{K_{OH}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{BH}$
8 "Hydrolysis" of entrapped organic nitrogen	$\rho_7(X_{ND} / X_S)$
Observed Conversion Rate, r_i $[ML^{-3}T^{-1}]$	$r_i=\sum_j \nu_{ij}\rho_j$
Stoichiometric parameters: Heterotrophic yield: Y_H Autotrophic yield: Y_A Fraction of biomass yielding slowly biodegradable substrate: f_P Mass N/mass COD in biomass: i_{XB} Mass N/mass COD in products from biomass decay: i_{XP}	*Kinetic parameters:* Heterotrophic growth and decay: $\hat{\mu}_H$, K_S, K_{OH}, K_{NO}, b_H Autotrophic growth and decay: $\hat{\mu}_A$, K_{NH}, K_{OA}, b_A Correction factor for anoxic growth of heterotrophs: η_g ammonification: k_a Hydrolysis: k_h, K_X Correction factor for anoxic hydrolysis: η_h

2.3.1.3 Comments

There have been many new developments in activated sludge process modeling since the publication of the task group's final report. One of them is wastewater characterization. Organic matter has been divided into more and more fractions (Henze, 1992). Biomass also needs to be further divided to accommodate the new organic matter fractions. While it is tempting to formulate new models by including more components and processes into Activated Sludge Model No. 1, one should not forget the purpose and the limitations of such models. Historically, activated sludge models have been most successful in predicting oxygen utilization related process behavior. That is also the area that the IAWQ Task Group recommended that the model be applied to (Henze *et al.* 1987). It is evident that some of these new efforts have moved away from this area. There is nothing wrong to develop and test new ideas. What is dangerous is that people do not realize the limits of these models.

Another potential trap is the interaction among substrate fractions and biomass groups. It is well known in microbiology that some microorganisms are capable of metabolizing more than one substrate. Therefore microorganism groups may overlap (Henze 1992). So far little is known of the impact of such substrate-biomass interactions and no consideration has been given to them in activated sludge modeling. As more fractions are created for substrate and biomass, such interactions will certainly become more pronounced.

Activated Sludge Model No. 1 already suffers from lack of identifiability with its current mathematical complexity (Lessard and Beck, 1991). The difficulty will certainly become more prominent when new substrate fractions and biomass groups are added to the model.

2.3.2 Nitrification

Nitrification is the biological process in which autotrophs convert ammonia to nitrate using inorganic carbon, such as CO_2, as carbon source. Nitrification is a two step reaction. In the first step, *Nitrosomonas* oxidizes ammonia into nitrite. In the second step, *Nitrobacter* oxidizes nitrite into nitrate. Under most conditions, the first step is a slower reaction and is the limiting step. The second step, however, can become the liming step under certain circumstances. When this happens, a nitrite build-up will occur. This phenomenon is referred to as partial nitrification (Turk and Mavinic, 1989). Nitrification is a naturally occurring microbial reaction. In wastewater treatment, the mechanisms of nitrification are the same except nitrification becomes an engineered, controlled, and enhanced process. Nitrification is required for most wastewater treatments for the following reasons: 1) ammonia, if discharged into receiving waters, exerts oxygen demand which could drag the dissolved oxygen to such a low level that it will adversely affects the ecological habitat. 2) nitrification is a prerequisite of denitrification which removes nitrogen from water by converting nitrate to nitrogen gas. Without efficient nitrification which oxidizes ammonia to nitrate, denitrification will not function.

Nitrification has been treated as a one-step reaction (ammonia to nitrate) in many cases for the sake of simplicity (Henze, *et al.* 1987). Nitrite build-up, however, has been identified as the major manifestation of nitrification inhibition. It is therefore necessary to model nitrification as a two-step reaction (step 1: ammonia to nitrite and step 2: nitrite to nitrate) in such situations.

Nitrification can be accomplished in a wide variety of biological treatment processes, such as activated sludge, trickling filter, rotating biological contactor, etc. Activated sludge is the most widely used process for nitrification.

In many cases, nitrification is achieved in a single-sludge activated sludge process which performs carbon oxidation, nitrification, and denitrification. Some nutrient removal systems also carry out biological phosphorus removal in addition to carbon oxidation, nitrification, and denitrification. In some cases carbon oxidation, nitrification, and denitrification is performed in separate stages as opposed to in a single-sludge system.

Denitrification is not investigated in this study. The following is an incomplete list of the recent publications on denitrification: Soares, *et al.* (1991, Clayton *et al.* (1991), Carley and Mavinic (1991), Brenner and Argaman (1990), Gayle, et al. (1989), Brenner (1986), Argaman and Brenner (1986), Esener (1986).

For the two types of activated sludge processes investigated in this research, nitrification is not required for the high-purity oxygen activated sludge process; single-sludge carbon oxidation and nitrification are required for the petroleum refinery activated sludge process. Thus the review in the next sections will be limited to single-sludge nitrification.

2.3.2.1 Stoichiometry

The Stoichiometry of nitrification is described by the following reactions:

$$NH_4^+ + 1.5\,O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + 2H^+ + H_2O \tag{2.26}$$

$$NO_2^- + 0.5\,O_2 \xrightarrow{\text{Nitrobacter}} NO_3^- \tag{2.27}$$

The overall reaction is:

$$NH_4^+ + 2O_2 \xrightarrow{\text{Nitrifier}} NO_3^- + 2H^+ + H_2O \tag{2.28}$$

2.3.2.2 Kinetics

The kinetic rate expressions of nitrification have been most frequently represented by the Monod equation. Poduska and Andrews were among the first to develop a dynamic model of nitrification for the activated sludge process. The kinetic expressions for substrate utilization and biomass growth were both represented by the Monod kinetics (Poduska and Andrews, 1975). Randall and Buth (1984a) found that temperature can cause the rates of nitrification to change to first-order to zero-order, or the reverse. Because of this, it was concluded that the Monod equation is a better kinetic model for nitrification than simpler kinetic models such as zero- or first-order.

Recent research, however, indicates that nitrification can be inhibited by high concentrations of ammonia. Accumulation of nitrite can also result in inhibition of nitrification. It is thus more mechanistically appropriate to represent the nitrification kinetics by the Haldane kinetics. Rozich and Castens (1986) investigated nitrification kinetics by using a two-stage continuous culture system. A synthetic ammonia wastewater with no organic carbon was fed to the reactor. The results indicated that nitrification kinetics are best represented with a substrate inhibitory function such as the Haldane kinetics. Gee *et al.* (1990) found that the oxidation of nitrite was inhibited by the concentration of nitrite only in the presence of a high concentration of ammonia. Nitrite alone, on the other hand, did not inhibit its own oxidation at the concentrations studied. Other investigations on nitrification include Bliss and Barnes (1986), Diab et al. (1993), Ng and Stenstrom (1987), and Shammas (1986).

2.3.3 Sulfur Oxidation

Study of sulfur oxidation is limited to the petroleum refinery activated sludge process in this investigation. Sulfur species in combined refinery wastewater is primarily hydrogen sulfide. Organic sulfur is negligible. This is because organic sulfur embedded in crude oil is converted into hydrogen sulfide via such processes as hydrogenation to enhance the quality of products, such as gasoline.

Not much has been reported in the literature on the oxidation of hydrogen sulfide in the petroleum refinery activated sludge process. Much information, however, exists about oxidation of reductive sulfur species in pure culture conditions. Overall the following conclusions have been made for the oxidation of hydrogen sulfur:

Hydrogen sulfide can be oxidized both chemically and biochemically; but bacteria-mediated biochemical oxidation is much faster than chemical oxidation. Buisman (1990a) found that the biological oxidation rate in cell suspensions from a bioreactor, measured in a phosphate buffered system at pH 8.0 and 25 °C, was found to be a factor 75 faster than the chemical no-catalyzed oxidation at sulfide concentrations around 10 mg/l. Thus chemical oxidation is negligible for the activated sludge process.

Possible oxidation products of hydrogen sulfide include elemental sulfur (S^0), sulfite (SO_3^{2-}), sulfate(SO_4^{2-}), etc. The biological oxidation of sulfide to sulfate proceeds in two stages. In the first stage, which proceeds faster than the second stage, sulfide looses two electrons and forms membrane-bound polymeric sulfur compounds. In the second step, membrane-bound sulfur is oxidized to sulfite and sulfate.

$$HS^- \rightarrow \text{membrane bound } [S^0] \leftrightarrow S^0$$

$$\text{membrane bound } [S^0] \rightarrow SO_3^{2-} \rightarrow SO_4^{2-}$$

Depending on the purpose of the treatment, the sulfur oxidation process can be designed and operated in such a way the production of a product is maximized. For sulfur harvest, the product is elemental sulfur (Buisman, *et al.* 1990b). For the refinery activated sludge process, the product is sulfate.

2.3.4 Factors Affecting Kinetics

Factors affecting activated sludge kinetics include dissolved oxygen (DO), temperature, pH, and the presence of toxic substances. The impact of these factors on heterotrophs and nitrifiers is different. The nitrifying population, being less robust than the heterotrophic population, requires more favorable environmental conditions (Painter, 1986).

2.3.4.1 Dissolved Oxygen

Dissolved oxygen (DO) is an important environmental factor that affects carbon oxidation and nitrification. This is especially true for nitrification (Stenstrom and

Poduska, 1980; Hanaki, *et al.* 1990a,, 1990b). Firstly, nitrification is oxygen intensive. For the complete oxidation of every mole of ammonia to nitrate, 4.57 mole of O_2 is required. Secondly, *nitrosomonas* and *nitrobacter* are more vulnerable than heterotrophs to oxygen deficiency. Thus for a single sludge carbon oxidation and nitrification system, DO level, as well as sludge age, is almost always controlled based on the requirement of nitrification.

Most modeling work of nitrification treats sludge as a homogenous substance, and the oxygen transfer between water and sludge is assumed to be fast enough such that it is not a limiting step. In other words the DO concentrations in bulk liquid and sludge flocs are always the same. This assumption is also adopted in this investigation. Other research, nevertheless, has shown that consideration of oxygen diffusion from bulk liquid to the center of sludge flocs resulted in better predictions (Stenstrom and Song, 1992).

The dependence of activated sludge kinetics on DO is often modeled by a DO 'switch' function (Henze *et al.* 1987):

$$f_{O_2} = \frac{S_O}{K_O + S_O} \tag{2.29}$$

where S_O is the dissolved oxygen concentration, mg O_2/l. K_O is the oxygen half-saturation coefficient, mg O_2/l. The value of K_O is small. For normal DO range (2 -4 mg/l for air systems), f_{O_2} approximately equals to 1; for low DO, f_{O_2} approaches to zero. The 'switch' function therefore turns aerobic reactions on and off depending on the DO concentration.

2.3.4.2 Temperature

Depending on the geographic location, the mean annual temperature of wastewater varies from about 10 to 21.1°C (50 to 70°F); 15.6°C is a representative value. Optimum temperatures for bacterial activity are in the range from about 25 to 35°C. Aerobic digestion and nitrification stop when the temperature rises to 50°C. When the temperature drops to about 15°C, methane-producing bacteria become quite inactive, and at about 5°C, the autotrophic-nitrify bacteria practically cease functioning. At 2°C even the chemoheterotrophic bacteria acting on carbonaceous material become essentially dormant (Metcalf & Eddy, Inc. 1991). For the typical wastewater temperature range of 10 to 35°C, reaction rates increase when temperature increases and the effect can be described by Van't Hoff-Arrhenius:

$$\ln K = -\frac{\Delta H^o}{RT} + C \tag{2.30}$$

where K - reaction rate constant; ΔH^o - standard enthalpy change of the reaction; R - universal gas constant; T - temperature, Kelvin; C - a constant. In wastewater engineering, a modified version of Van't Hoff-Arrhenius is often used:

$$k_T = k_{20}\theta^{(T-20)} \tag{2.31}$$

where k_T, k_{20} - rate coefficient at T (°C) and 20 (°C) respectively. θ has been found to vary with temperature ranges of interest. A value of θ often quoted in the literature is 1.024.

It should be realized that Equation (2.33) is only applicable to a narrow temperature range, such as 10 to 20 °C. The effect of temperature on kinetics no longer follows Van't Hoff-Arrhenius equation when the temperature is out of this range (Figure 2.16). A equation that covers a broader range of temperature is needed if the temperature range of interest is out of the 10 to 30 C range (see Chapter 3, Section 3.2 for the handling of temperature effect in the model petroleum refinery activated sludge process).

Randall and Buth (1984a) studied the effects of temperature on nitrification kinetics by performing a series of continuous-flow, laboratory-scale reactor experiments at temperatures 5, 6, 10, 14, 17, and 30°C. Their results reveal that nitrification can be very sensitive to small changes in temperature over the range of 10 to 17°C. The inhibitory effect of decreased temperature is greater for *Nitrobacter* than for *Nitrosomonas*. This results in a build-up of nitrites in the reactor until the temperature drops to a point where nitrification is completely suppressed.

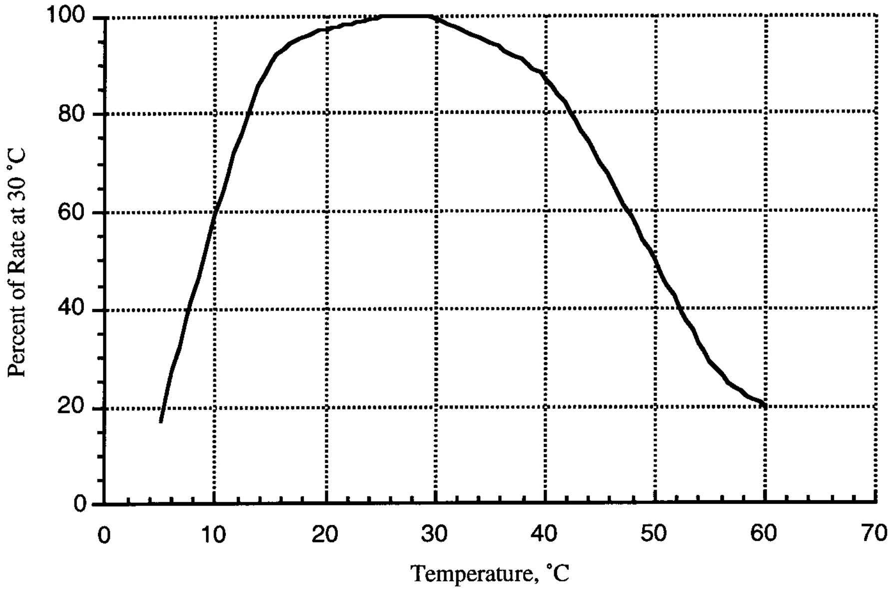


Figure 2.16 Effect of temperature on kinetics (Borchardt, 1966)

2.3.4.4 Inhibition

As aforementioned both heterotrophs and autotrophs are subject to inhibition with autotrophs being more vulnerable. Many investigators have observed inhibition of both *Nitrosomonas* and *Nitrobacter* by free ammonia, with *Nitrobacter* being the most sensitive genera. Many chemical compounds have been found inhibitory to nitrification, such as phenol, hexavalent chromium, trivalent arsenic, fluoride, toxic organics, etc. (Stafford, 1974).

Haldane kinetics have been increasingly used in lieu of Monod kinetics to describe the inhibitory effect due to excessive concentrations of substrate (Haldane, 1965). If the inhibitor is not the substrate itself, a wide variety of inhibition patterns exist, including competitive, noncompetitive, etc. (Beg and Atiqullah, 1983; Bailey and Ollis, 1986). When the inhibitor is the substrate itself the general noncompetitive kinetics becomes the Haldane kinetics. Haldane kinetics is therefore a special case of the noncompetitive kinetics. Modeling of inhibition has been limited to Haldane kinetics so far.

2.3.4.5 pH

It is well documented in the literature that both high and low pH environments are inhibitory to microorganisms. Optimal pH range for microbial growth is 6-9 (Metcalf & Eddy, Inc., 1991; Wild *et al.* 1971). When acclimated, heterotrophs and autotrophs are able to live under higher (pH > 9) and lower (pH < 6) pH conditions. It is the sudden change in pH that upsets the microbial metabolism most.

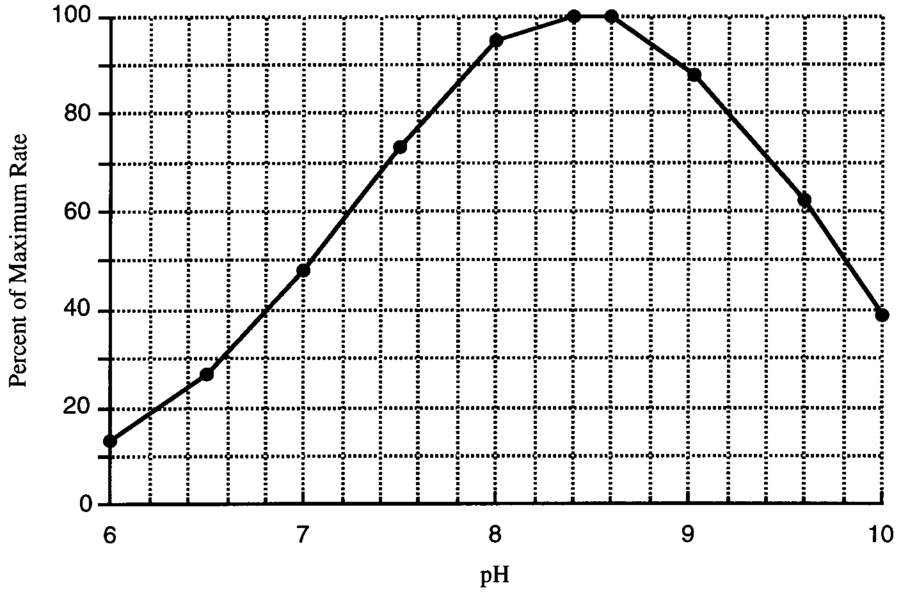


Figure 2.17 Effect of pH on nitrification rate at 20 °C (Wild *et al.* 1971)

The effect of pH, as depicted in Figure 2.17, can be modeled using the Michaelis pH functions which describe the effect of pH on enzyme kinetics in solution (Bailey and Ollis, 1986). There is room to argue if mechanisms of pH effects are the same for enzyme kinetics and activated sludge kinetics; but it is conceivable that enzyme kinetics is a good analog to activated sludge kinetics. Further more, from the perspective of modeling, the more important thing is that the mathematical form of the Michaelis pH functions is ideal for representing the effect of pH on activated sludge (Antoniou, *et al.* 1990).

2.4 Process Models

Of numerous process models that have been developed using the various kinds of conventional activated sludge models, the following are two examples which the author is familiar with - Lawrence and McCarty (1970) and Rozich and Gaudy (1992). These models are still valuable tools for activated sludge process design. The limitations of conventional activated sludge models, as reviewed above, prohibit them from playing more important roles. In this research, efforts are devoted to structured activated sludge models only.

Process models developed from structured activated sludge models are reviewed next for the two types of activated sludge process investigated in this research.

2.4.1 High-purity Oxygen Activated Sludge Process

The use of high-purity oxygen in biological wastewater treatment is considered by many to be the only major advance that has occurred in the area of activated sludge treatment since the early sixties. Furthermore, within the past thirty years oxygen activated sludge has become a viable alternative in those situations where the choice of activated sludge for secondary treatment is considered to be cost-effective (Benefield, *et al.*, 1983). The high purity oxygen activated sludge process is frequently used for large municipal applications where only small land areas are available for expansion. This situation frequently occurs in mature cities where large infrastructures have been developed around existing treatment plants.

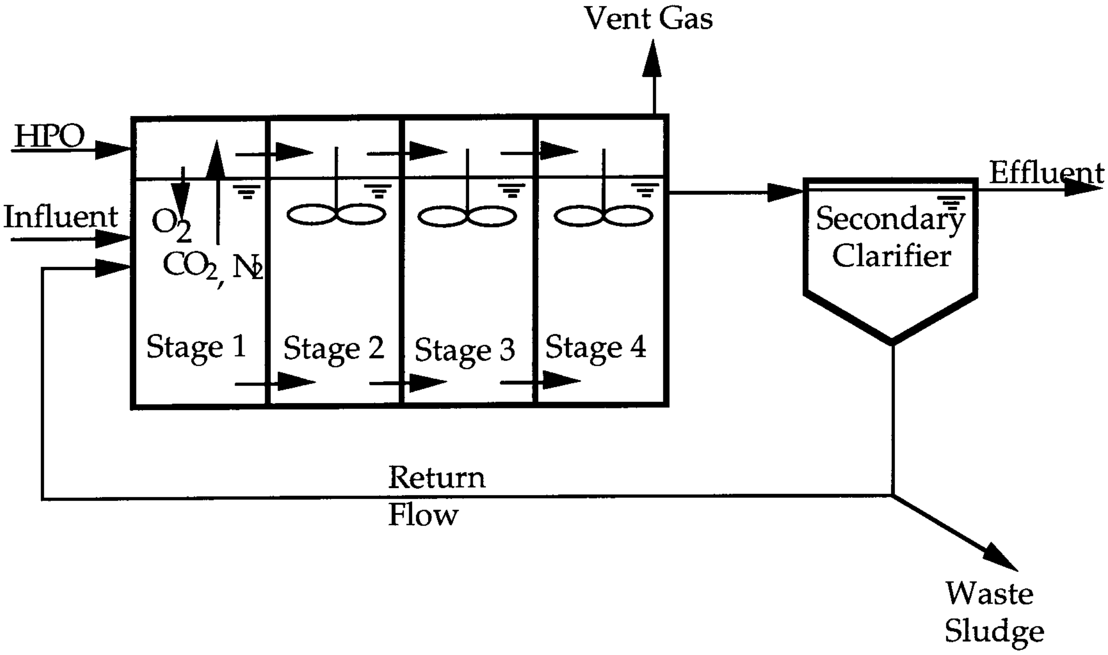


Figure 2.18 Flow Diagram of The High-Purity Oxygen Activated Sludge Process

The high purity oxygen activated sludge process is more complicated than a conventional air system. The complexity of the HPO process results from the use of high purity oxygen and multi-stage (usually 3-4 stages), closed aeration tanks (Figure 2.18). The design of the HPO process is based on steady-state mathematical models of the process, but for real HPO plants, process dynamics, caused by the diurnal variations of raw wastewater in both flow and concentrations, are intrinsic parts of the process operation.

The complexity and the dynamic nature of the oxygen activated sludge process make it difficult to understand the process dynamics. The importance of understanding process dynamics can not be over emphasized. It is difficult to achieve satisfactory process operation and control if process dynamics are not well understood.

Different approaches exist to understanding process dynamics. One approach is to build bench-scale and/or pilot-scale plants and perform tests using the plants. The shortcoming of this approach is obvious. There may be numerous different sized pilot plants that need to be tested. There are numerous tests and combinations of tests that need to be performed in order to fully test all possible scenarios. It is easily conceivable that such an approach is costly and time consuming. A more reasonable approach is to build a reliable process model, and investigate process dynamics by running simulations for different design options and/or control strategies. In this way, only a few tests are actually needed to verify the most important/prominent scenarios. Considerable time and money can be saved.

Several applications of HPO process modeling and simulation have been reported in the literature. Mueller *et al.* (1973) developed a model to investigate the gas transfer kinetics in the HPO process. The mass transfer equations were formulated in a dynamic form, but only a steady-state solution was pursued. The model was developed for process design, not for studying process dynamics. McWhirter and Vahldieck (1978) developed a generalized mathematical model to describe the multi-component mass transfer and physical, chemical and biological interactions in the HPO process. Their model, however, was a steady state model, and was developed for the purpose of process design. Thus it is not appropriate for investigating process dynamics. It is not clear what kind of activated sludge model, called biochemical oxidation model by McWhirter and Vahldieck, was used in their model and simulations. It is believed to be a conventional activated sludge model, as it is called now, based on Monod kinetics. Linden (1979) developed a model for minimizing energy requirement in the pure oxygen activated sludge process. The process model, which is part of the optimization model, is a steady-state model. The activated sludge model is a conventional activated sludge model based on Monod kinetics. Clifft and Andrews (1986) applied the structured activated sludge model they developed (Clifft and Andrews, 1981; Clifft, 1980), called Clifft-Andrews Model here, to the HPO process, and dynamically simulated the HPO process. Gas-liquid interactions were the focus of their investigation. Clifft and Barnett (1988) investigated the gas transfer kinetics in a full-scale HPO process. The validity of a liquid film limited, two-film theory model was examined for systems that rely strictly on surface mixers. Stenstrom *et al.* (1989) estimated the oxygen transfer capacity of a full-scale pure oxygen activated sludge plant. The activated sludge model used was the conventional (unstructured) activated sludge model, as documented by Lawrence and McCarty (1970). Stenstrom (1990) simulated the oxygen transfer of a pilot HPO plant. Oxygen transfer capacity and kinetics were examined. A sensitivity analysis was conducted for design variables to identify possible changes of design which were expected to bring in potential improvements in process performances. The activated sludge model used was the structured Cliff and Andrews activated sludge model. Tzeng (1992) theoretically investigated the VOC emission from the HPO process and concluded that VOC emissions from the HPO process is much less than an equivalent air system. Tzeng (1992) also simulated the dynamic performance of PID controllers in controlling first stage total pressure, dissolved oxygen, and stage 4 oxygen utilization. The Clifft and Andrews model was modified to incorporate the VOC components.

As illustrated above, the activated sludge models used in previous research evolved from the conventional/unstructured model to the structured Clifft-Andrews model. The IAWQ Activated Sludge Model No. 1 has not been applied to the high-purity oxygen activated sludge process despite its increasing use in recent years. Activated Sluge Model No. 1 and the Clifft-Andrews Model are different in many aspects. The author was interested in finding out how well Activated Sludge Model No. 1 is capable of predicting process dynamics of the high purity oxygen activated sludge system. It was my objective in this study to develop an overall process model for the high-purity oxygen activated sludge process by use of Activated Sludge Model No. 1, verify the new model using data from both pilot- and full-scale plants, and compare it with previous models.

2.4.2 Petroleum Refinery Activated Sludge Process

A complex combination of many different unit petrochemical processes is used in a modern petroleum refinery to change crude oil physically and chemically in order to produce the various products in desired qualities and quantities. Various wastewaters are generated during the refining process. It is a typical practice in most refineries to collect all process wastewaters and combine them into a single wastewater stream, which is then treated in a central facility - often called "end-of-pipe" treatment. The "end-of-pipe" treatment technology in the petroleum refining industry relies heavily upon the use of biological wastewater treatment methods. Of all the biological wastewater treatment methods, the activated sludge process is the most widely used secondary treatment technique. Figure 2.19 depicts the flow diagram of the Effluent Treatment Plant (ETP) in the model petroleum refinery.

Not much has been reported in the literature on the modeling of the petroleum refinery activated sludge process. Conventional activated sludge models have been applied to the design of petroleum refinery activated sludge processes (Ramalho, 1978; Ramalho, 1979). Mathematical models have been developed for the removal of specific pollutants in the petroleum refinery activated sludge process, such as phenolics and ammonia; but no system model have been developed which is capable of describing all the important reactions, e.g. carbonaceous oxygen demand removal, nitrification, sulfur

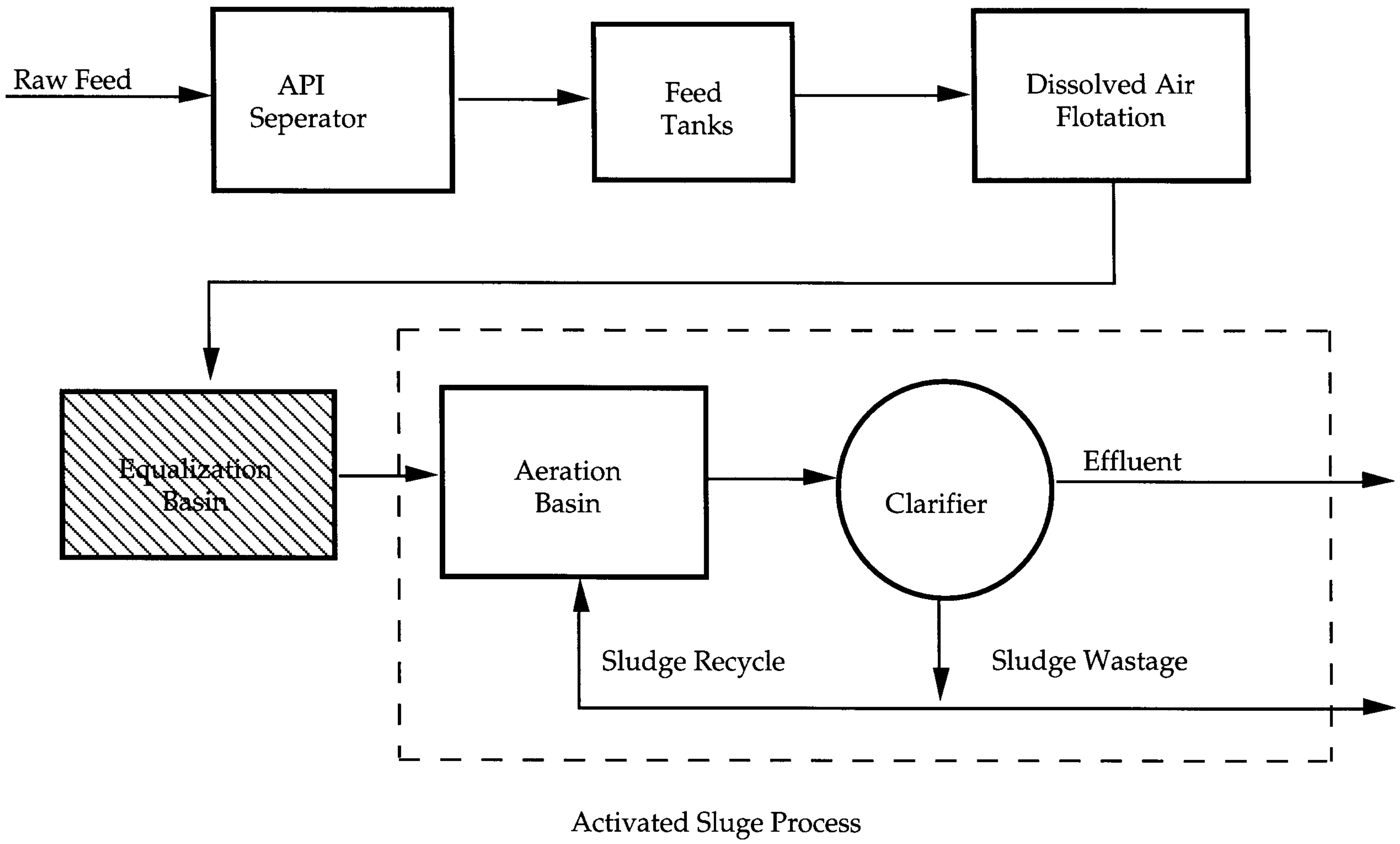


Figure 2.19 Flow Diagram of the Effluent Treatment Plant (ETP) in the Model Petroleum Refinery

oxidation, and biodegradation of phenolics.

A dynamic model is developed for the petroleum refinery activated sludge process in this research. The model is based on the IAWQ Activated Sludge Model No. 1 but includes more components and reactions specific to petroleum refinery wastewater.

2.5 Expert Systems

Substantial efforts have been made towards the application of expert system technology to wastewater treatment systems. Ozgur and Stenstrom (1994) documents the development of an expert system to assist the control of nitrification in a petroleum refinery wastewater treatment plant. Yuan *et al.* (1993a) reported the development of an expert system to assist the operation and control of the effluent treatment plant in the model refinery. The expert system was designed with special emphasis on the integration of data management and process diagnosis. Other publications on this subject were reviewed by Yuan *et al.* (1993a) (Chapter 6). Most of these expert systems are protocol type programs which present developments of methodologies and demonstrate potentials of expert system technology; but few of them have been applied to the real-world. There is a gap between research and application which is in part caused by the lack of real-time capability and user friendliness of the programs. Yuan *et al.* (1993a) attempted to shrink the gap by adopting a sophisticated real-time oriented shell.

A recent trend in expert system development is the combination of expert systems and mathematical model. Yuan *et al.* (1992) proposed the structure of an integrated expert system and illustrated additional benefits to be derived from such an integration using the effluent treatment plant in the model refinery as an example (Chapter 7).

The expert system development effort in this investigation is devoted to a petroleum refinery activated sludge wastewater treatment plant. An expert system for the high-purity oxygen activated sludge process is currently under development, as an independent research project.

3. MODEL DEVELOPMENT

Dynamic models are developed in this chapter for the two types of activated sludge processes investigated in this research - the high-purity oxygen activated sludge process and the petroleum refinery activated sludge process.

3.1 High-Purity Oxygen Activated Sludge

A new dynamic model was developed for the high-purity oxygen activated sludge process. As reviewed in Chapter 2, Section 2.4.1, a number of models have been developed for and applied to the high-purity oxygen activated sludge process. None of them, however, used the IAWQ Activated Sludge Model No. 1, which has become the most widely used activated sludge model. The new HPO-ASP model developed in this dissertation is the first such model that incorporates the IAWQ Activated Sludge Model No. 1.

3.1.1 Modification of Activated Sludge Model No. 1

The IAWQ Activated Sludge Model No. 1 was modified for the high-purity oxygen activated sludge process. The oxygen activated sludge process carries out carbon oxidation only. Nitrification, if required, is always performed separately after carbon oxidation. The high-purity oxygen activated sludge process is usually controlled at a sludge age of 1-2 days. Almost no nitrification occurs when the process is operated at such a short sludge age. Dissolved oxygen is usually maintained at 6 mg/l or higher. Thus anoxic condition does not exist in the high-purity oxygen activated sludge process and consequently no denitrification occurs. The flow diagram of the carbon oxidation portion of Activated Sludge Model No. 1 is depicted in Figure 3.0.

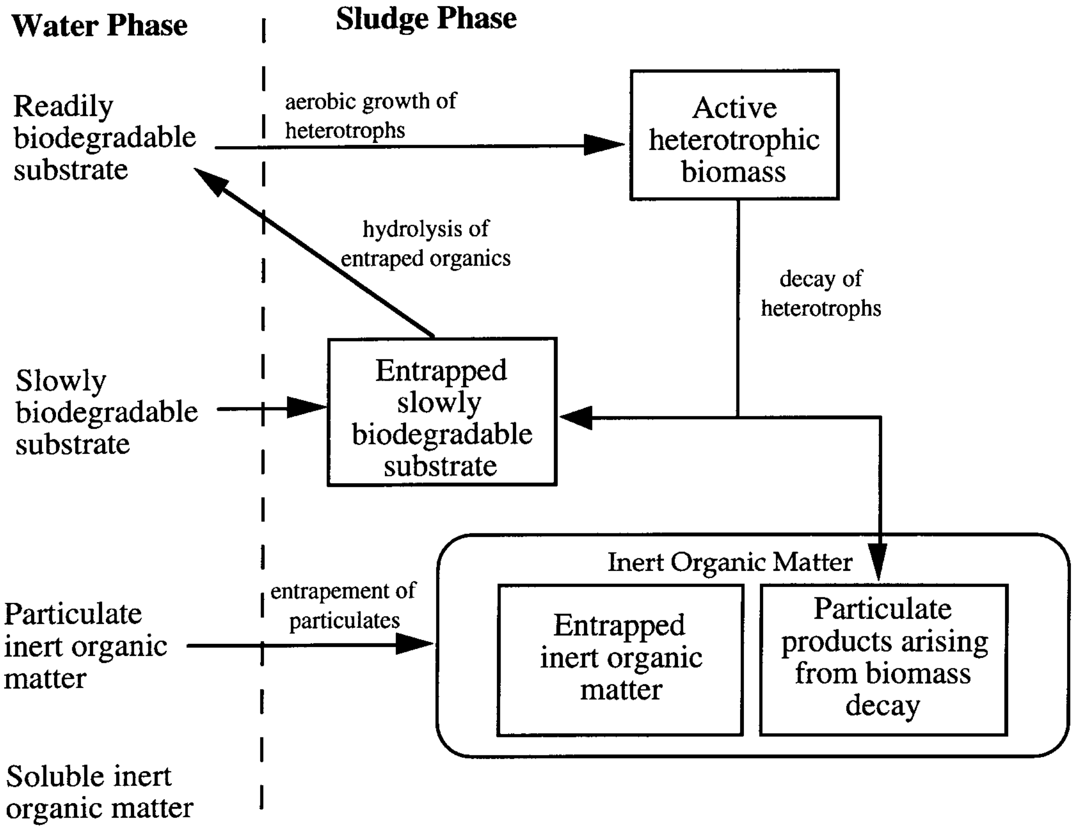


Figure 3.0 Flow diagram of carbon Oxidation in Activated Sludge Model No. 1

Activated Sludge Model No. 1 was modified for the HPO-ASP as follows: Three processes were removed from the original IAWQ Activated Sludge Model No. 1. They are process 2 - anoxic growth of heterotrophs (denitrification), process 3 - aerobic growth of autotrophs (nitrification), and process 5 - decay of autotrophs. Anoxic hydrolysis was removed from process rate expressions of process 7 - "hydrolysis" of entrapped organics and process 8 - "hydrolysis" of entrapped organic nitrogen. Two components were removed from the model. They are component 6 - active autotrophic biomass X_{BA} and component 9 - nitrite and nitrate nitrogen X_{NO}.

Table 3.1 Modified IAWQ Activated Sludge Model No. 1 for the High Purity Oxygen Activated Sludge Process

Component → i j ↓ Process	1 S_I	2 S_S	3 X_I	4 X_S	5 X_{BH}	6 X_P	7 S_O	8 S_{NH}	9 S_{ND}	10 X_{ND}	11 S_{ALK}	Process Rate, ρ_i $[ML^{-3}T^{-1}]$
1 Aerobic growth of Heterotrophs		$-\frac{1}{Y_H}$			1		$-\frac{1-Y_H}{Y_H}$	$-i_{XB}$			$-\frac{i_{XB}}{14}$	$\mu_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_O}{K_{OH}+S_O}\right)X_{BH}$
2 Decay of Heterotrophs				$1-f_P$	-1	f_P				$i_{XB}-f_P i_{XP}$		$b_H X_{BH}$
3 Ammoinification of Soluble Organic Nitrogen								1	-1		$\frac{1}{14}$	$k_a S_{ND} X_{BH}$
4 Hydrolysis of Entrapped Organics		1		-1								$k_h \frac{X_S/X_{BH}}{K_X+(X_S/X_{BH})}\left(\frac{S_O}{K_{OH}+S_O}\right)X_{BH}$
5 Hydrolysis of Entraped Organic Nitrogen									1	-1		$\rho_7(X_{ND}/X_S)$
Observed Conversion Rates $[ML^{-3}T^{-1}]$	$r_i = \sum_{j=1}^{5} \nu_{ij}\,\rho_j$											
Stoichiometric parameters: Heterotrophic yield: Y_H Fraction of biomass yielding particulate products: f_P Mass N/Mass COD in biomass: i_{XB}	Soluble inert organic matter $(M(COD)L^{-3})$	Readily biodegradable substrate $(M(COD)L^{-3})$	Particulate inert organic matter $(M(COD)L^{-3})$	Slowly biodegradable substrate $(M(COD)L^{-3})$	Active heterotrophic biomass $(M(COD)L^{-3})$	Particulate products arising from biomass $(M(COD)L^{-3})$	Oxygen (negative COD) $(M(COD)L^{-3})$	NH +NH nitrogen $(M(N)L^{-3})$	Soluble biodegradable organic nitrogen $(M(N)L^{-3})$	Particulate biodegradable organic nitrogen $(M(N)L^{-3})$	Alkalinity - Molar units	*Stoichiometric parameters:* Mass N/Mass COD in products from biomass decay: i_{XP} *Kinetic parameters:* Heterotrophic growth and decay: μ_H, K_S, K_{OH}, b_H Ammonification: k_a Hydrolysis: k_h, K_X

The original Activated Sludge Model No. 1 has 13 components, 8 processes, and 18 stoichiometric and kinetic coefficients. The modified Activated Sludge Model No. 1 has 11 components, 5 processes, and 11 stoichiometric and kinetic coefficients (Table 3.1).

3.1.2 Process Model Development

This section describes the development of the new dynamic model for the high-purity oxygen activated sludge process. The modules of the high-purity oxygen activated sludge process model are illustrated by Figure 3.1. The process model is composed of an aeration tank model and a secondary clarifier model. The aeration tank model further consists of a gas phase model, a liquid phase model, and a gas transfer model. The activated sludge model, which is a biokinetic model, is part of the liquid phase model. Notice that the arrows linking gas phase model and liquid phase model via the gas transfer model can go in both directions, which indicates that gas can either be dissolved into liquid or stripped off liquid. The two-direction arrows between aeration tank and secondary clarifier represents their interactive relation - mixed liquor suspended solid (MLSS) from the last stage of the aeration tank is fed into the clarifier and the sludge is withdrawn from the bottom of the clarifier and recycled to the first stage of the aeration tank. It should be noted that previous high-purity oxygen activated sludge process models have similar structures as that depicted in Figure 3.1; but none of them explicitly presented the information.

The gas phase model is a "must-have" module for any high-purity oxygen activated sludge process model.

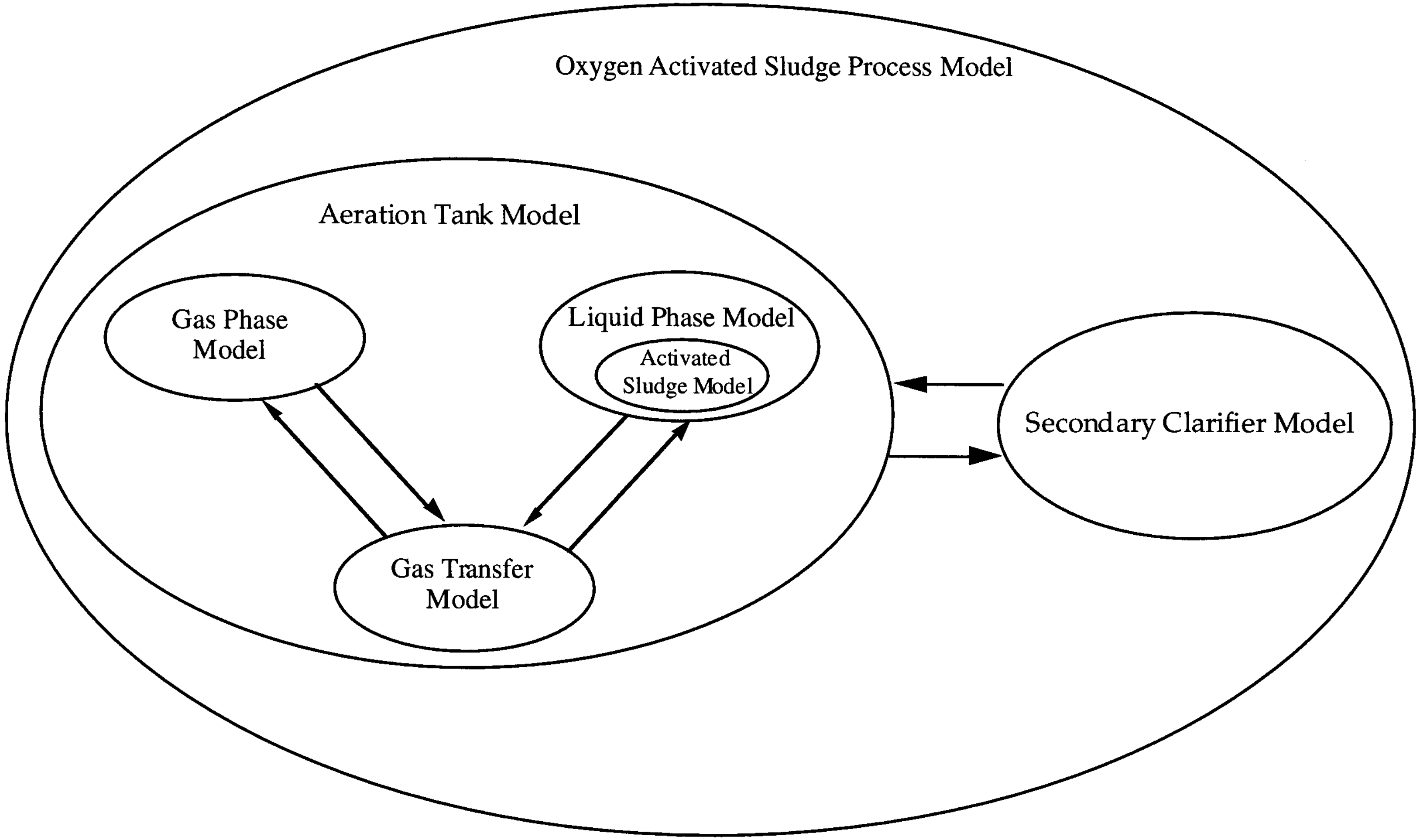


Figure 3.1 Modules of the High-purity Oxygen Activated Sludge Process Model

3.1.2.1 Aeration Tank

The core of the new HPO-ASP model, the aeration tank model, is the focus of the model development effort. Its development is presented in this section. A number of assumptions are made to facilitate the derivation of the governing equations. Although they may appear restrictive, many actual engineering situations may be adequately represented by the mathematical models obtained within the limitations of the assumptions. The assumptions made here are similar to those of Clifft and Andrews (1986).

- The gas phase is composed of oxygen, nitrogen, carbon dioxide, and water vapor.
- All gases and gas mixtures behave like ideal gas.
- Both the gas phase and liquid phase are completely mixed.
- Gas and liquid volumes are constant.
- Atmospheric pressure is 760 mm Hg.
- Activity coefficients are 1.0.

Mass balance equations are written for each gas and liquid component in each stage (Figure 3.2). SI units are used throughout the process model: m^3 for gas and liquid phase volumes, m^3/hr for flow rates, atm for partial and total pressures, mole/m^3 for the concentrations of gas components, and mg/l for the concentrations of dissolved gases. Note that gas transfer terms are formulated based on liquid concentrations in this study (Equation 3.11 -3.13). Their units need to be converted from mg/l/hr to mole/m^3/hr when incorporated into gas phase mass balance equations. The general form of the mass balance equation for a component i_c in stage i is as follows:

$$V(i)\frac{d}{dt}\begin{bmatrix}\text{concentration of}\\ \text{component } i_c\end{bmatrix}=\sum_{i_{is}}\begin{bmatrix}\text{flow rate of}\\ \text{inlet stream } i_{is}\end{bmatrix}\begin{bmatrix}\text{conc. of component } i_c\\ \text{in inlet stream } i_{is}\end{bmatrix}$$
$$-\sum_{i_{os}}\begin{bmatrix}\text{flow rate of}\\ \text{outlet stream } i_{os}\end{bmatrix}\begin{bmatrix}\text{conc. of component } i_c\\ \text{in outlet stream } i_{os}\end{bmatrix}+V(i)\begin{bmatrix}\text{source or sink terms}\\ \text{of component } i_c\end{bmatrix} \quad (3.1)$$

where V(i) = volume of gas phase for gas components or volume of liquid phase for liquid components, [m^3]; i_c = index of component; i_{is} = index of inlet stream; i_{os} = index of outlet stream. For gas phase components, inlet streams of stage i include high-purity oxygen feed (to the first stage only) and gas flow from preceding stage (i-1) (not applicable to the first stage). Outlet streams include outflow of stage i (to stage i+1) and gas leakage (to ambient atmospheric air). Outflow changes from stage to stage because of the utilization of oxygen. It decreases gradually from the first stage to the last stage. Source/sink terms are due to gas transfer. There is no chemical/biological reaction in gas phase. For liquid phase components, inlet streams to stage i include influent feed (to stage 1 only under conventional mode; to stage 2 only for under reaeration mode), return sludge (to stage 1 only) and liquid flow from preceding stage (i-1) (not applicable for stage 1). Outlet stream is the outlet flow of stage i to stage i+1 (next stage), which equals to the sum of all inlet flows to stage i. Most source/sink terms are described by the activated sludge model. For non-reactive liquid phase components, such as dissolved nitrogen, source/sink terms are attributed to gas transfer.

First stage total pressure and vent gas oxygen purity are important control variables . The set point of first stage total pressure is usually 4-6 inch of water column. Vent gas oxygen purity is usually controlled at 40%, which, under steady state, results in an oxygen utilization rate of approximately 90%. First stage total pressure is controlled by manipulating the pure oxygen feed to the first stage. Vent gas oxygen purity can be controlled by adjusting the valve openings of the vent gas exit.

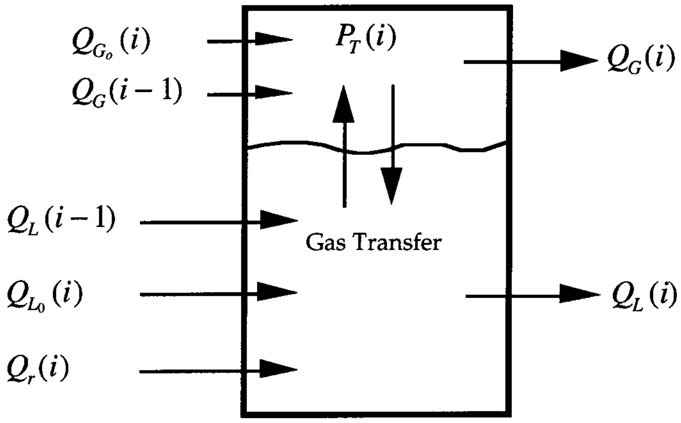


Figure 3.2 Mass balance diagram for stage i of a multi-stage high-purity oxygen activated sludge process

Notation used in Figure 3.2: Q = flow rate, [m^{3}hr^{-1}], with subscript G, L, and r indicating flows of gas, liquid, and return sludge respectively; 0 = as subscript, denotes influent; i, i-1 = in parentheses, denote stage i and stage i-1; P_T = total gas pressure, atm.

3.1.2.1.1 Gas Phase

The mass balance equations of oxygen, nitrogen, and carbon dioxide are:

$$\frac{dO_2(i)}{dt} = \frac{Q_{G_o}(i)O_{2_o} + Q_{G_T}(i-1)O_2(i-1) - Q_{G_T}(i)O_2(i)}{V_G(i)} + GTR_{O_2}(i) \tag{3.2}$$

$$\frac{dN_2(i)}{dt} = \frac{Q_{G_o}(i)N_{2_o} + Q_{G_T}(i-1)N_2(i-1) - Q_{G_T}(i)N_2(i)}{V_G(i)} + GTR_{N_2}(i) \tag{3.3}$$

$$\frac{dCO_2(i)}{dt} = \frac{Q_{G_o}(i)CO_{2_o} + Q_{G_T}(i-1)CO_2(i-1) - Q_{G_T}(i)CO_2(i)}{V_G(i)} + GTR_{CO_2}(i) \tag{3.4}$$

where O2(i), N2(i), CO2(i) are concentrations of oxygen, nitrogen, and carbon dioxide in stage i gas phase, mole/m^3; V_G(i) is the gas phase volume of stage i; $GTR_{O_2}(i)$, $GTR_{N_2}(i)$, $GTR_{CO_2}(i)$ are gas transfer rates of oxygen, nitrogen, and carbon dioxide, mole/m^3/hr; 0, as subscript, denotes high-purity oxygen feed. Equations of the gas transfer terms are presented next in the gas transfer model.

Note that high-purity oxygen is fed to the first stage only. $Q_{G_o}(i)$ is zero for stage 2 through 4. Therefore $Q_{G_o}(i)O_{2_o}(i)$, $Q_{G_o}(i)N_{2_o}(i)$, and $Q_{G_o}(i)CO_{2_o}(i)$ become zero for stage 2, 3 and 4. Also note that $Q_G(i-1)$ is zero for stage 1 which does not have a preceding stage. The composition of the high-purity oxygen feed is about 97% oxygen, 3% nitrogen, and 0% carbon dioxide (molar fractions).

The relation between partial pressure and molar concentration is described by the gas law:

$$p_{O_2}(i) = O_2(i) \bullet RT \tag{3. 5}$$

$$p_{N_2}(i) = N_2(i) \bullet RT \tag{3. 6}$$

$$p_{CO_2}(i) = CO_2(i) \bullet RT \tag{3. 7}$$

where $p_{O_2}(i)$, $p_{N_2}(i)$, $p_{CO_2}(i)$ - partial pressures of oxygen, nitrogen, and carbon dioxide in stage i, atm; R - universal gas constant, 8.2057 x 10^{-5} m^3 atm K^{-1} mol^{-1}; T - gas phase temperature, K.

The total gas pressure of stage i is:

$$P_T(i) = p_{O_2}(i) + p_{N_2}(i) + p_{CO_2}(i) + p_{H_2O} \tag{3. 8}$$

where p_{H_2O} is water vapor pressure, atm. The expression of p_{H_2O} is:

$$p_{H_2O} = (5.0538 - 0.021092T + 0.030783T^2)/760 \tag{3.9}$$

Equation (3.9) results from the polynomial fit of handbook water vapor pressure data (in mm Hg) (Stenstrom, 1990; Tzeng, 1992).

Gas flow from stage i to stage i+1 is model as that through an orifice:

$$Q_G(i) = K_{flow}\sqrt{P_T(i) - P_T(i+1)} \tag{3.10}$$

where K_{flow} is the gas flow coefficient. Note that for the last stage (i=4) $P_T(i+1)$ represents atmospheric pressure.

3.1.2.1.2 Gas Transfer

Gas transfer model used here is based on the two-resistance (two-film) gas transfer theory.

$$GTR_{O_2}(i) = \alpha K_L a_{o_2}(i)\left(S^*_{O_2} - S_{O_2}(i)\right) \tag{3.11}$$

$$GTR_{N_2}(i) = \alpha K_L a_{N_2}(i)\left(S^*_{N_2} - S_{N_2}(i)\right) \tag{3.12}$$

$$GTR_{CO_2}(i) = \alpha K_L a_{CO_2}(i)\left(S^*_{CO_2} - S_{CO_2}(i)\right) \tag{3.13}$$

where α is the alpha factor of the aeration system (K_La actual/K_La tap water) $K_La_{O_2}$, $K_La_{N_2}$, $K_La_{CO_2}$ are liquid phase gas transfer coefficients for oxygen, nitrogen, and carbon dioxide respectively, hr^{-1}; $S^*_{O_2}$, $S^*_{N_2}$, $S^*_{CO_2}$ are saturation concentrations of dissolved oxygen, nitrogen, and carbon dioxide, mg/l; S_{O_2}, S_{N_2}, S_{CO_2} are concentrations of dissolved oxygen, nitrogen, carbon dioxide in liquid phase, mg/l.

The saturation concentrations of oxygen, nitrogen, and carbon dioxide are:

$$S^*_{O_2} = 5.5555 \times 10^4 \frac{MW_{O_2}}{H_{O_2}} \cdot p_{O_2}(i) \cdot \beta \cdot f_h \tag{3. 14}$$

$$S^*_{N_2} = 5.5555 \times 10^4 \frac{MW_{N_2}}{H_{N_2}} \cdot p_{N_2}(i) \cdot \beta \cdot f_h \tag{3.15}$$

$$S^*_{CO_2} = 5.5555 \times 10^4 \frac{MW_{CO_2}}{H_{CO_2}} \cdot p_{CO_2}(i) \cdot \beta \cdot f_h \tag{3.16}$$

where MW_{O_2}, MW_{N_2}, MW_{CO_2} are molecular weights of oxygen, nitrogen, and carbon dioxide respectively, g/mole; H_{O_2}, H_{N_2}, H_{CO_2} are henry's law coefficients of oxygen, nitrogen, and carbon dioxide respectively, atm/mole fraction; β is the beta factor for the aeration system; f_h is the hydrostatic correction factor (=1 for surface aeration, =1.38 for the submerged aeration in the model high-purity oxygen activated sludge process).

3.1.2.1.3 Liquid Phase

Most liquid phase components are the components of the modified Activated Sludge Model No. 1 except dissolved nitrogen and carbon dioxide.

Soluble inert organic matter does not undergo any transformation; it becomes part of the effluent COD.

$$\frac{dS_I(i)}{dt} = \frac{Q_{L_o}(i)S_{I_o} + Q_r S_{I_r} + Q_{L_T}(i-1)S_I(i-1) - Q_{L_T}(i)S_I(i)}{V_L(i)} \tag{3.17}$$

Readily biodegradable substrate S_S is utilized by heterotrophs in aerobic growth, and is generated from hydrolysis of entrapped particulate substrate X_S.

$$\begin{aligned} \frac{dS_S(i)}{dt} &= \frac{Q_{L_o}(i)S_{S_o} + Q_{L_r} S_{S_r} + Q_{L_T}(i-1)S_S(i-1) - Q_{L_T}(i)S_S(i)}{V_L(i)} \\ &\quad - \frac{1}{Y_H}\mu_H\left(\frac{S_S(i)}{K_S + S_S(i)}\right)\left(\frac{S_{O_2}(i)}{K_{OH} + S_{O_2}(i)}\right)X_{BH}(i) + k_h\left(\frac{X_S(i)/X_{BH}(i)}{K_X + X_S(i)/X_{BH}(i)}\right)X_{BH}(i) \end{aligned} \tag{3.18}$$

Particulate inert organic matter X_I does not undergo any biochemical reaction, but is entrapped into sludge flocs, and becomes part of MLVSS.

$$\frac{dX_I(i)}{dt} = \frac{Q_{L_o}(i)X_{I_o} + Q_{L_r}(i)X_{I_r} + Q_{L_T}(i-1)X_I(i-1) - Q_{L_T}(i)X_I(i)}{V_L(i)} \tag{3.19}$$

Slowly biodegradable substrate (particulate substrate) X_S is hydrolyzed into readily biodegradable substrate (soluble substrate), and produced from biomass decay.

$$\begin{aligned} \frac{dX_S(i)}{dt} &= \frac{Q_{L_o}(i)X_{S_o} + Q_{L_r}(i)X_{S_r} + Q_{L_T}(i-1)X_S(i-1) - Q_{L_T}(i)X_S(i)}{V_L(i)} \\ &\quad + (1 - f_P)b_H X_{BH}(i) - k_h\left(\frac{X_S(i)/X_{BH}(i)}{K_X + X_S(i)/X_{BH}(i)}\right)\left(\frac{S_{O_2}(i)}{K_{OH} + S_{O_2}(i)}\right)X_{BH}(i) \end{aligned} \tag{3.20}$$

Active heterotrophic biomass is synthesized from the metabolism of soluble substrate.

$$\frac{dX_{BH}(i)}{dt}=\frac{Q_{L_o}(i)X_{BH_o}+Q_{L_r}(i)X_{BH_r}+Q_{L_T}(i-1)X_{BH}(i-1)-Q_{L_T}(i)X_{BH}(i)}{V_L(i)} \\ +\mu_H\left(\frac{S_S(i)}{K_S+S_S(i)}\right)\left(\frac{S_{O_2}(i)}{K_{OH}+S_{O_2}(i)}\right)X_{BH}(i) \tag{3.21}$$

Particulate organic matter arising from biomass decay X_P is generated from biomass decay. It is considered as inert. The only difference between X_I and X_P is their origin. X_I comes from influent, and X_P comes from biomass decay.

$$\frac{dX_P(i)}{dt}=\frac{Q_{L_o}(i)X_{P_o}+Q_{L_r}(i)X_{P_r}+Q_{L_T}(i-1)X_P(i-1)-Q_{L_T}(i)X_P(i)}{V_L(i)}+f_Pb_HX_{BH}(i) \tag{3.22}$$

The sink term of dissolved oxygen is the oxygen uptake rate by heterotrophic growth (OUR), and the source term is the gas transfer rate of oxygen (GTR_{O2}).

$$\frac{dS_{O_2}(i)}{dt}=\frac{Q_{L_o}(i)S_{O_{2_o}}+Q_{L_r}(i)S_{O_{2_r}}+Q_{L_T}(i-1)S_{O_2}(i-1)-Q_{L_T}(i)S_{O_2}(i)}{V_L(i)} \\ -\frac{1-Y_H}{Y_H}\mu_H\left(\frac{S_S(i)}{K_S+S_S(i)}\right)\left(\frac{S_{O_2}(i)}{K_{OH}+S_{O_2}(i)}\right)X_{BH}(i)+GTR_{O_2}(i) \tag{3.23}$$

Ammonia (S_{NH}) is consumed as nutrient by heterotrophs and is generated by ammonification (conversion of soluble organic nitrogen to ammonia).

$$\frac{dS_{NH}(i)}{dt}=\frac{Q_{L_o}(i)S_{NH_o}+Q_{L_r}(i)S_{NH_r}+Q_{L_T}(i-1)S_{NH}(i-1)-Q_{L_T}(i)S_{NH}(i)}{V_L(i)} \\ -i_{XB}\mu_H\left(\frac{S_S(i)}{K_S+S_S(i)}\right)\left(\frac{S_{O_2}(i)}{K_{OH}+S_{O_2}(i)}\right)X_{BH}(i)+k_aS_{ND}X_{BH}(i) \tag{3.24}$$

Soluble organic nitrogen is consumed by ammonification and generated by hydrolysis of particulate biodegradable organic nitrogen.

$$\begin{aligned}\frac{dS_{ND}(i)}{dt} &= \frac{Q_{L_o}(i)S_{ND_o} + Q_{L_r}(i)S_{ND_r} + Q_{L_T}(i-1)S_{ND}(i-1) - Q_{L_T}(i)S_{ND}(i)}{V_L(i)} \\ &\quad + k_a S_{ND} X_{BH}(i) - k_h \left(\frac{X_S(i) / X_{BH}(i)}{K_X + X_{BH}(i)} \right) \left(\frac{S_{O_2}(i)}{K_{OH} + S_{O_2}(i)} \right) X_{BH}(i)(X_{ND}(i) / X_S(i))\end{aligned} \qquad (3.25)$$

Particulate biodegradable organic nitrogen (X_{ND}) is hydrolyzed into soluble organic nitrogen, and is generated by decay of biomass.

$$\begin{aligned}\frac{dX_{ND}(i)}{dt} &= \frac{Q_{L_o}(i)X_{ND_o} + Q_{L_r}(i)X_{ND_r} + Q_{L_T}(i-1)X_{ND}(i-1) - Q_{L_T}(i)X_{ND}(i)}{V_L(i)} \\ &\quad + (i_{XB} - f_P i_{XP}) b_H X_{BH}(i) - k_h \left(\frac{X_S(i) / X_{BH}(i)}{K_X + X_{BH}(i)} \right) \left(\frac{S_{O_2}(i)}{K_{OH} + S_{O_2}(i)} \right) X_{BH}(i)(X_{ND}(i) / X_S(i))\end{aligned}$$

(3.26)

The sink term of alkalinity is the depletion of ammonia by aerobic growth and the source term is the generation of ammonia from soluble organic nitrogen by ammonification.

$$\begin{aligned}\frac{dS_{ALK}(i)}{dt} &= \frac{Q_{L_o}(i)S_{ALK_o} + Q_{L_r}(i)S_{ALK_r} + Q_{L_T}(i-1)S_{ALK}(i-1) - Q_{L_T}(i)S_{ALK}(i)}{V_L(i)} \\ &\quad - \frac{1}{14} i_{XB} \mu_H \left(\frac{S_S(i)}{K_S + S_S(i)} \right) \left(\frac{S_{O_2}(i)}{K_{OH} + S_{O_2}(i)} \right) X_{BH}(i) + \frac{1}{14} k_a S_{ND}(i) X_{BH}(i)\end{aligned} \qquad (3.27)$$

The source term of dissolved carbon dioxide is the respiration of heterotrophs, and the sink term is the stripping of dissolved carbon dioxide from water phase to gas phase.

$$\frac{dS_{CO_2}(i)}{dt}=\frac{Q_{L_o}(i)S_{CO_{2_o}}+Q_{L_r}(i)S_{CO_{2_r}}+Q_{L_T}(i-1)S_{CO_2}(i-1)-Q_{L_T}(i)S_{CO_2}(i)}{V_L(i)}$$
$$-RQ\cdot\frac{1-Y_H}{Y_H}\mu_H\left(\frac{S_S(i)}{K_S+S_S(i)}\right)\left(\frac{S_{O_2}(i)}{K_{OH}+S_{O_2}(i)}\right)X_{BH}(i)+GTR_{co_2}(i) \qquad (3.28)$$

The only source/sink term included in dissolved nitrogen mass balance is the gas transfer term.

$$\frac{dS_{N_2}(i)}{dt}=\frac{Q_{L_o}(i)S_{N_{2_o}}+Q_{L_r}(i)S_{N_{2_r}}+Q_{L_T}(i-1)S_{N_2}(i-1)-Q_{L_T}(i)S_{N_2}(i)}{V_L(i)}+GTR_{N_2}(i) \qquad (3.29)$$

3.1.2.1.4 pH Calculation

The method of pH calculation in this dissertation is different from those of Clifft and Andrews (1986), Stenstrom *et al.* (1989), Stenstrom (1990), and Tzeng (1992). Clifft and Andrews (1986) considered carbon dioxide-bicarbonate equilibrium to be the only significant reaction for the normal pH range of 6.0 to 8.0 when no nitrification occurs. Rate of change of bicarbonate was correlated to rates of change of dissolved carbon dioxide and $[H^+]$. Mass balance equations were established for both dissolved carbon dioxide and bicarbonate. pH was calculated from the following equations:

$$K_{a1}=\frac{[H^+]\,[HCO_3^-]}{[H_2CO_3^*]} \qquad (3.30)$$

$$S_{CO2}=[H_2CO_3^*]=[CO_{2(aq)}]+[H_2CO_3]\sim[CO_{2(aq)}]) \qquad (3.31)$$

$$[H^+]=\frac{K_{a1}\,[H_2CO_3^*]}{[HCO_3^-]} \qquad (3.32)$$

$$pH = -\log_{10}([H^+]) \tag{3.33}$$

In this new HPO-ASP model, alkalinity is a state variable. The source/sink terms of alkalinity equation (Equation 3.27) are from the modified IAWQ Activated Sludge Model No. 1. Alkalinity is depleted in aerobic growth of heterotrophs because ammonia is consumed as nutrient in cell synthesis. Alkalinity is generated in ammonification because of the generation of ammonia from soluble organic nitrogen.

The following ionic equilibria and mass balance are used for pH calculation:

Alkalinity:

$$S_{ALK} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] + [NH_3] \tag{3.34}$$

Ion product of water:

$$K_W = [H^+]\,[OH^-] \tag{3.35}$$

Acidity constants of carbonic acid (carbon dioxide):

$$K_{a1} = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3^*]} \tag{3.36}$$

$$K_{a2} = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]} \tag{3.37}$$

Basicity constant of ammonia:

$$K_{NH_3} = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} \tag{3.38}$$

Ammonia nitrogen (mole/l):

$$[NH_3]_T = [NH_3] + [NH_4^+] \tag{3.39}$$

Combine Equation 3.34 through 3.39, we get:

$$S_{ALK} = \frac{K_{a1}[H_2CO_3^*]}{[H^+]} + \frac{2K_{a1}K_{a2}[H_2CO_3^*]}{[H^+]^2} + \frac{K_w}{[H^+]} - [H^+] + \frac{[NH_3]_T}{1 + \frac{K_{NH_3}[H^+]}{K_W}} \tag{3.40}$$

Notice that $[H_2CO_3^*] = S_{CO_2}$ and $[NH_3]_T = S_{NH}$ using the notation of the activated sludge model. pH is calculated implicitly and iteratively from the concentrations of alkalinity, dissolved carbon dioxide, and total ammonia nitrogen using Equation (3.40).

Stenstrom(1990) and Stenstrom *et al.* (1989) used the same implicit iteration technique to calculate pH from the values of alkalinity, dissolved carbon dioxide, and total ammonia nitrogen, but calculated alkalinity differently. Alkalinity was not treated as a state variable; instead, alkalinity was calculated as follows:

$$\text{Salk} = \text{Salk}_0 - \frac{[NH_3]_0 - [NH_3]}{14\text{x}10^3} \tag{3.41}$$

Equation 3. 41 basically correlates the change of alkalinity with the decrease of ammonia. This approach works well under steady-state conditions, but under dynamic condition, Equation 3.27 provides more realistic predictions. The factor in the denominator, $14\text{x}10^3$, converts unit of ammonia from mg N/l to mole/l.

3.1.2.2 Secondary Clarifier

The clarifier model included in the new high-purity oxygen activated sludge process model is the one-dimensional model developed by Bryant (1972), Busby (1973), and Stenstrom (1976). The model was later expanded by Vitasovic (1986) and Vitasovic (1989). The model divides the clarifier into horizontal layers along the vertical direction. Ten layers have often been found adequate in most cases. A mass balance equation is written for sludge solids in each layer. The model predicts the sludge concentration at the bottom of the secondary clarifier (thickening). The model is not capable of predicting effluent suspended solid concentration (clarification). Recently G. G. Patry and his colleagues have developed a new secondary clarifier model which is capable of handling both thickening and clarification (Takács *et al.* 1991).

3.1.2.3 Environmental Effects

The effect of dissolved oxygen was considered in the form of a "switch" function which turns off oxygen dependent reactions when DO approaches to zero (Equation 2.29). The effect of temperature on gas was considered through the gas law (Equation 3.5-3.7). The effect of temperature on kinetic rate coefficients is described by the modified Van't Hoff-Arrhenius (Equation 2.31). The amount of inhibitory chemical compounds is negligible. The pH does not vary significantly in the HPO-ASP; so its effect on activated sludge kinetics does not need to be considered in the model.

3.2 Petroleum Refinery Activated Sludge

This section documents the development of a dynamic model for the single-sludge carbon oxidation-nitrification activated sludge process treating combined petroleum refinery wastewater. Chevron El Segundo Refinery Effluent Treatment Plant (ETP) serves as a model for this study.

3.2.1 Background for Model Development

Petroleum refinery wastewater is a complex mixture of a wide variety of pollutants, usually characterized by such conventional pollutant parameters as BOD_5, COD, TOC, TSS, ammonia, sulfide, oil and grease, and phenolic compounds. Table 3.2 shows typical concentration ranges of these conventional pollutant parameters in raw petroleum refinery wastewater. Figure 3.3 to Figure 3.8 illustrates the effluent concentrations of the equalization basin. Treatment processes in the model refinery effluent treatment plant (ETP) include American Petroleum Institute (API) separator, dissolved air flotation (DAF), equalization basin, and activated sludge process (Figure 2.19). The effluent of equalization basin is the influent of the activated sludge unit. Although API separator and DAF are most efficient at removing oil and grease, a certain degree of removal has been observed for all pollutants. The NPDES discharge limitations of the model refinery is listed in Table 3.3.

Table 3.2 Raw wastewater characterization (adapted from Vernick, *et al.*, 1984)

Pollutant (mg/l)	Range	Median
BOD5	50-800	144
COD	300-600	418
TOC	100-250	135
TSS	50-200	
Ammonia, as N	4-300	42.1
Phenolic compounds	0.5-50	10.0
Sulfide, as S	0-200	176
Oil and Grease	20-250	44.9
Total Chromium	0-5	0.471

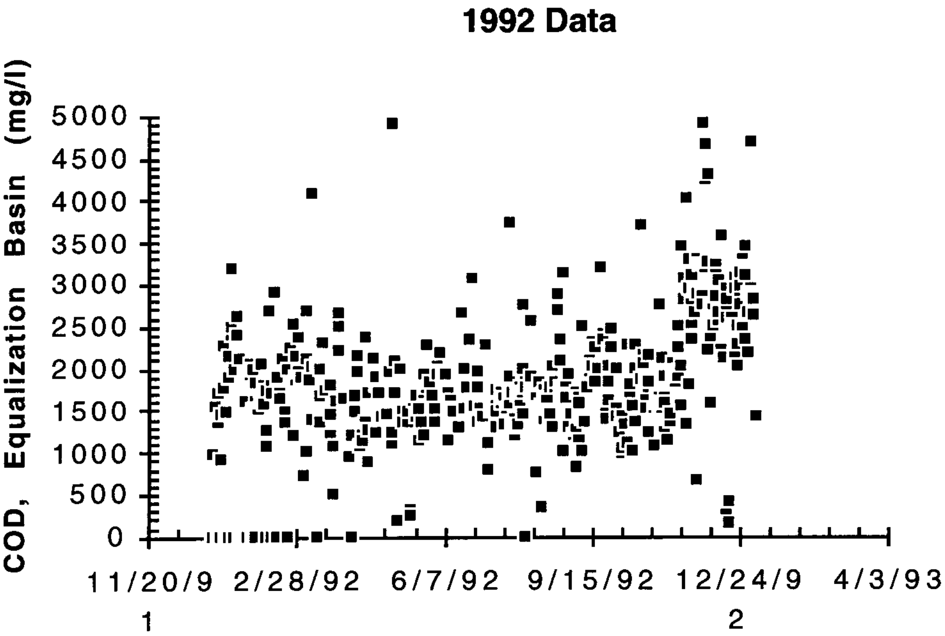


Figure 3.3 Equalization basin COD concentration

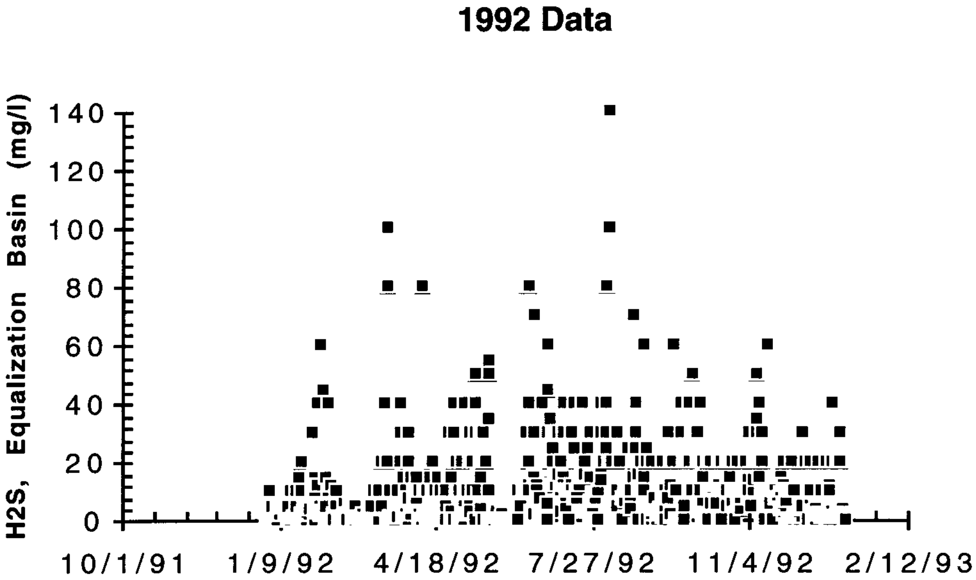


Figure 3.4 Equalization basin sulfide concentration

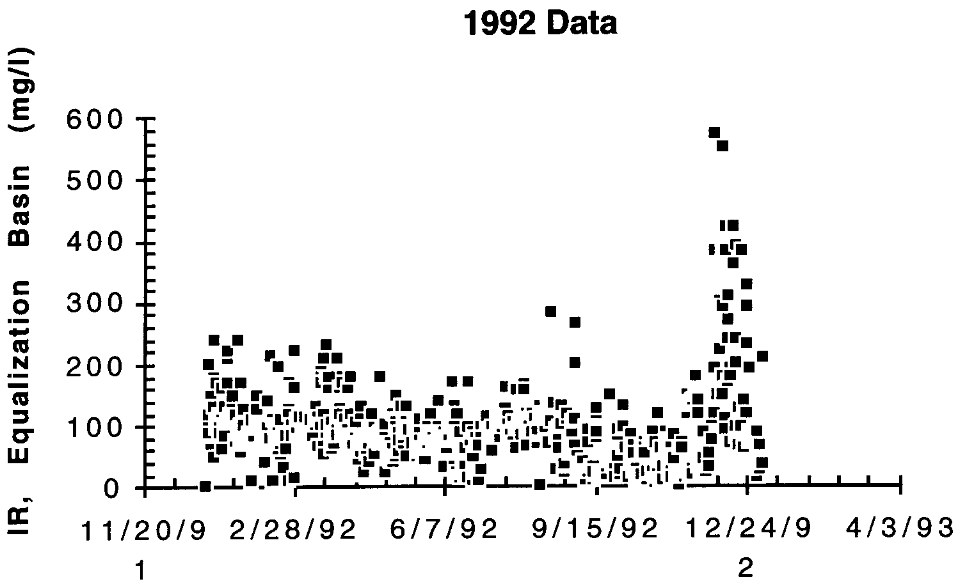


Figure 3.5 Equalization basin oil and grease concentration

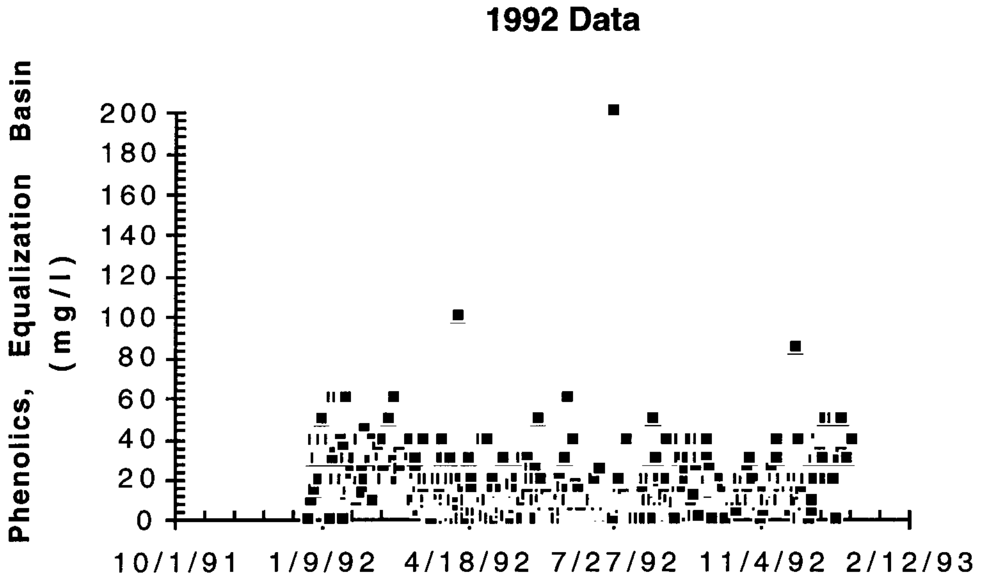


Figure 3.6 Equalization basin phenolics concentration

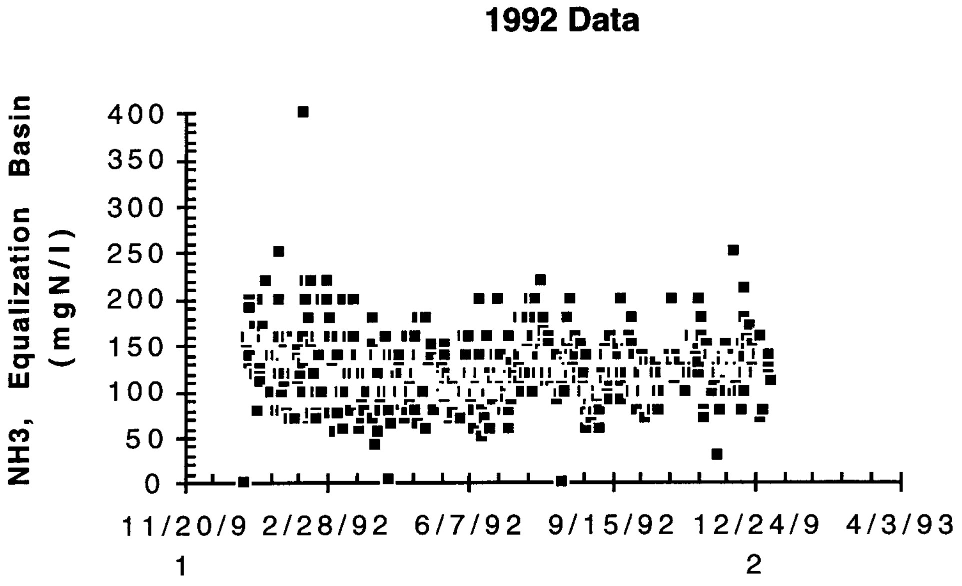


Figure 3.7 Equalization basin ammonia concentration

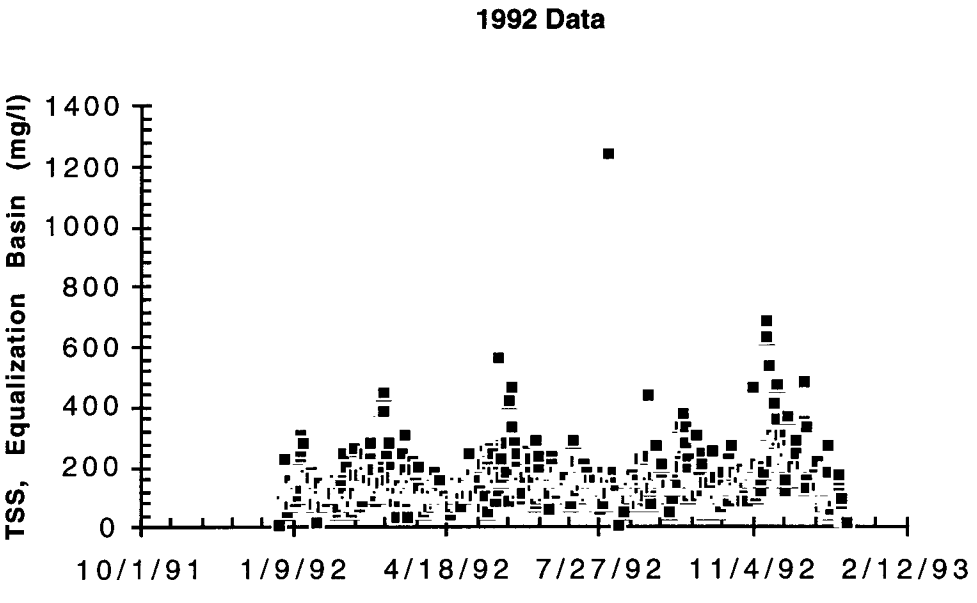


Figure 3.8 Equalization basin TSS concentration

The activated sludge process is a single-sludge carbon oxidation and nitrification process. Nitrification is very important because of the high strength of ammonia in the raw wastewater. Loss of nitrification is the most frequently encountered problem in the model refinery.

Process model development consists of two steps. First, an activated sludge model is developed for refinery activated sludge. Second, a process model was developed for the single sludge carbon oxidation nitrification petroleum refinery activated sludge process based on the activated sludge model.

Table 3.3 NPDES limitations for the selected petroleum refinery ETP

Constituent	Units	30 Day Average	Daily Maximum
BOD5 20 °C	lbs/day mg/l	2,420 66	4,360 119
Suspended solids	lbs/day mg/l	1,940 53	3,040 83
COD	lbs/day mg/l	16,900 462	32,600 890
Oil and Grease	lbs/day mg/l	710 20	1,320 37
Phenolic Compounds	lbs/day	10.9	45.3
Ammonia (as N)	lbs/day	1,320	2910
Sulfide (as S)	lbs/day mg/l	12.8 0.35	28.6 0.78
Total Chromium	lbs/day	12.8	37.1
Hexavalent Chromium	lbs/day mg/l	1.05 0.029	2.37 0.065

3.2.2 Refinery Activated Sludge Model Development

An activated sludge model (biokinetic model) is developed for the petroleum refinery activated sludge process which performs carbon oxidation and nitrification. The development of the model follows the modeling principles embedded in the IAWQ Activated Sludge Model No. 1 (Henze, *et al.*, 1987). In addition to biodegradation, stripping of volatile organic compounds (VOCs) could be another important removal mechanism for hydrocarbons in refinery wastewater (Rebhun and Galil, 1988; Cardinal and Stenstrom, 1991; Hsieh *et al.*, 1993a, 1993b). Volatilization, nevertheless, is not included in the current version of the dynamic model for the petroleum refinery activated sludge process. It is speculated that a significant percentage of VOCs has been removed in the preceding units of the activated sludge process - API separator, dissolved air flotation (DAF), and equalization basin, which is aerated. Thus the amount of VOCs available for stripping from the aeration tank may not be significant. There are, however, few data to prove or disprove this speculation. Another concern is that the inclusion of VOC emission also would make the model prohibitively large and complex (Tzeng, 1992), which is something that should be avoided for this first comprehensive model for petroleum refinery activated sludge.

The structure of the proposed model is shown in Figure 3.9. The processes included in the model are aerobic growth of heterotrophs, decay of heterotrophs, nitrification, decay of nitrifiers, oxidation of sulfide, decay of sulfide oxidizers, and hydrolysis of entrapped organics. Components of the model include soluble inert organic matter, readily biodegradable substrate, particulate inert organic matter, slowly biodegradable substrate, particulate inert organic matter from decay, active biomass, dissolved oxygen, ammonia, nitrate, sulfide, sulfate, and alkalinity. Organic nitrogen and sulfur are assumed to be negligible in the raw wastewater. The reason is that organic nitrogen and sulfur in crude oil are removed as impurities and converted into ammonia and hydrogen sulfide by refining processes such as hydrotreating. According to Henze *et al.* (1987) soluble and particulate nitrogen, nevertheless, could be found in the aeration

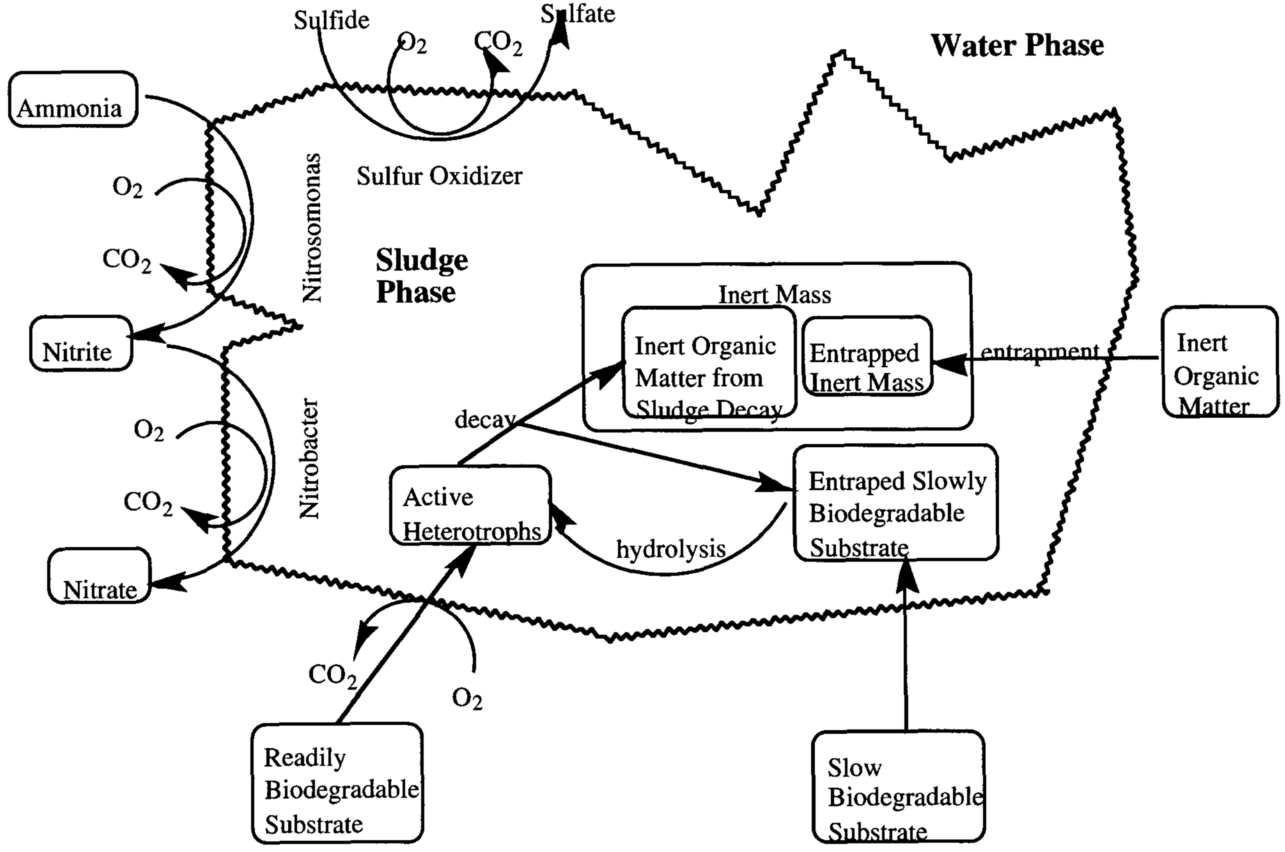


Figure 3.9 Schematic Diagram of the Refinery Activated Sludge Model

tank. They originate from the decay of active biomass. When active biomass decays, a fraction of the decayed mass becomes particulate inert organic matter and the rest of it becomes slowly biodegradable substrate. Organic nitrogen is part of slowly biodegradable substrate and is converted to soluble organic nitrogen by hydrolysis. Soluble organic nitrogen is then transformed to ammonia through ammonification (Henze, *et al.* 1987). Organic nitrogen transformation, however, could be simplified as follows: ammonia is released from biomass to liquid when biomass decays (Clifft and Andrews, 1981). This would eliminate two nitrogen components from the model - soluble and particulate organic nitrogen. The fact that there is little organic nitrogen in raw wastewater and influent ammonia concentration is high makes such a simplification reasonable. The simplified approach, nevertheless, was not employed in this research.

The mixed liquor volatile suspended solids (MLVSS) consists of the following four fractions: inert particulate (from influent and biomass decay), slowly biodegradable substrate (particulate), active heterotrophs, and active autotrophs (nitrifiers and sulfur oxidizers). The division of MLVSS, together with the division of organics, establishes a model structure which overcomes the shortcomings of the conventional (or unstructured) activated sludge models, such as that influent BOD is treated as soluble and readily biodegradable, and MLVSS is considered as active biomass. This make it possible to correctly predict process responses, particularly oxygen utilization patterns (Henze, *et al.*, 1987; Clifft and Andrews, 1981).

3.2.2.1 Carbon Oxidation

The organic matter is divided into four fractions - soluble inert, readily biodegradable (soluble), particulate inert, and slowly biodegradable (particulate).

Although BOD_5, COD, TOC, phenolics, oil and grease, and TSS all represent the organic matter, these parameters have been developed and used mainly for regulatory purposes instead of for the description of the physical, chemical, and biological mechanisms of petroleum refinery activated sludge. Oil and grease, for example, is defined by the method used for its determination (Standard Method, 1989). Sun *et al.* (1987) demonstrated that organic matter measured as oil and grease actually include some phenolics, short-chain carboxylic acids, naphthenic acids, and other compounds. These soluble oil and grease components have been found to be easily biodegradable. This indicates that different components of the organic matter follows different reaction mechanisms. It is therefore necessary to divide the organic matter into different fractions.

Soluble inert organic matter does not participate any biological process but contributes to the effluent soluble COD. The readily biodegradable fraction (soluble substrate) is metabolized following Monod kinetics. Particulate inert is entrapped into sludge flocs and becomes part of MLVSS. The slowly biodegradable fraction (particulate substrate) is hydrolyzed into soluble readily biodegradable substrate (Table 3.3).

A wide variety of toxic pollutants exists in refinery wastewater. Table 3.4 lists the name, concentration range, and solubility of the EPA priority pollutants which typically exist in petroleum refinery raw wastewater. Of all priority compounds, phenol, or phenolic compounds, is the most important in terms of its abundance in refinery wastewater and has been studied extensively (Colvin and Rozich, 1986; Rozich and Gaudy, 1985). Figure 3.6 illustrates the concentration of phenolic compounds in the model refinery ETP raw wastewater. The inhibition of aerobic growth of heterotrophs is not considered in the model though it has been the subject of much research (Galil *et al.*, 1988; Rebhun and Galil, 1988; Patoczka, *et al.*, 1989). Noncompetitive kinetics, such as

Haldane kinetics, could have been used to describe the aerobic growth of heterotrophs had more information been available on the mechanism of phenol inhibition to the aerobic growth of heterotrophs utilizing soluble substrate. Instead, the influence of hazardous compounds is considered as being included into the half-velocity coefficient, K_S, which is larger than the 'real' K_S if inhibition is explicitly included in the rate expression. K_S is called apparent K_S, $K_{S_{ap}}$, by Rebhun and Galil (1988).

Table 3.4 US EPA Priority Pollutants typically detected in petroleum refinery raw wastewater (adapted from Vernick *et al.*, 1984)

US EPA Priority Pollutants	Typical Conc. $\mu g / l$	Note
volatile organics		
benzene	430	(a)
ethylbenzene	130	
toluene	1300	
semi-volatile organics		
2,4-dimethylphenol	80	(a) In a particular plant actual concentration may vary from undetectable to ten times the typical value given.
phenol	1500	
acenaphthene	270	
fluoranthene	7	
chrysene	15	
phenanthrene	170	
metals		
Arsenic	120	(b) Variable to as much as 35 times the typical concentration given.
Chromium	700	
Copper	65(b)	
Cyanide	150(b)	
Lead	140(b)	
Nickel	20(b)	
Zinc	360	

The way that inhibitory effects of hazardous compounds are considered is also supported by the fact that microorganisms in refinery activated sludge have been acclimated to toxic compounds as well as conventional pollutants, e.g. BOD$_5$, ammonia, sulfide, phenolics, etc. Activated sludge kinetics does not change much except under extreme conditions, such as spill of concentrated phenol solutions. Therefore use of Monod kinetics is justified for normal operations. Consequently it is conceivable that the model might fail to predict process dynamics under the extreme conditions discussed above. As more information becomes available, a more detailed description should be included on the inhibitory effects of toxic compounds in petroleum refinery wastewater.

3.2.2.2 Nitrification

Nitrification is perhaps the most important biological process in the model refinery for a number of reasons. First, the NPDES discharge permit requires that ammonia be nitrified into nitrate before the effluent is discharged. Secondly, high ammonia concentration in refinery wastewater makes the nitrification process heavily loaded. Thirdly, the vulnerability of nitrifiers, as opposed to heterotrophs, renders the process vulnerable to upsets. Fourth, a number of toxic compounds exist in refinery wastewater which are inhibitory to nitrification. The oxidation of ammonia is performed by chemoautotrophs (*nitrosomonas* and *nitrobacter*) (Table 3.5).

Table 3.5 Physical Groups of Aerobic Chemoautotrophs (after Stanier, *et al.*, 1986)

Group of Aerobic Chemoautotrophs	Oxidizable Substrate	Oxidized Product	Terminal Electron Acceptor
Ammonia Oxidizers (*nitrosomonas*)	NH_4^+	NO_2^-	O_2
Nitrite Oxidizers (*nitrobacter*)	NO_2^-	NO_3^-	O_2
Sulfur Oxidizers	H_2S, S^0, $S_2O_3^{2-}$	SO_4^{2-}	O_2, sometimes NO_3^-

Nitrification is a two-step process, with ammonia being oxidized into nitrite first by *nitrosomonas*, and nitrite being oxidized into nitrate second by *nitrobacter*. Normally step 1 is the limiting step for nitrification. Step 2 of nitrification, however, could become the limiting step under certain conditions and result in nitrite build-up (Randall and Buth, 1984a, 1984b). Phenol, as well many other toxic compounds, has been found to inhibit nitrification. Furthermore ammonia inhibits nitrification at high concentrations. It has been suggested that Haldane, instead of Monod, kinetics be used for describing nitrification (Gee, *et al.* 1988; Rozich and Castens, 1986). Possible interactions among toxic compounds, synergistic or antagonistic, render the adoption of inhibition kinetics unrealistic. Therefore Monod kinetics is used for the same reason as for carbon oxidation. In addition, nitrification is modeled as an one step reaction for the simplicity of modeling. The IAWQ Activated Sludge Model No. 1 handles nitrification in the same way.

Ammonia nitrogen is in the form of NH_4^+ for $pH < 9.3$ (Snoeyink and Jenkins, 1980). Thus stripping of ammonia from the aeration tank is negligible because the pH range in refinery activated sludge is 7.5 to 9.

3.2.2.3 Sulfur Oxidation

Sulfide is another important inorganic pollutant in refinery wastewater. The typical concentration of sulfide in the model refinery is 15 mg/l, with a fluctuation range of 0-50 mg/l. The oxidation of sulfide is performed by chemoautotrophs (Table 3.5). The following sulfur oxidation reactions occur in an aerobic sulfide oxidation system, e.g. petroleum refinery activated sludge process:

$$HS^- + 0.5O_2 + H^+ \rightarrow S^0 + H_2O \tag{3.42}$$

$$S^0 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \tag{3.43}$$

The overall reactions is

$$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+ \tag{3.44}$$

The distribution of sulfide species is as follows: $pH < 7.1$, H_2S; $7.1 < pH < 14$, HS^-; $pH > 14$, S^{2-} (Snoeyink and Jenkins, 1980). Therefore for typical refinery activated sludge pH range (7.5 - 9) sulfide is primarily in the form of HS^-. Stripping of sulfide is negligible.

Sulfide can be oxidized both chemically and biologically in the aeration tank. Chemical oxidation, however, is insignificant compared with bacteria-mediated biological oxidation. Element sulfur and sulfite can be formed as intermediates, but will be further oxidized into sulfate quickly. Hence sulfide oxidation is treated as a single-step reaction here, with sulfate as the end product. Possible inhibitory effects are not explicitly described but can be taken into consideration by reflecting them in existing model coefficients.

3.2.2.4 Summary

An activated sludge model was developed for the single-sludge carbon oxidation nitrification activated sludge process in the mode refinery. Biological processes included in the model are aerobic growth of heterotrophs, decay of active heterotrophic biomass, aerobic growth of nitrifiers (nitrification) and sulfur oxidizers (sulfur oxidation), decay of nitrifiers and sulfur oxidizers, and hydrolysis of entrapped particulate organics. Total organic matter is divided into four fractions - soluble inert organic matter, readily biodegradable substrate, particulate inert organic matter, and slowly biodegradable substrate. Nitrification is modeled as a two-step reaction - *nitrosomonas* mediated oxidation of ammonia to nitrite and *nitrobacter* mediated oxidation of nitrite to nitrate. The oxidation of sulfide was handled as an one step reaction, with the final oxidation product sulfate being sulfate. Inhibitory effects of toxic compounds, such as phenolics, were not explicitly modeled but were considered by reflecting them in existing coefficients. In addition to the description of reactions involving reactants such as organics, ammonia, sulfide, and phenolics, the model also describes important process variables such as oxygen uptake rate (OUR) nitrogen and phosphate (as nutrients) uptake rates. Oxygen uptake rate and phosphorus uptake rate are important for the design, operation, and control of the aeration system and phosphorus dosing system in the model refinery.

The single sludge carbon oxidation nitrification activated sludge model developed in this Section is shown in Table 3.6 in matrix format.

Table 3.6 Petroleum Refinery Activated Sludge Model (Part I)

Component →i j ↓Process	**1** S_I	**2** S_S	**3** X_I	**4** X_S	**5** X_P	**6** X_{BH}	**7** X_{BA_N}	**8** X_{BA_S}	**9** S_{O_2}	**10** S_{NH}
1 Aerobic growth of Heterotrophs		$-\frac{1}{Y_H}$				1			$-\frac{1-Y_H}{Y_H}$	$-i_{XB}$
2 Nitrification							1		$-\frac{4.57-Y_{A_N}}{Y_{A_N}}$	$-i_{XB}-\frac{1}{Y_{A_N}}$
3 Oxidation of Sulfide								1	$-\frac{2-Y_{A_S}}{Y_{A_S}}$	$-i_{X_B}$
4 Decay of Heterotrophs				$1-f_P$	f_P	-1				
5 Decay of Nitrifiers										
6 Decay of Sulfide Oxidizers				$1-f_P$	f_P			-1		
7 Hydrolysis of Entrapped Organics		1		-1						
Observed Reaction Rate $[ML^{-3}T^{-1}]$	$r_i=\sum_j \nu_{ij}\rho_j$									
Stoichiometric coefficients: Y_H, Y_{AN}, Y_{AS} - yield coefficients, mass of heterotrophs, nitrifiers, and sulfur oxidizers produced per unit mass of readily biodegradable substrate, ammonia nitrogen, and sulfide sulfur utilized f_P - mass of inert organic matter generated per unit mass of active biomass decayed [M(COD)/M(COD)]	Soluble inert organic matter $[M(COD)L^{-3}]$	Readily biodegradable substrate $[M(COD)L^{-3}]$	Particulate inert organic matter $[M(COD)L^{-3}]$	Slowly biodegradable substrate $[M(COD)L^{-3}]$	Particulate inert organic matter from biomass decay $[M(COD)L^{-3}]$	Active heterotrophic biomass $[M(COD)L^{-3}]$	Active autotrophic biomass (nitrifiers) $[M(COD)L^{-3}]$	Active autotrophic biomass (sulfur oxidizers) $[M(COD)L^{-3}]$	Dissolved oxygen $[M(-COD)L^{-3}]$	Ammonia nitrogen $[M(N)L^{-3}]$

Table 3.6 Petroleum Refinery Activated Sludge Model (Part II)

Component →**i** **j** ↓Process	**11** S_{NO}	**12** S_{HS}	**13** S_{SO}	**14** S_{ALK}	Process Rate, r_i $[ML^{-3}T^{-1}]$
1 Aerobic growth of Heterotrophs				$-\frac{i_{XB}}{14}$	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_{O_2}}{K_{OH}+S_{O_2}}\right)X_{BH}$
2 Nitrification	$\frac{1}{Y_{A_N}}$			$-\frac{i_{XB}}{14}-\frac{1}{7Y_{A_N}}$	$\hat{\mu}_{A_N}\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_N}$
3 Oxidation of Sulfide		$-\frac{1}{Y_{A_S}}$	$\frac{1}{Y_{A_S}}$	$-\frac{i_{XB}}{14}-\frac{1}{16Y_{A_S}}$	$\hat{\mu}_{A_S}\left(\frac{S_{HS}}{K_{HS}+S_{HS}}\right)\left(\frac{S_{O_2}}{K_{OA_S}+S_{O_2}}\right)X_{BA_S}$
4 Decay of Heterotrophs					$b_H X_{BH}$
5 Decay of Nitrifiers					$b_{A_N} X_{BA_N}$
6 Decay of Sulfide Oxidizers					$b_{A_S} X_{BA_S}$
7 Hydrolysis of Entrapped Organics					$k_h\left(\frac{X_S/X_{BH}}{K_X+(X_S/X_{BH})}\right)\left(\frac{S_{O_2}}{K_{OH}+S_{O_2}}\right)X_{BH}$
Observed Reaction Rate $[ML^{-3}T^{-1}]$	$r_i=\sum_j \nu_{ij}\rho_j$				
Stoichiometric coefficients: Y_H, Y_{AN}, Y_{AS} - yield coefficients, mass of heterotrophs, nitrifiers, and sulfur oxidizers produced per unit mass of readily biodegradable substrate, ammonia nitrogen, and sulfide sulfur utilized f_P - mass of inert organic matter generated per unit mass of active biomass decayed [M(COD)/M(COD)]	Nitrate nitrogen $[M(N)L^{-3}]$	**Sulfide sulfur $[M(S)L^{-3}]$**	Sulfate sulfur $[M(S)L^{-3}]$	Alkalinity, molar unit	Kinetic coefficients: heterotrophs: μ_H, K_S, K_{OH}, b_H, k_h, K_X autotrophs: nitrifiers: μ_{AN}, K_{NH}, K_{OA}, b_{AN} sulfur oxidizers: μ_{AS}, K_{HS}, K_{OA}, b_{AS}

3.2.3 Process Model Development

The refinery activated sludge model developed in Section 3.2.2 is used to develop a process model for the refinery activated sludge process.

3.2.3.1 Aeration Tank

The aeration tank is completely mixed, and is treated here as a CSTR (continuous stirred tank reactor). State equations are established by writing mass balance equations for each component in the aeration tank.

$$V\frac{d}{dt}\begin{bmatrix}\text{concentration of}\\ \text{component } i\end{bmatrix}=\begin{bmatrix}\text{flow rate of}\\ \text{influent Q}\end{bmatrix}\begin{bmatrix}\text{conc. of component}\\ i \text{ in influent } \mathrm{C}_{\mathrm{i}_\mathrm{o}}\end{bmatrix}$$
$$+\begin{bmatrix}\text{flow rate of}\\ \text{return sludge } \mathrm{Q}_\mathrm{r}\end{bmatrix}\begin{bmatrix}\text{conc. of component}\\ i \text{ in return sludge } \mathrm{C}_{\mathrm{i}_\mathrm{r}}\end{bmatrix}$$
$$-\begin{bmatrix}\text{flow rate of}\\ \text{outflow } \mathrm{Q}+\mathrm{Q}_\mathrm{r}\end{bmatrix}\begin{bmatrix}\text{conc. of component}\\ i \text{ in outflow } \mathrm{C}_\mathrm{i}\end{bmatrix}+[\text{source / sink}]$$

where subscript o and r denote influent and return sludge respectively.

Soluble inert organic matter:

$$\frac{dS_I}{dt}=\frac{QS_{I_o}+Q_rS_{I_r}-(Q+Q_r)S_I}{V} \tag{3.45}$$

Readily biodegradable substrate:

$$\frac{dS_S}{dt}=\frac{QS_{S_o}+Q_rS_{S_r}-(Q+Q_r)S_S}{V}+\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_{O_2}}{K_S+S_{O_2}}\right)X_{BH} \tag{3.46}$$

Inert particulate:

$$\frac{dX_I}{dt}=\frac{QX_{I_o}+Q_rX_{I_r}-(Q+Q_r)X_I}{V} \tag{3.47}$$

Slowly biodegradable substrate:

$$\frac{dX_S}{dt}=\frac{QX_{S_O}+Q_rX_{S_r}-(Q+Q_r)X_S}{V}+(1-f_P)b_HX_{BH}+(1-f_P)b_{AN}X_{AN}$$
$$+(1-f_P)b_{AS}X_{AS}-k_h\left(\frac{X_S/X_{BH}}{K_X+X_S/X_{BH}}\right)\left(\frac{S_{O_2}}{K_{OH}+S_{O_2}}\right)X_{BH} \qquad (3.48)$$

Particulate Inert organic matter from decay:

$$\frac{dX_P}{dt}=\frac{QX_{P_O}+Q_rX_{P_r}-(Q+Q_r)X_P}{V}+f_Pb_HX_{BH}+f_Pb_{AN}X_{AN}+f_Pb_{AS}X_{AS} \qquad (3.49)$$

Active heterotrophs:

$$\frac{dX_{BH}}{dt}=\frac{QX_{BH_O}+Q_rX_{BH_r}-(Q+Q_r)X_{BH}}{V}+\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_{O_2}}{K_{OH}+S_{O_2}}\right)X_{BH}-b_HX_{BH} \qquad (3.50)$$

Active autotrophs:

$$\frac{dX_{BA_N}}{dt}=\frac{QX_{BA_{N_O}}+Q_rX_{BA_{N_r}}-(Q+Q_r)X_{BA_N}}{V}$$
$$+\hat{\mu}_{A_N}\left(\frac{S_{NH}}{K_S+S_{NH}}\right)\left(\frac{S_{O_2}}{K_{OH}+S_{O_2}}\right)X_{BA_N}-b_{A_N}X_{BA_N} \qquad (3.51)$$

$$\frac{dX_{BA_S}}{dt}=\frac{QX_{BA_{S_O}}+Q_rX_{BA_{S_r}}-(Q+Q_r)X_{BA_S}}{V}$$
$$+\hat{\mu}_{A_S}\left(\frac{S_{HS}}{K_{HS}+S_{HS}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_S}-b_{A_S}X_{BA_S} \qquad (3.52)$$

Dissolved Oxygen:

$$\frac{dS_O}{dt}=\frac{QS_{O_O}+Q_rS_{O_r}-(Q+Q_r)S_O}{V}-\frac{1-Y_H}{Y_H}\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_{O_2}}{K_{OH}+S_{O_2}}\right)X_{BH}$$
$$-\frac{4.57-Y_{A_N}}{Y_{A_N}}\hat{\mu}_{A_N}\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_N} \qquad (3.53)$$
$$-\frac{2-Y_{A_S}}{Y_{A_S}}\hat{\mu}_{A_S}\left(\frac{S_{HS}}{K_{HS}+S_{HS}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_S}+GTR_{O_2}$$

where GTR_{O_2} is the oxygen transfer rate which can be describe by Equation (3.11) except that the partial pressure of oxygen is constant and equals to 0.21 atm for air system.

Total ammonia-N:

$$\frac{dS_{NH}}{dt}=\frac{QS_{NH_o}+Q_rS_{NH_r}-(Q+Q_r)S_{NH}}{V}-i_{XB}\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_{O_2}}{K_{OH}+S_{O_2}}\right)X_{BH}$$
$$-\left(i_{XB}+\frac{1}{Y_{A_N}}\right)\hat{\mu}_{A_N}\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_N} \tag{3.54}$$
$$-i_{XB}\hat{\mu}_{A_S}\left(\frac{S_{HS}}{K_{HS}+S_{HS}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_S}$$

Nitrate:

$$\frac{dS_{NO}}{dt}=\frac{QS_{NO_o}+Q_rS_{NO_r}-(Q+Q_r)S_{NO}}{V}+\frac{1}{Y_{A_N}}\hat{\mu}_{A_N}\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_N} \tag{3.55}$$

Sulfide:

$$\frac{dS_{HS}}{dt}=\frac{QS_{HS_o}+Q_rS_{HS_r}-(Q+Q_r)S_{HS}}{V}-\frac{1}{Y_{A_S}}\hat{\mu}_{A_S}\left(\frac{S_{HS}}{K_{HS}+S_{HS}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_S} \tag{3.56}$$

Sulfate:

$$\frac{dS_{SO}}{dt}=\frac{QS_{SO_o}+Q_rS_{SO_r}-(Q+Q_r)S_{SO}}{V}+\frac{1}{Y_{A_S}}\hat{\mu}_{A_S}\left(\frac{S_{HS}}{K_{HS}+S_{HS}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_S} \tag{3.57}$$

Alkalinity:

$$\frac{dS_{ALK}}{dt}=\frac{QS_{ALK_O}+Q_rS_{ALK_r}-(Q+Q_r)S_{ALK}}{V}-\frac{i_{XB}}{14}\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_{O_2}}{K_{OH}+S_{O_2}}\right)X_{BH}$$
$$-\left(\frac{i_{XB}}{14}+\frac{1}{7Y_{A_N}}\right)\hat{\mu}_{A_N}\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_N} \tag{3.58}$$
$$-\left(\frac{i_{XB}}{14}+\frac{1}{32Y_{A_S}}\right)\hat{\mu}_{A_S}\left(\frac{S_{HS}}{K_{HS}+S_{HS}}\right)\left(\frac{S_{O_2}}{K_{OA}+S_{O_2}}\right)X_{BA_S}$$

The particulate components, X_I, X_S, X_P, X_{BH}, X_{BAN} and X_{BAS} are combined together to form MLVSS, and their units are converted from COD to mg/l using a conversion factor of 1.48 (COD mg/l)/(VSS mg/l) (Dold *et al.*, 1986). X_{nv} is combined with MLVSS to form MLSS.

3.2.3.2 Secondary Clarifier

The secondary clarifier model included in the petroleum refinery activated sludge process model is the same as that of the new high-purity oxygen activated sludge process model (see Section 3.1.2.2 of this chapter).

3.2.3.3 Environmental Effects

The limitation of dissolved oxygen on aerobic activities is reflected by the incorporation of DO switching functions in the model. A simplified approach was adopted for the consideration of inhibition through the use of apparent half-velocity coefficients. The effects of temperature and pH, however, deserve more detailed description.

3.2.3.3.1 Temperature

Temperatures of both influent and effluent of the activated sludge unit in the model refinery can go over 100 °F (Figure 3.10 and Figure 3.11). Operating experience reveals that loss of nitrification has been frequently observed whenever the temperature goes over 100 °F. This suggests that the upper bound of the temperature range is high enough that it becomes inhibitory to activated sludge kinetics. It also indicates that Van't Hoff-Arrhenius is no longer valid for the whole temperature spectrum. The equation used to describe temperature effect is adopted from Bailey and Ollis (1986):

$$\hat{\mu}_T = \frac{\hat{\mu} e^{-\frac{E}{RT}}}{1 + e^{\frac{\Delta S_d}{R}} \cdot e^{-\frac{\Delta H_d}{RT}}} \tag{3.59}$$

where $\hat{\mu}_T$ - rate coefficient at temperature T (K); $\hat{\mu}$ - rate constant; E - activation energy; ΔS_d - change of standard entropy; ΔH_d - change of standard enthalpy; R - universal gas constant. Equation 3.59 may be called extended Arrhenius. Figure 3.12 is a plot of Equation (3.59) using the following parameter values: $\hat{\mu}$ = 258 mm3/min, E = 3.5 kcal/mol, ΔS_d = 168 kcal mol^{-1} K^{-1}, ΔH_d = 168 kcal mol^{-1} K^{-1}. For activated sludge process modeling, the physical implication of these constants is less important. The more important thing is that Equation (3.59) predicts a temperature effect similar to that observed in experiment (Figure 2.16). For engineering purposes, Equation (3.59) can be formulated as

$$\hat{\mu}_T = \frac{\hat{\mu} e^{-\frac{a}{T}}}{1 + b e^{-\frac{c}{T}}} \tag{3.60}$$

where a, b, c = constants. The values of a, b, and c can be obtained when Equation (3.60) is used to fit experimentally observed temperature pattern, such as Figure 2.16.

It is not explicitly stated above if the inhibitory effect of temperature, as described by Equation (3.60), is reversible or irreversible. The way it is modeled, however, implicitly states that the inhibitory effect is reversible. That is, when temperature goes back to the normal range, the kinetics also resumes back to normal. This, however, may not be always true.

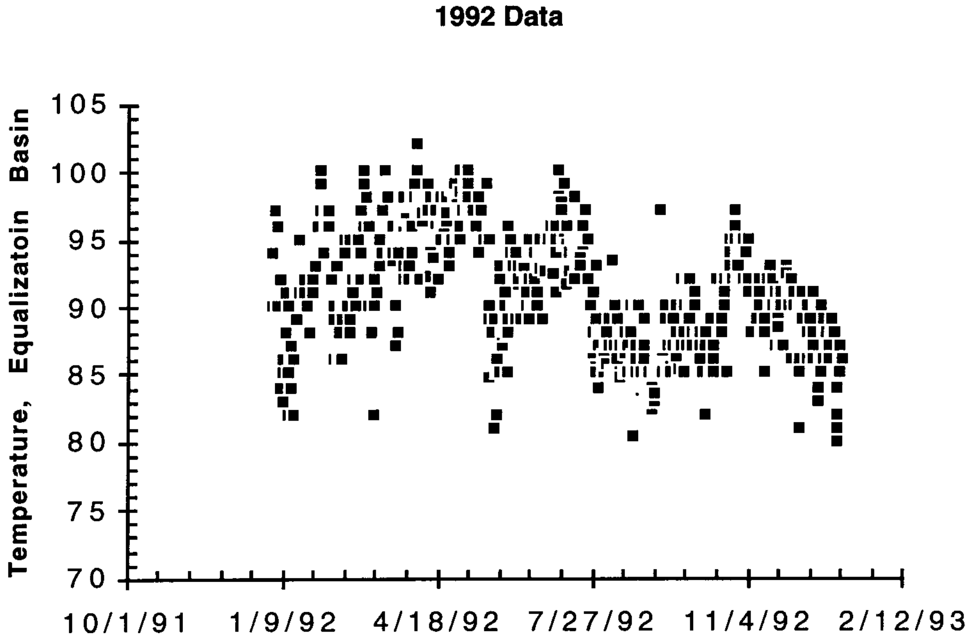


Figure 3.10 Observed equalization basin temperature (influent to activated sludge unit)

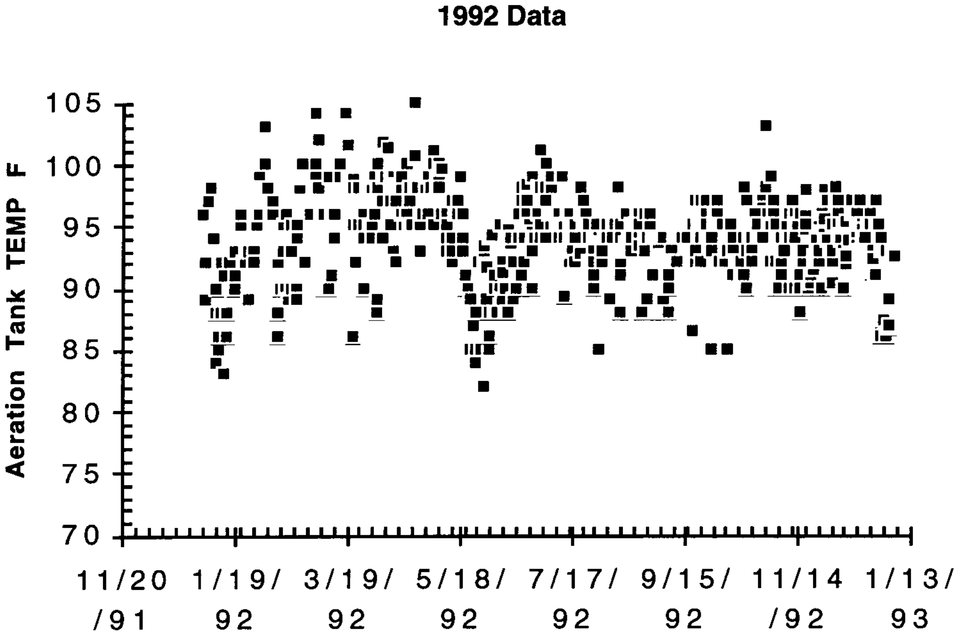


Figure 3.11 Observed aeration tank temperature

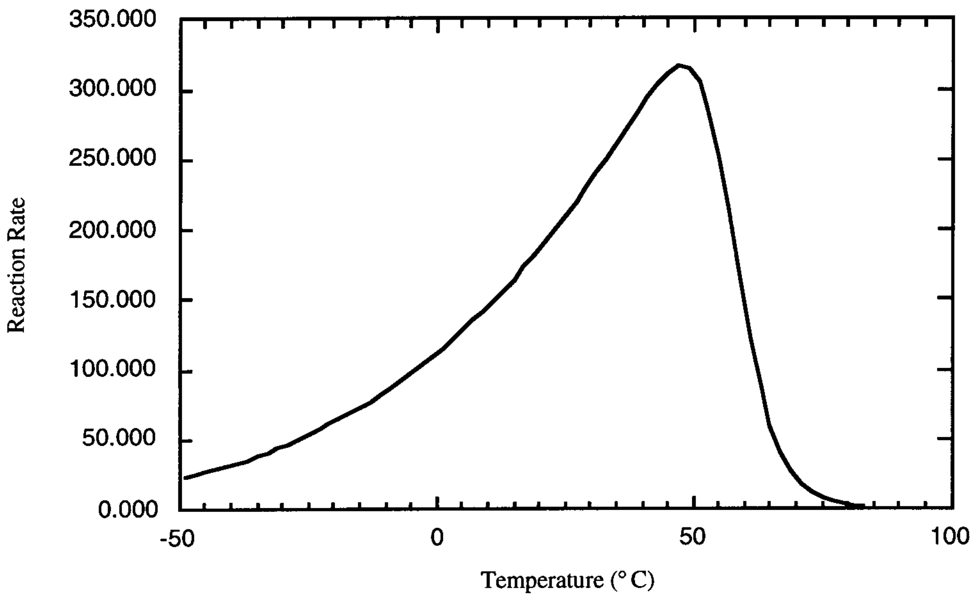


Figure 3.12 Modeled temperature effect

3.2.3.3.2 pH

The observed pH effect, as shown in Figure 2.17, can be described by the following equation:

$$\alpha = \frac{1}{\frac{[\mathrm{H}^+]}{K_1} + 1 + \frac{K_2}{[\mathrm{H}^+]}} \tag{3.61}$$

where α- fraction of the rate at optimum pH; K_1, K_2 - constants; $[\mathrm{H}^+]$ - hydrogen ion concentration. If we substitute $[\mathrm{H}^+]$ with pH then

$$\alpha = \frac{1}{\frac{10^{-pH}}{K_1} + 1 + \frac{K_2}{10^{-pH}}} \tag{3.62}$$

Equation 3.62 was originally derived from enzyme kinetics. Perhaps the most important thing is the mathematical form of Equation 3.60 which exhibits a shape like the one depicted in Figure 2.17. Equation (3.62) is similar to the ionization fraction α_1 of a diprotic acid H_2A and K_1 and K_2 are equivalent to K_{a1} and K_{a2} of H_2A. When pH falls into the range of $pK_{a1}<pH<pK_{a2}$, the fraction of HA^- approaches to 1. For Equation (3.62) the optimum pH is $pH_{optimum} = \frac{pK_1 + pK_2}{2}$ and the curve is symmetrical about this optimum pH. α equals to 0.50 when $pH=pK_1$ or $pH=pK_2$. For $pH < pK_1 - 1$ or $pH > pK_2 + 1$ α approaches to zero (< 0.0909). For $pK_1 + 1 < pH < pK_2 - 1$ α approaches to 1 (> 0.9091). The characteristic of the pH function (Equation 3.60) makes it easy to adjust K_1 and K_2 to fit observed pH effects. For example if the optimum pH range is 7 to 10 we can set $pK_1 = 6$ and $pK_2 = 11$. The optimum pH is thus 8.5 and within $7 < pH < 10$ α is between 0.9 and 1 (Figure 3.13). When pH drops below 7 and rise above 10 α quickly drops to zero.

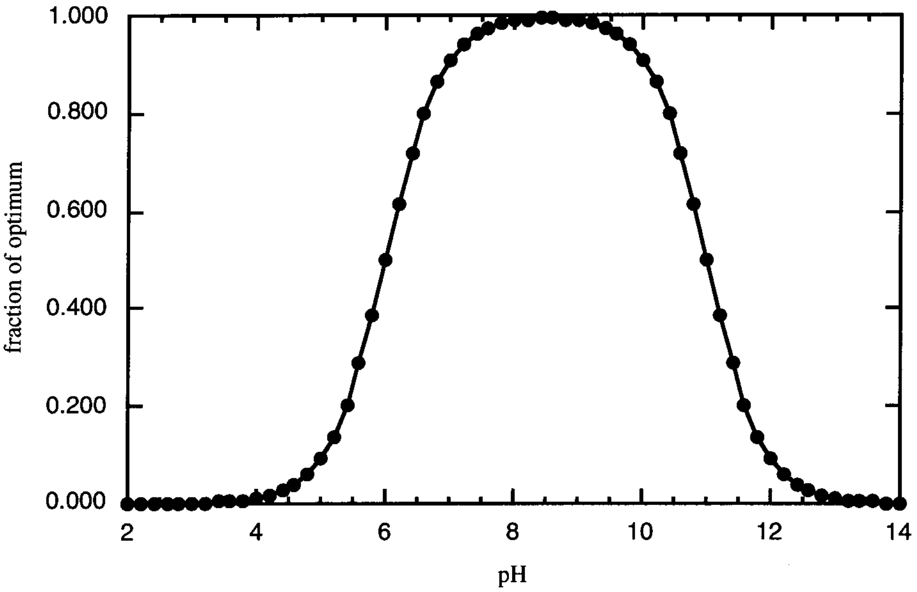


Figure 3.13 Modeled pH effect

4. MODEL IMPLEMENTATION, CALIBRATION, VERIFICATION AND VALIDATION

The implementation, calibration, verification and validation of the two dynamic models are presented in this chapter. The two mathematical models developed in Chapter 3 are composed of ordinary differential equations (ODEs) as well as algebraic equations. Although the mathematical model governs the behavior of a process, it has to be solved in order to reveal the relation between model inputs and outputs. In most cases, the solution of a ODE mathematical model requires numerical methods and the implementation of the numerical solution is almost always done by using a computer. Strictly speaking, there is a difference between the mathematical model and its corresponding computer model; practically they are considered as the same since mathematical models of most engineering problems are in forms of either ODE or PDE (partial differential equation) which can only be solved numerically on computer. In this investigation, model implementation is defined as the development of a computer code which solves the mathematical models numerically.

Model credibility must be established before it can be applied to assist the design, optimization, operation, and control of the activated sludge process. Most often this is accomplished through model calibration, a process in which simulations are made to match observations through the "tuning" of model coefficients within acceptable bounds established in the literature. Model verification, the demonstration of model fit for a distinctly different set of environmental conditions, with the same suite of coefficients used in calibration, establishes a much enhanced level of credibility. A model is said to be validated in cases where all inputs are kinetic coefficients are independently measured and simulations match observations.

4.1 Model Implementation

The mathematical models developed in Chapter 3 are implemented into FORTRAN codes - HIPURE2 and PRASIM. HIPURE2 and PRASIM are the computer versions (simulation programs) of the new high-purity oxygen activated sludge process model and the petroleum refinery activated sludge process model respectively.

4.1.1 High-purity Oxygen Activated Sludge Process

The code of the new high-purity oxygen activated sludge process model, HIPURE2, is written in FORTRAN 77 and is compatible with Microsoft FORTRAN (versions 5.1), IBM AIX XL FORTRAN (versions 2.2 and 2.3), and IBM VS FORTRAN. The codes have been thoroughly checked and have been compiled using the following FORTRAN compilers, machines, and operation systems: 1) Microsoft FORTRAN on an IBM PC compatible 486 machine (50 MHz) using the MS-DOS/MS-Windows operating system; 2) IBM AIX XL FORTRAN in an IBM RISC 6000 POWERstation machine (Model 520) using the AIX operation system; 3) IBM VS FORTRAN on UCLA's IBM 3090 super computer using the MVS operation system. All machines produced virtually identical outputs. Small differences in the sixth significant digit are due to the way each machine stores floating point variables.

The governing equations developed in Chapter 3 produce a large collection of different equations. For the high-purity oxygen activated sludge process, the current configuration, including DO controllers and gas purity controller, results in 86 ordinary differential equations (ODEs) with each stage requiring 19 ODEs. The clarifier requires

10 ODEs and two more are required for stage 4 purity and system pressure controllers (Table 4.1).

Table 4.1 Number of Equations

Equation Type	Aeration Tank (one stage only)			Clarifier	Total Aeration Tank (4 stages) + Clarifier
	Gas	Gas-Liquid	Liquid		
ODE	3	0	16	10	86
AE	5	3	4	4	48

ODE - Ordinary Differential Equation
AE - Algebraic Equations

The code structure of HIPURE2 is similar to HIPURE, which is Stenstrom's version of the high-purity oxygen activated sludge process simulation program (Stenstrom, 1990). The first version of HIPURE used the conventional activated sludge model documented by Lawrence and McCarty (1970) and the second version used the structured Clifft and Andrews Activated Sludge Model (Stenstrom, *et al.*, 1989; Stenstrom, 1990; Clifft and Andrews, 1981). The most significant difference between HIPURE2 and HIPURE is that HIPURE2 substituted the IAWQ Activated Sludge Model No. 1 for the Clifft and Andrews Activated Sludge Model. HIPURE2 is written in a modular fashion using subroutines and functions as much as possible to produce an efficient, readable code. The modular fashion also facilitates the use of the MAKE utilities of Microsoft FORTRAN and IBM AIX XL FORTRAN compilers which makes it possible that only the module changed is recompiled while the objective file of other modules are linked directly without recompilation. The code uses a total of 21 subprograms and a total of 1600 lines of source code and comments. The code is structured in such a way that it can be expanded to include as many equations as necessary. There are no design aspects that limit the size of the code; only the capacity and speed of the computer limit the number of equations that can be included in the model. Figure 4.0 shows an overview of HIPURE2.

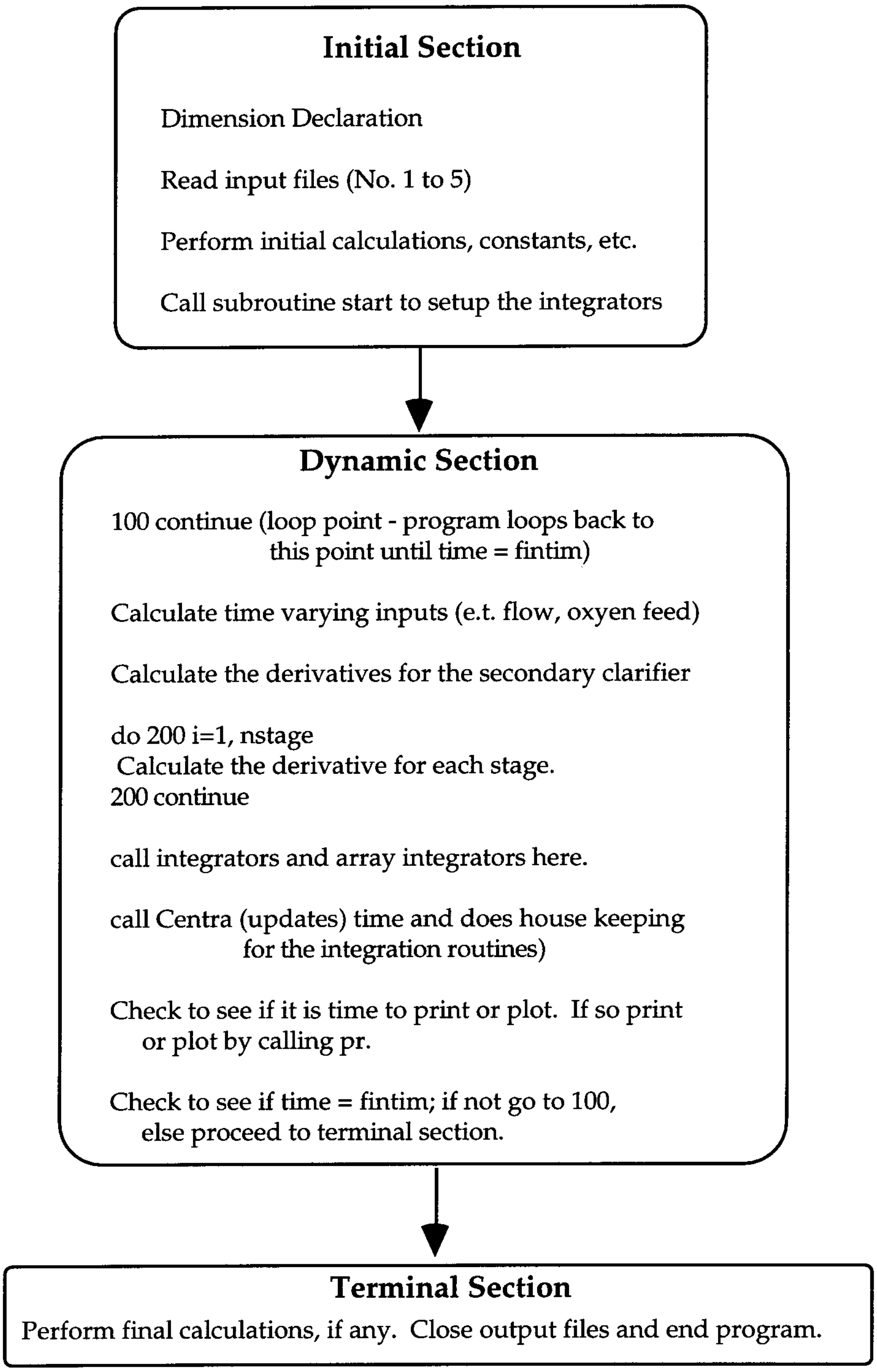


Figure 4.0 Block diagram of HIPURE2

Four integration methods are provided - Euler (or Rectangular), Modified Euler (or Trapezoidal), fixed step Runge Kutta, and variable step Runge Kutta. The variable step method may be the best choice for many problems and may save time. For problems with abrupt changes in the inputs, a fixed step procedure may be preferable. The procedures are common and described in a number of numerical analysis textbooks, including James *et al.* (1985). The code was developed to resemble IBM's CSMP program; however, none of the code came from IBM.

The process model uses five files for input. Four are required for all simulations. The fifth is required only if arbitrary input functions are needed.

The TIMERS input file is read first. Table 4.2 shows a sample of the TIMERS file. TIMERS is formatted in such a format that the first ten columns of each line are reserved for the value of a parameter, which is read and assigned to the parameter when the code is executed. The rest of the line describes the parameter and its symbol. The first line contains an integer which must appear in column 1. This integer defines the method and the numerical codes are shown in the table. The next line contains the integration step size. For the variable method, this value as a starting point, and the step may increase or decrease in size. An internal variable DELMIN specifies the minimum step size, and this value has been arbitrarily set to DELT/10^4. It can be changed by editing the START.FOR subprogram. PRDEL and OUTDEL define the intervals for printing and plotting. The current version of HIPURE2 does not plot but writes output to file OUTPUT.DAT which can be read into a plotting software, such as Microsoft EXCEL and plotted. Like DELMIN, the ABSERR and RELERR terms are used only for the variable step Runge Kutta procedure. Default values will be substituted if they are not included in the input file. TIMERS is read on FORTRAN I/O unit 8. Format for this file and others are F10.0, which requires that input data be contained within the first 10 spaces and the data must include a decimal point (e.g. 10., not 10). If the code is compiled with a different compiler other than the ones used here, different rules may apply.

Table 4.2 Timers File

4	method	integration method (1 = Euler, 2 = modified Euler, 3 = Runge Kutta, 4 = variable time step Runge-Kutta
0.0010	delt	integration time step, hour
1.0	prdel	time interval for printing output on screen, hour
1.0	outdel	time interval for writing output to data file, hour
24.	fintim	finish time (total time of simulation), hour
0.001	abserr	absolute error (variable time step Runge-Kutta method)
0.001	abserr	relative error (variable time step Runge-Kutta method)

Table 4.3 shows a sample of the PARAMS file. This file contains the parameters and coefficients, such as those described in the governing equations in Chapter 3. The model includes provisions for DO and stage 4 oxygen purity control. The limits for the controlled and the controller gains are included in this file as well. To restrict the values of K_La or the stage 4 oxygen purity (partial pressure), specify the appropriate limits in this file. If no control is required or wanted, set controller gains to zero. The values of K_La specified in the file are initial estimates if the controllers are used. Otherwise the initial values will be used throughout the program. The program assumed that K_La can be changed if the controller is active and the upper and lower bounds are not equal. The format for this file is similar to the other file in that the first 10 spaces of each line are reserved for the variables, which must include a decimal point. The remaining spaces can be used for comments.

The clarifier area and depth are specified in this file as well as the reactor volumes; both liquid and gas reactor volumes are required. The clarifier area is the total area of all clarifiers. The reactor volume is the volume of a single train, stage-by-stage. The PARAMS file is read on FORTRAN I/O unit 9.

Table 4.3 PARAMS File

0.46	alpha1 (0.46) stage 1 alpha factor of the aeration tank
0.55	alpha2 (0.55) stage 2
0.64	alpha3 (0.64) stage 3
0.67	alpha4 (0.67) stage 4
0.95	beta beta factor of the aeration system
5.8	kla1 (kla for stage 1, 1/hour) **************************
2	kla2 (kla for stage 2, 1/hour)
0.8	kla3 (kla for stage 3, 1/hour)
0.7	kla4 (kla for stage 4, 1/hour)
0	Lower limit for kla1 **************************
0	Lower limit for kla2
0	Lower limit for kla3
0	Lower limit for kla4
50	Upper limit for kla1 **************************
40	Upper limit for kla2
30	Upper limit for kla3
20	Upper limit for kla4
6	DO set point for Stage 1 ***************************
6	DO set point for Stage 2
6	DO set point for Stage 3
6	DO set point for Stage 4
10	Proportional gain for DO control (set to zero for no control
5	Reset (integral) gain for DO control (set to zero for no
0.4	O2 purity in stage 4 set point
2	Proportional gain for stage 4 purity control
1	Rest (integral) gain for stage 4 purity control
0	pgs4po2
0	rgs4po2
1.005	Stage 1 total pressure set point 2-6 mmHg
0	Proportional gain for stage 1 total pressure control
0	Reset (integral) gain for stage 1 total pressure control
0.67	yh - heterotrophic yield (g cell COD formed/g COD oxidize
0.08	fp - fraction of biomass yielding particulate products
0.086	ixb - mass N/mass COD in biomass 0.086
1.375	co2o2 mass co2/mass O2 consumed

Table 4.3 PARAMS File (cont.)

1.48	codvss - converting the unit of MLVSS from COD to VSS
0.06	ixp - mass N/mass COD in products from biomass decay
6	uh - maximum specific growth rate of heterotrophs, 1/day
20	ks - saturation coefficient (heterotrophic growth)
0.2	koh - saturation coefficient (DO 'switch' function)
0.62	bh - decay rate constant (heterotrophs)
0.08	ka - ammonification rate constant, m^3/(gCOD.day)
3	kh - hydrolysis rate constant
0.03	kx - saturation coefficient (hydrolysis)
212372	area - clarifier area (ft^2) 1/4*pi*(130)^2x16
20	adepth - clarifier depth (ft)
10	anelem - number of element in
1	ameth - flag, indicates SRT calculation methods
11520	VG1 (gas, ft^3) (48x48x5?)
11520	VG2 (gas, ft^3)
11520	VG3 (gas, ft^3)
11520	VG4 (gas, ft^3)
69120	VL1 (liquid, ft^3)(48x48x30)
69120	VL2 (liquid, ft^3)
69120	VL3 (liquid, ft^3)
69120	VL4 (liquid, ft^3)
10000	Kflow

The model works by dividing the inputs equally among the specified number of trains. Therefore, the volume of only one train is required. To obtain global mass balances, the values associated with each are multiplied by the number of trains in service. This procedure assumes that all trains are operated in identical fashions. The procedure for handling the clarifier area is different. The total area must be specified, and it divided equally among trains. This procedure is required because clarifiers may not be assigned to specific trains, and could be shared among trains.

The INITS file is next read on FORTRAN I/O unit 10 and is shown in Table 4.4. This file specifies the initial conditions of all the state variables. The values are read across the page into an array. The format of the file is 5F10.0. Each entry must have a decimal point. The initial concentrations of each state variable (e.g. readily biodegradable substrate, particulate substrate, active heterotrophs, etc.) must be specified. At the end of a normal run of the model, the final values of the state variables are written into a file called NINITS. This file may be renamed INITS in order to restart the model at the conclusion of a run. The restart using this procedure will be nearly equal to the pervious simulation, with the exception of inputs that may have been changed by controllers, such as the $K_L$as or the oxygen feed rate.

Table 4.4 INITS File

0	23	23	23	23	Si	
0	23.739	4.992	2.251	1.728	Ss	
0	978.334	978.155	977.974	977.794	Xi	
0	27.126	19.261	14.883	12.549	Xs	
0	205.139	205.101	205.063	205.026	Xnv	
0	1396.391	1408.67	1407.897	1404.282	Xb	
0	90.582	91.667	92.752	93.834	Xp	
0	7.531	9.056	8.944	9.373	S_{O2}	
0	16.576	16.708	17.436	18.082	NH_3	
0	1.776	1.333	1.042	0.862	Snd	
0	2.652	1.824	1.371	1.134	Xnd	
0	160.773	161.242	163.842	166.149	Salk	
0.058	0.068	0.072	0.075		CO2	
0.85	0.793	0.764	0.738		O2	
6.192	6.159	6.15	6.143		pH	
1266.725	1264.852	1265.103	1263.235	1610.212		2802
3805.576	4676	5583.347	6896.848	Clarifier solids conc.(mg/l)		

* See Table 3.1 for notations of the last column

The INPUTS file is read next on FORTRAN I/O unit 11 and is shown in Table 4.5. This file contains the influent flows and concentrations. Input variables are read from the first 10 columns, as before, with a decimal point. This feature has not been tested thoroughly for the current version of HIPURE2 because no appropriate diurnal data was available. The step feed option, which is available in many activated sludge processes, is also allowed in HIPURE2. The lines which have "Percent flow to Stage 1," etc. specify what percent of the influent flow is diverted to each stage. The percents for all four stages should total to 100. The recycle flow is specified as a fraction (0 to 1) of the input flow and always enters stage 1. For cases where the flow rate is changing, the recycle flow rate will change also (ratio recycle control).

Table 4.5 INPUTS Files

23	Conc. influent Si (mg COD/L)
140	Conc. influent Ss (mgCOD/L)
62	Conc. influent particulate inert Xi (mgCOD/L)
80	Conc. influent particulate biodegradable Xs (mgCOD/L)
13	Conc. Influent non-volatile solids Xnv (mg/L)
0	Conc. Influent active biomass Xbh(mgCOD/L)
0	Conc. Influent decay products Xp (mgCOD/L)
0	Conc. influent dissolved oxygen So2 (mgO2/L)
20	Conc. Influent ammonia Snh3 (mg/L)
3	Conc. influent soluble organic nitrogen Snd (mgCOD/L)
4	Conc. influent particulate organic N Xnd (mgCOD/L)
173	Conc. Influent alkalinity Salk (as CaCO3, mg/L)
7	Influent pH
0	Leak parameter
6	Number of Basins
143.2	Flow rate Q (MGD)
100	Percent flow to Stage 1 (step feed)
0	Percent flow to Stage 2 (step feed)
0	Percent flow to Stage 3 (step feed)
0	Percent flow to Stage 4 (step feed)
0.353	Recycle Rate (fraction of input flow rate)
2	SRT (set point, days)
23.72	Temperature (deg C)
120	Oxygen feed in tons per day
0.97	Fractional oxygen purity of O2 feed
1	Input type (1=constant, 2=sinusoidal, 3=actual diurnal data)
20	Percent sinusoidal variation in flow input (input type = 2)
20	Percent sinusoidal variation in Ss (input type = 2)
20	Percent sinusoidal variation in Xs (input type = 2)

The input type parameter needs further explanation. If the input type is specified as 1, the liquid inputs are constant. If the input type is specified as 2, the liquid inputs assumed to vary in a sinusoidal fashion with a period of 1 day. The magnitude of the variation is specified on the following lines. For example, if the flow rate Q were specified as 200 MGD with input = 2 and a percent variation of 20, the flow would vary sinusoidally between a 160 MGD minimum to a 240 MGD maximum with a period of 1 day . If the input is specified as 3, the file DIURNAL is read, which allows an arbitrary input to be specified.

The file DIURNAL is read on FORTRAN I/O number 13 and is shown in Table 4.6. The first line of the file contains a two digit integer in columns 1 and 2 which specifies the number of flow data pairs that follow. The flow data pairs consist of a timer of the day (0. = midnight, 24 = midnight) and a normalized value of flow. The average of the normalized values of flow should always have a mean of 1.0. The data must be entered in ascending order and the intervals need not to be constant. Interesting input functions can be created (e.g. square waves) using this procedure. The particulate BOD and soluble data pairs follow in the file in a similar fashion. The time intervals need not match the flow time intervals. A minimum of two data pairs is required. A maximum of 200 pairs is allowed for each function, but this number can be increased, if desired, by changing the dimensions and recompiling the main program and function AFGEN.FOR.

Table 4.6 DIURNAL file

```
13                        number of data pairs for flow
0           1.1           time=12 midnight
2           1.02          time=2 AM
4           0.9           time=4 AM
6           0.78          time=6 AM
8           0.71          time=8 AM
10          0.83          time=10 AM
12          1             time=12 Noon
14          1.1           time=2 PM
16          1.12          time=4 PM
```

Table 4.6 DIURNAL file (cont.)

18	1.13	time=6 PM
20	1.15	time=8 PM
22	1.1	time=10 PM
24	1.1	time=12 midnight
14		number of data pairs Ss
0	1	
1.5	1.06	
3.5	1.11	
5.5	0.9	
7.5	1.06	
9.5	0.94	
11.5	1.06	Readily biodegradable substrate Ss
13.5	1.18	
15.5	1.02	
17.5	0.94	
19.5	0.92	
21.5	0.85	
23.5	0.94	
24	0.97	
14		number of data pairs
0	1.2	
1.5	1.23	
3.5	1.58	
5.5	1.43	
7.5	1.14	
9.5	0.45	
11.5	0.39	Slowly biodegradable substrate Xs
13.5	0.39	
15.5	0.94	
17.5	1.04	
19.5	1.17	
21.5	1.06	
23.5	1.17	
24	1.19	

4.1.2 Petroleum Refinery Activated Sludge Process

The structure of PRASIM, the computer implementation of the petroleum refinery activated sludge process model developed in Chapter 3, is similar to that of HIPURE2 except the following:

- The aeration tank of the high-purity oxygen activated sludge process model has four stages while the petroleum refinery activated sludge process model is a single-sludge carbon oxidation-nitrification process. Arrays were declared in HIPURE2 for state variables. Single variables were used in PRASIM for state variables.
- PRASIM has less state variables than HIPURE2 because PRASIM does not have a gas-phase model. As a result the PRASIM is not capable of predicting the composition of aeration tank off-gas. PRASIM, nevertheless, has more components in the liquid phase because of the complex nature of the refinery wastewater.

4.2 Model Calibration

The calibration of HIPURE2 and PRASIM is presented in this section. A significant portion of this chapter is devoted to development and evaluation of a model calibration algorithm for the high-purity oxygen activated sludge process.

Process models must be calibrated before being applied. Model calibration represents the process of assigning values to the parameters used in the model such that the difference between model predictions and observations is at its minimum. Good fit, however, is not always guaranteed. When it is difficult to fit model predictions to the observations, the following are all possible causes:

1) The calibration algorithm is not good enough.

2) The process model is not good enough. The model structure needs to be changed.

3) The data set is not good enough. The data set may contain systematic errors. This usually can be accomplished by performing repeated tests and take parallel samples provided enough resources are available.

Many questions need to be answered before a model calibration algorithm is developed and the corresponding calibration program is implemented, such as: what observations should be used for the calibration? how many data points are adequate and what is the appropriate sampling frequency? how many parameter can be rigorously estimated for a given set of observations? The answers to these questions are crucial to the success of the calibration.

Model calibration has been done by hand in many cases in the past and is still widely used. The advantage of this approach, which is called model calibration based on human expertise by Wanner *et al.* (1991), is that it offers an excellent opportunity for model users to feel the model and understand its behavior. This approach, if well performed, delivers the same results as calibration based on mathematical optimization does. The disadvantage is that it is expertise-intensive. Only people who understand the model well are expected to conduct the calibration. The manual approach or calibration based on human expertise also suffers from its inability to handle a large number of data quickly and reliably. The calibration based on mathematical optimization approach, however, could give misleading results if one does not have answers to the questions raised above.

The objective of this section is to present the development and evaluation of a model calibration algorithm for the high-purity oxygen activated sludge process. More specifically, I intend to find out the effects of the following factors on the performance of

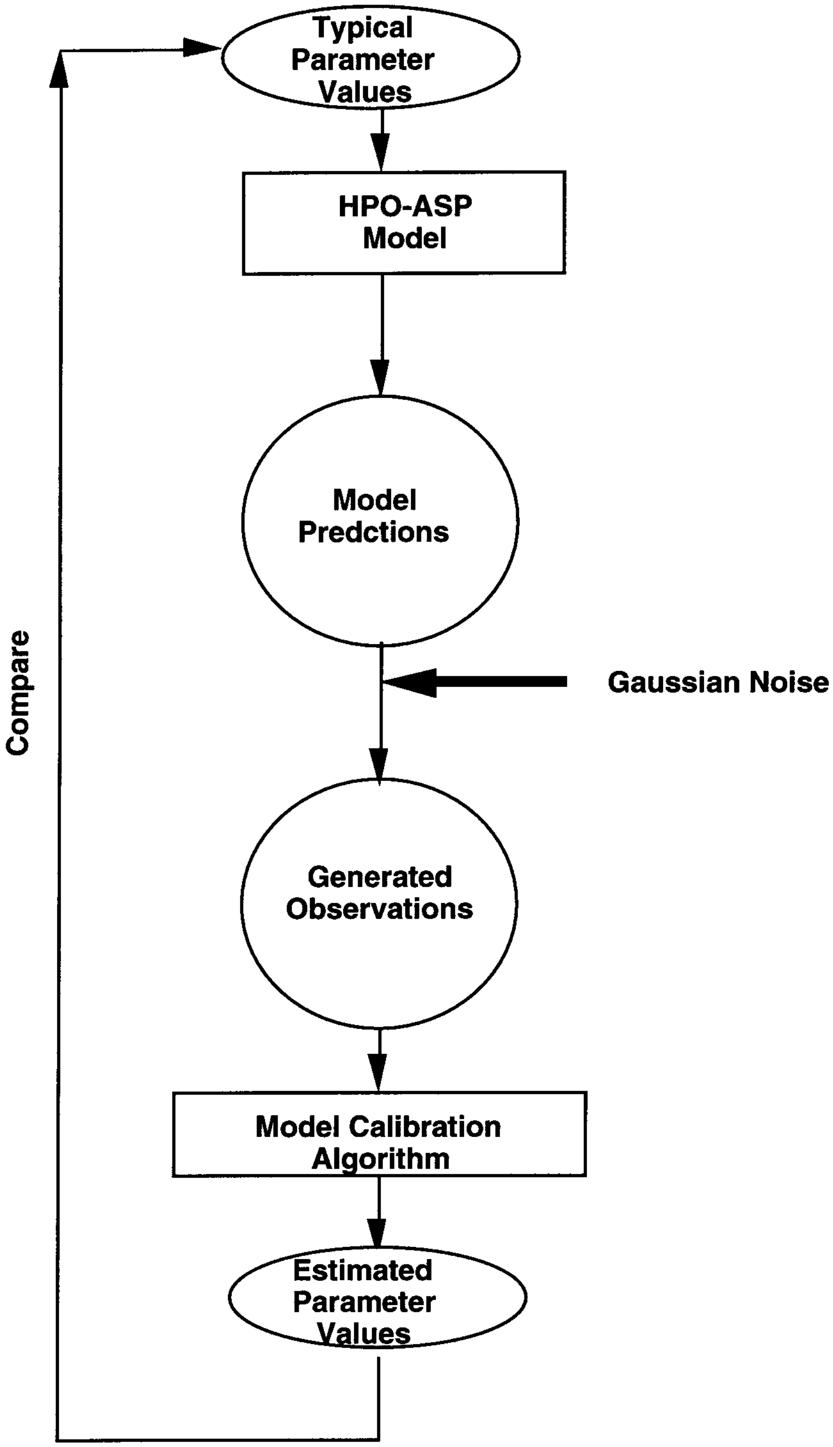


Figure 4.1 Procedures for model calibration algorithm evaluation

the calibration algorithm - data quality, number of data points, and the number of measured variables. The investigation is accomplished through numerical experiments in which the observations are generated numerically by corrupting model predictions with Gaussian noise (Figure 4.1). By doing so, it can be guaranteed that the model is not the cause if the a good fit is not achieved. Other merits of the numerical experiment approach include the advantage of knowing the 'true' values of the parameters and the flexibility of adjusting the data quality (Yuan *et al.* 1994, 1993b).

4.2.1 High-purity Oxygen Activated Sludge Process

The modified IAWQ Activated Sludge Model No. 1 has 11 biokinetic parameters - 4 stoichiometric coefficients and 7 kinetic coefficients (Table 3.1). The total number of parameters are well over 30 (Table 4.3). The necessity of developing a model calibration algorithm is obvious. Tzeng (1992) should be credited for performing the first model calibration based on mathematical optimization using the observations from a full-scale oxygen activated sludge treatment plant. Tzeng, however, did not perform a systematic evaluation of algorithms that he used.

4.2.1.1 Model Calibration Method

The basic approach in all calibrations is usually the same: A objective function (or merit function) is designed that measures the agreement between the data and the model with a particular choice of parameters. The objective function is conventionally arranged so that small values represent close agreement. The parameters of the model are then adjusted to achieve a minimum in the objective function. The adjustment process is thus a problem in minimization in many dimensions.

4.2.1.1.1 Objective Function

Least-squares is the most common form of objective function used. Three kinds of least-squares objective functions can be used: absolute least-squares (ALS) (Equation 4.1), weighted absolute least-squares (WALS) (Equation 4.2), and relative least-squares (RLS) (Equation 4.3). ALS is not appropriate for the activated sludge process because the magnitudes of observations differ significantly. For example, the ranges of some observations in a full-scale HPOASP are: DO 5-12 mg/l; vent gas oxygen purity 0.40-0.80; MLSS 1000-2000 mg/l. One possible solution to the uneven-weight problem associated to the ALS objective function is WALS which solves the problem by assigning an appropriate set of weights to different variables measured. Another possible solution is to normalize the function by dividing the difference between the model-predicted and observed values by the model-predicted value. This is RLS (Equation 4. 3). Equation (4.4) represents the relative least-squares objective function that uses observations of first stage DO, fourth stage DO, vent gas oxygen purity, and MLSS.

$$f = \sum_{j=1}^{m}\left(\sum_{i=1}^{n}\varepsilon_{a_{ij}}^{2}\right) = \sum_{j=1}^{m}\left(\sum_{i=1}^{n}\left(S_{ij} - S_{ij}^{*}\right)^{2}\right) \tag{4.1}$$

$$f = \sum_{j=1}^{m}\left(\sum_{i=1}^{n}\gamma_{ij}\varepsilon_{a_{i}}^{2}\right) = \sum_{j=1}^{m}\left(\sum_{i=1}^{n}\gamma_{ij}(S_{ij} - S_{ij}^{*})^{2}\right) \tag{4.2}$$

$$f = \sum_{j=1}^{m}\left(\sum_{i=1}^{n}\varepsilon_{r_{ij}}^{2}\right) = \sum_{j=1}^{m}\left(\sum_{i=1}^{n}\left(\frac{S_{ij} - S_{ij}^{*}}{S_{ij}^{*}}\right)^{2}\right) \tag{4.3}$$

$$f = \sum_{i=1}^{n}\left(\left(\frac{p_{O_{24}}^{*} - p_{O_{24}}}{p_{O_{24}}^{*}}\right)_{i}^{2} + \left(\frac{S_{O_{21}}^{*} - S_{O_{21}}}{S_{O_{21}}^{*}}\right)_{i}^{2} + \left(\frac{S_{O_{24}}^{*} - S_{O_{24}}}{S_{O_{24}}^{*}}\right)_{i}^{2} + \left(\frac{MLSS^{*} - MLSS}{MLSS^{*}}\right)_{i}^{2}\right) \tag{4.4}$$

where

S = observed variable

i = as subscript, denotes the ith observation

j = as subscript, denotes the jth observed variable

$*$ = as superscript, denotes predicted value

m = total number of observed variables

n = total number of observations

γ = weighting coefficient

ε_a = absolute error

ε_r = relative error

Most measurements in biological systems have normally or log-normally distributed relative errors instead of absolute errors. Saez and Rittmann (1992) demonstrated that the relative least-squares objective function (Equation 4.3) is superior to absolute least-square criterion (Equation 4.1) where observations (state variables) differ significantly in magnitude, such as in the activated sludge process.

4.2.1.1.2 Constraints

The parameters in the high-purity oxygen activated sludge are from mechanistic models and have clear physical meanings. For example, the heterotrophic yield Y_H, which has a unit of g cell COD formed/ g COD substrate metabolized, must have a value between 0 and 1. Lower bound 0 and upper bound 1 are theoretical extremes. In reality, Y_H has an even narrower bound, such as between 0.5 and 0.8. This is true for all parameters in the process model. To ensure that the parameter values selected by the calibration program are physically feasible, if is necessary to impose constraints on them. In the calibration program, the constraints are given in the form of upper and lower bounds. With well defined parameters bounds, it takes less iterations for the objective function to converge to its minimum. However, if the calibration algorithm is robust, the constraints should not be too stringent, that is, the range between the upper and lower bound should not be too narrow.

4.2.1.1.3 Observations

The observations used in this study are 'synthetic' data which are generated mathematically as follows. For a state variable S at time t, the relative error of the observation, S_i, to the exact solution S_i^*, is defined as:

$$\varepsilon_r = \frac{S_i - S_i^*}{S_i^*}$$

thus $S_i = S_i^* + \varepsilon_r S_i^*$. If ε_r is normally distributed, with mean $\mu=0$ and variance $=\sigma$, then the observation S_i is also normally distributed, with mean $\mu= S_i^*$, and variance $=\sigma S_i^*$. If $\sigma=0.10$, this means the variance of the observation equals to 10% of the exact solution S_i^*.

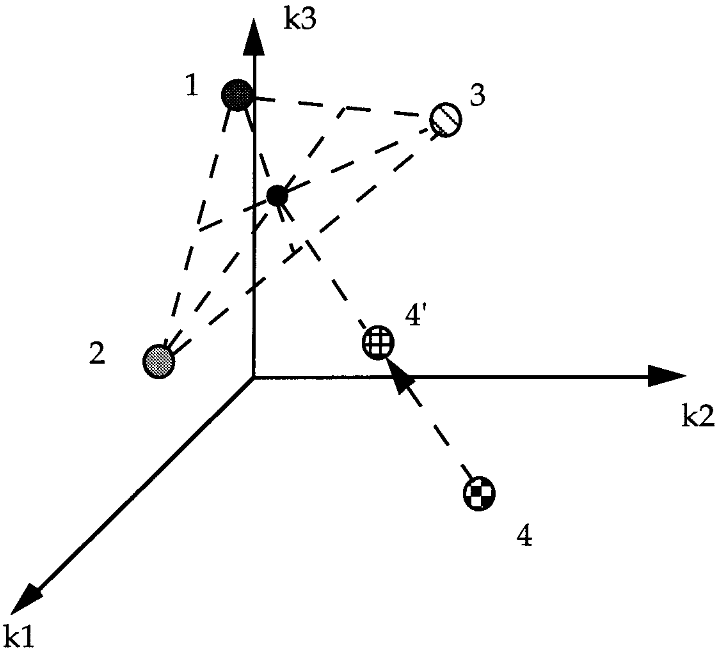


Figure 4.2 Illustration of the Complex Method

4.2.1.1.4 Optimization Method

After the objective function and constraints of parameters are defined, the calibration problem is transformed into a nonlinear, constrained optimization problem. Many optimization techniques are available for this purpose, such as Gauss-Newton method. The particular algorithm used in the research is the Complex Method. The Complex Method was developed in 1965 by Box (Box, 1965). Its derivation is not rigorously based mathematical theory. It is an empirical method. It, however, has been proved to be a very robust optimization algorithm for many messy engineering problems (Little and Williams, 1992). The Complex method is derivative-free, and thus remarkably robust to messy problems such as discontinuities and difficult-to-evaluate or nonexistent derivatives.

Figure 4.2 illustrates the basic idea of the Complex method for a 3-parameter system. Each point (k_1,k_2,k_3) in 3-D space represents a set of parameters to be estimated. The method requires at least four sets of parameters to be initially selected, and scatters them randomly in the domain. For this 3-parameter system, four sets of parameters are chosen. They are denoted as points 1, 2, 3, 4 in Figure 4.2. Mathematically, this is implemented as:

$$\theta_{i,j} = L_i + r_{i,j}(U_i - L_i)$$

where

i = as subscript, denotes the ith parameter ($i=1,2, ..., N$),

j = as subscript, denotes the jth set of parameter ($j=1, 2, 3, ..., K$),

N = number of parameters,

K = number of parameter sets,

$r_{i,j}$ = a random real number between 0 and 1,

$\theta_{i,j}$ = value of the ith parameter in the jth set of parameters,

U_i = upper bound of the ith parameter, and

L_i = lower bound of the ith parameter

Table 4.7 Parameters in the modified IAWQ Activated Sludge Model No. 1

Symbol	Name	Unit	Value[a]
	Stoichiometric parameters		
Y_H	yield for heterotrophic biomass	g Cell COD formed/g substrate COD oxidized	0.67
f_p	fraction of biomass yielding particulate products	dimensionless	0.08
i_{XB}	mass N/Mass COD in biomass	g N(g COD in biomass)-1	0.086
i_{XP}	Mass N/Mass COD in products from biomass decay	g N (g COD)-1 in endogenous mass	0.06
	Kinetic Parameters		
μ_H	Maximum specific growth rate of heterotrophs	day-1	6.0
K_S	Half-velocity coefficient of heterotrophs	g COD m^{-3}	20.0
K_{OH}	oxygen half-saturation coefficient for heterotrophs	g O_2 m^{-3}	0.20
b_H	decay coefficient of heterotrophic biomass	day^{-1}	0.62
k_a	ammonification rate	$m^3 \cdot (g\ COD.day)^{-1}$	0.08
k_h	maximum specific hydrolysis rate	g slowly biodegradable COD $(g\ cell\ COD \cdot day)^{-1}$	3.0
K_X	half-saturation coefficient for hydrolysis of slow biodegradable substrate	g slowly biodegradable COD $(g\ cell\ COD)^{-1}$	0.03

[a] typical value at 20 °C

Each point (each set of parameters) is used to make predictions and the objective function is calculated from model predictions and observations. The point (set of parameters) which causes the largest objective function (largest error) is identified, say, as point 4. Point 4 is then moved half way to the middle point between the centroid of points 1, 2, and 3 and point 4. Now point 4 becomes point 4'. The parameter values of point 4' are used to make predictions, the objective function is calculated and its value is compared to those of points 1, 2, and 3. A highest value is found, and that point is adjusted through the same procedure as described. This is iterated again and again, until all set of parameters give the same function value (Kuester and Mize, 1973).

4.2.1.1.5 Other

The initial conditions and inputs used for observation generation and prediction are the same. Sinusoidal inputs are to used to represent the diurnal changes in influent quantity and quality. Tabulated in Table 4.7 are the values of the stoichiometric and kinetic coefficients used for observation generation.

4.2.1.2 Algorithm Evaluation

The effects of the following factors on the performances of the calibration algorithm - quality of observations, number of observations, number of measured variables, and number of parameters estimated- are evaluated in the following case studies.

4.2.1.2.1 Quality of Observations

The quality of observations are indicated by the values of the variances of the Gaussian noises. Hourly observations of first stage DO, fourth stage DO, vent gas oxygen purity, and MLSS are used for calibration. A total of 72 hours of observations is used. The variance of the Gaussian noises are set to 0.10, 0.20, 0.30, and 0.40 respectively.

4.2.1.2.2 Number of Observations

The observations used are the same as in A except the number of observations are change from 24, 48, 72, to 96. This analysis is intended to find the optimum sampling period which suffices the requirements of correctly calibrating the model but avoids wasting resources by not taking too many observations. The variances of the Gaussian noises is fixed as 0.20 in this analysis (σ=0.20).

4.2.1.2.3 Number of Measured Variables

The observations used here are the same as above except that the measurements of ammonia nitrogen are added. The results obtained are compared with those in which ammonia nitrogen is not considered in the objective function.

4.2.1.3 Calibration Results and Discussion

A. The relationship between the variances of the relative errors and the quality of data may be explained as: the larger the values of the variances are, the worse the quality of the data is. The results of this study are shown in Figure 4.3. The line denoted as 'exact' represents the exact solution of process model. The line denoted as 'estimated' represents the solutions of the process model using the estimated parameter values. For a given set of observations of reasonable quality, if the calibration is reliable, then the 'predicted' should be very close to the 'exact'. As we can see from figure 3, the 'predicted' fits the 'exact' quite well in all cases though it deteriorates gradually and slowly with the increase of σ.

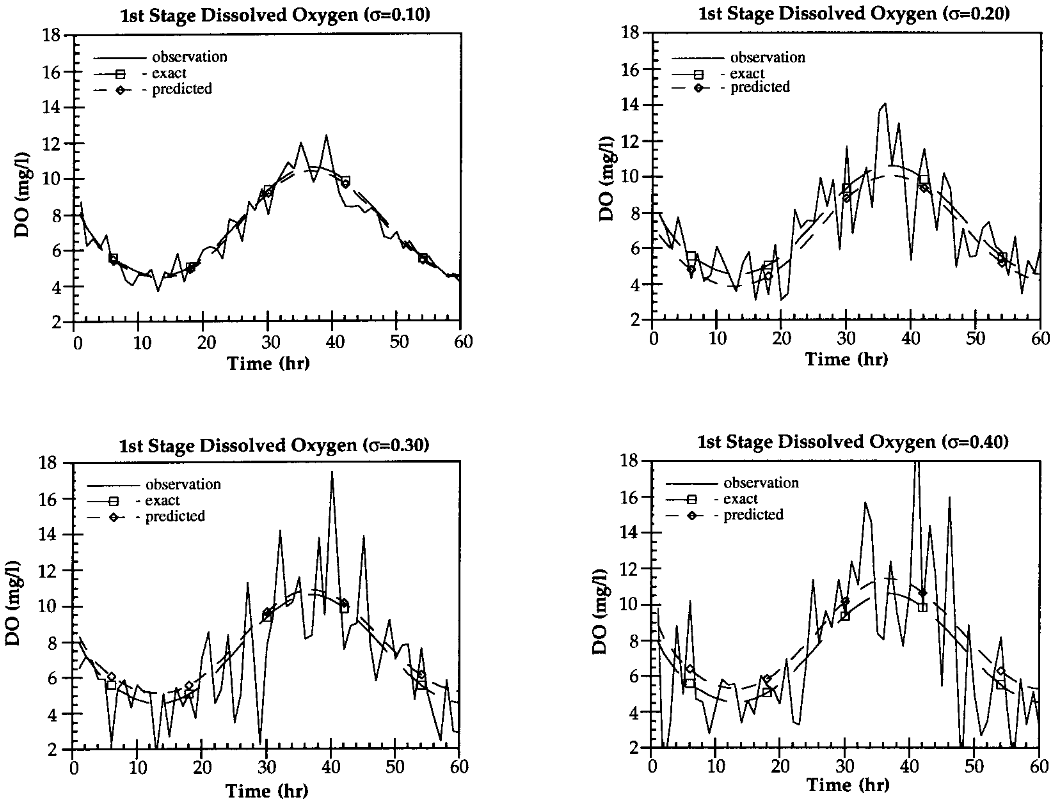


Figure 4.3 Effect of observation quality (σ) on 1st stage DO calibration

B. The results of this analysis is shown in Figure 4.4 and Table 4.8. There is no significant difference between n=24 and n=96 so far as the fit between the 'predicted' and the 'exact' solutions is concerned, but it is true the fit improves as the number of observations increases. The estimated parameters show the same pattern: the relative error between the estimated value and the 'true' value decreases when the number of observations increases (Table 4.8).

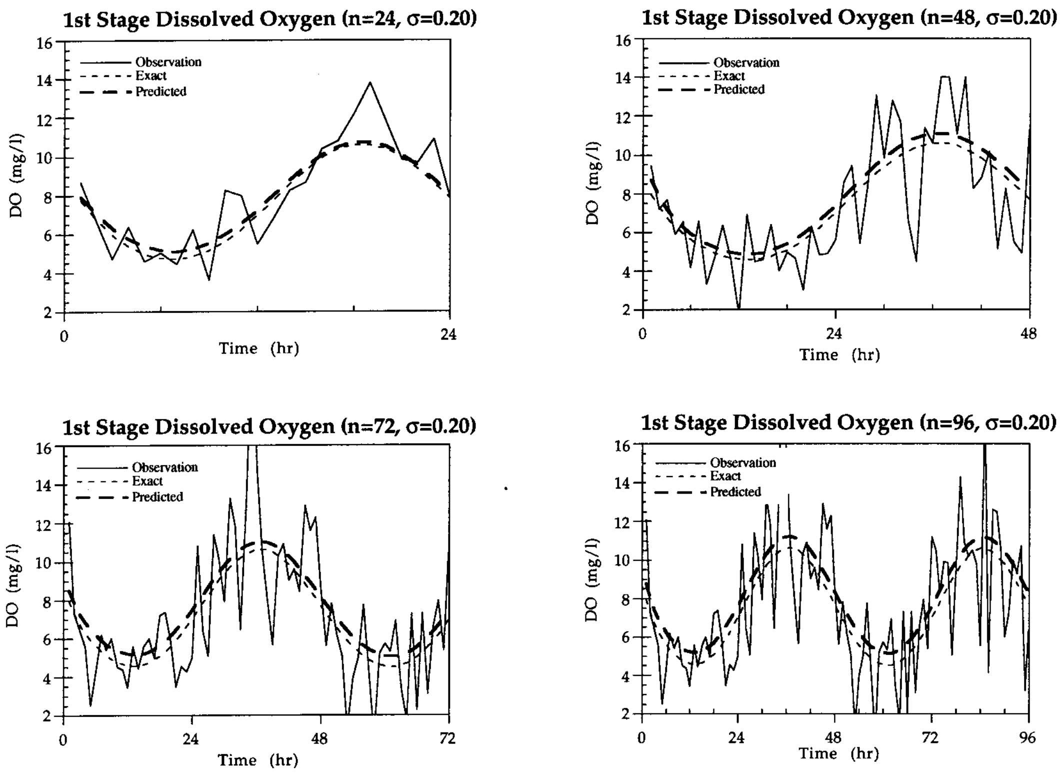


Figure 4.4 First stage dissolved oxygen for different n

Table 4.8 Estimated parameter values for different n (number of observations)

parameter	n=24	n=48	n=72	n=96
Y_H	5.76%	2.05%	1.34%	0.36%
μ_H	8.50%	4.34%	2.61%	0.79%

Theoretically, the longer the sampling period is, the more accurate the calibration is. In the real world, however, the sampling period is always limited to a finite time interval due to the limitations in resources. This analysis provides useful information when a decision needs to be made on a possible tradeoff between accuracy and resources.

C. The results of A and B reveal that some parameters, such as i_{XB} and i_{XP}, can not be accurately estimated if the objective function only includes 1st stage DO, 4th stage DO, vent gas oxygen purity, and MLSS (Table 4.9).

Table 4.9 Relative errors between the 'true' and 'estimated' values of parameters

parameter	σ=0.10	σ=0.20	σ=0.30	σ=0.40
Y_H	0.60%	1.34%	0.10%	2.30%
i_{XB}	25.47%	35.58%	49.88%	49.19%
i_{XP}	2.83%	12.30%	49.83%	16.00%

A steady-state sensitivity analysis is then conducted to systematically identify the sensitivities of observations to the changes of parameters. The sensitivity of the *ith* state variable S_i with respect to the *jth* parameter θ_j is defined by the following formula:

$$\Sigma(S_i,\theta_j)=\frac{\frac{\partial S_i}{S_i}}{\frac{\partial\theta_j}{\theta_j}}\cong\frac{\frac{\Delta S_i}{S_i}}{\frac{\Delta\theta_j}{\theta_j}}$$

From the definitions of i_{XB} and i_{XP}, it is natural to conclude that i_{XB} and i_{XP} have little effect on 1st stage DO, 4th stage DO, and 4th stage oxygen purity (vent gas oxygen purity), but strongly affect the nitrogen balance in the system. Table 4.10 confirms this point. In contrast, DO_1 and DO_4 are much more sensitive to Y_H and μ_H. Vent gas oxygen purity is not sensitive to any parameter, thus its measurements are of limited value for model calibration.

Table 4.10 Sensitivities

$\Sigma(DO_1, i_{XB}) = 5.8306 \times 10^{-4}$	$\Sigma(DO_4, i_{XB}) = 6.1926 \times 10^{-4}$	$\Sigma(p_{O_{24}}, i_{XB}) = 1.6484 \times 10^{-4}$
$\Sigma(DO_1, i_{XP}) = -1.9889 \times 10^{-4}$	$\Sigma(DO_4, i_{XP}) = -4.3348 \times 10^{-4}$	$\Sigma(p_{O_{24}}, i_{XP}) = 3.5604 \times 10^{-3}$
$\Sigma(DO_1, Y_H) = 2.4264 \times 10^{-2}$	$\Sigma(DO_4, Y_H) = 6.0553 \times 10^{-2}$	$\Sigma(p_{O_{24}}, Y_H) = 4.6264 \times 10^{-3}$
$\Sigma(DO_1, \mu_H) = 7.6667 \times 10^{-3}$	$\Sigma(DO_4, \mu_H) = -3.5814 \times 10^{-3}$	$\Sigma(p_{O_{24}}, \mu_H) = 5.0330 \times 10^{-3}$

It is obvious that for a given set of information (observations) only a certain number of parameters can be rigorously estimated. If the observations are not sensitive to a parameter , then the parameter can not be rigorously estimated from the given observations. On the other hand, if a parameter is to be estimated, only observations sensitive to the parameter should be used. If we intend to estimate i_{XB} and i_{XP}, additional observations, such as measurements of ammonia nitrogen, should be used.

This analysis is useful for the design and implementation of a model calibration. It provides insights into the algorithm, and lets one know what parameters can be reliably estimated from given observations, and what possible improvements may be brought up by adding additional measurements.

4.2.1.4 Summary and Conclusions

A model calibration algorithm is developed for the high-purity oxygen activated sludge process. The objective function is formulated as a relative least-squares function and the optimization method is the Complex Method. The effects of the following factors on the performance of the algorithm are evaluated: data quality, number of observations, and number of estimated parameters.

The following conclusions are drawn from this study:

1. The model calibration algorithm is robust to the quality of observations. As long as the errors are random (no systematic errors), the algorithm is capable of estimating the parameters to an acceptable accuracy.
2. The accuracy of calibration improves as the number of observations increases. However, the improvement slows down as the number of observations increases. No significant improvement is observed beyond n=96 (hourly observations of 4 days). In this study n=24 (hourly data of 1 day) is able to estimate Y_H and μ_H within 10% of their true values. For applications in which 10% is an acceptable estimation error, hourly sampling for 24 hours should be an adequate sampling scheme.
3. For a given set of observations, only a certain number of parameters can be reliably estimated. A sensitivity analysis should be performed before the calibration is performed to determine what parameters are to be estimated. If additional variables are to be measured and used for calibration, the potential benefits resulted from the addition should be quantitatively evaluated in advance.

4. The calibration algorithm is robust to constraints. Stringent constraints are not required and the range between the upper and lower bound do not need to be too narrow.

It should be noted that the evaluation of model calibration algorithm does not have the ability to reveal or identify any deficiency of the mathematical model. It is designed for algorithm evaluation and is only good for that purpose. This is because the synthetic data are derived from the model, which implicitly excludes the possibility that model deficiency is a cause of observation-prediction discrepancy.

4.2.2 Petroleum Refinery Activated Sludge Process

The model calibration algorithm developed for the high-purity oxygen activated sludge process should be readily applicable to the petroleum refinery activated sludge process. The general conclusions drawn from the algorithm evaluation are also useful for petroleum refinery activated sludge. Rigorous calibration based on mathematical optimization, nevertheless, was not attempted for the petroleum refinery activated sludge process because that the author was concerned that not enough information was available to justify such an attempt. It is premature to engage in a ambitious mathematical optimization for the following reasons: 1) Not enough data is available; 2) Data quality is of concern; 3) The behavior of the model is not revealed. The data, however, should still be helpful for the verification of the model under steady-state. This will be discussed in the following section.

4.3 Verification and Validation

It is evident that the work presented in Section 4.2 emphasizes the development and evaluation of a model calibration algorithm. The algorithm, however, was not used to calibrate the high-purity oxygen activated sludge model developed in this study. The reason is that the data set from the model high-purity oxygen activated sludge wastewater treatment plant does not permit a rigorous model calibration to be performed. There is only one observation per day for each variable and the sampling time is not recorded. The monthly report of the model high-purity oxygen activated sludge wastewater treatment plant indicates clearly that the flow and concentrations of influent changes diurnally; but only the maximum and minimum flows are recorded. There are changes from day to day but these changes does not necessarily reflect true process dynamics since some of these changes could be caused merely by the way the data were collected - one measurement per day. Furthermore the 'cause-effect' relation between inputs and outputs is ill defined because of the possibility that they are not measured at the same time and consequently not correlated. As a result the monthly averaged inputs and outputs were used to verify and validate the new high-purity oxygen activated sludge process model. This is equivalent to steady-state analysis. Another data set available for the high-purity oxygen activated sludge process verification and validation is the steady-state results from a pilot plant (Stenstrom, 1990; Tzeng, 1992). Therefore the verification and validation of the new high-purity oxygen activated sludge process is limited to steady-state scenarios. The same steady-state approach was also applied to the petroleum refinery activated sludge process which has even more limited data available. Field trips to the model refinery and conversations with the operation personnel make me less confident on the quality of the data set. The author does not feel that the data set could be used to validate the refinery activated sludge model. Consequently it was only used to verify the model. A data set of better quality will have to be collected and more supporting studies be conducted before the petroleum refinery activated sludge model can be validated.

4.3.1 High-purity Oxygen Activated Sludge Process

Two data sets were available for model verification and validation. The first data set is from a pilot plant study (Stenstrom, 1990; Tzeng, 1992). The pilot plant was operated in reaeration mode (sludge recycled to 1st stage, influent fed to second stage) under steady state. The data represents an average of about 20 days of operation. Another data set is from a full-scale high-purity oxygen activated sludge wastewater treatment plant - Sacramento Regional Wastewater Treatment Plant (SRWTP). Influent to this treatment plant changes diurnally in both flow rate and substrate concentration; but only one measurement is made every day. The data manifest changes from day to day but the changes can not be considered as true process dynamics since they could be created merely by the way the samples were collected - one sample per day with no indication of sampling time. In other words, it is possible the observations and inputs are not collected at the same of the day. Serious discrepancy could result from it. In this investigation, monthly averages of data are used which is believed to be a good representation of process behavior on an average basis. Random errors associated with the data could also be significantly reduced by taking a monthly average . The full-scale treatment plant has been previously described by Stenstrom *et al.* (1989) and Tzeng (1992).

Since the major contribution of the new high-purity oxygen activated sludge process model is the incorporation of the modified Activated Sludge Model No. 1, the typical values of stoichiometric and kinetic coefficients recommended by the IAWQ Task Group was first tried for model verification (Henze, et. 1987). Parameter values of the gas phase model and the gas transfer model were based on those of Stenstrom *et al.* (1989), Stenstrom (1990), and Tzeng (1992) which have been thoroughly evaluated. No effort was made to adjust these parameters. The typical values of stoichiometric and kinetic coefficients, however, were found to result in a poor fit between model predictions and observations from the model high-purity oxygen activated sludge wastewater treatment plant. The model was found to require only two thirds of the real oxygen feed to provide similar profiles of dissolved oxygen and gas phase oxygen purity (the average oxygen feed is about 120 tons/day in June 1990; the model only required a feed of 80 tons/day to provide a similar oxygen utilization pattern). Adjustment of a number of parameters resulted in minor improvements in the fit but none of the improvements was substantial enough to rectify the discrepancy in oxygen utilization. In order to identify the cause HIPURE2 was changed to output all the terms of the dissolved oxygen mass balance (Equation 3.23). The same thing was also done for HIPURE, which is Stenstrom's version of the high-purity oxygen activated sludge simulation program and has been applied to the model high-purity oxygen activated sludge wastewater treatment plant (Stenstrom *et al.* 1989; Tzeng, 1992). The same inputs were used wherever possible for the two codes, HIPURE2 and HIPURE, except the stoichiometric and kinetic coefficients in PARAMS (Table 4.3). Table 4.11 shows some results from these trial runs. There is no oxygen uptake rate (OUR) data in the full-scale high-purity oxygen activated sludge process data set. Thus the validity of the prediction can not be verified. The output of HIPURE, however, can serve as a reference here since its credibility has been established. It was found that the total OUR (sum of OURs through stage 1 to 4) calculated by HIPURE2 is significantly lower than that by HIPURE. Furthermore the OUR profile calculated by HIPURE2 exhibited a sharp decrease while HIPURE predicted a much dampened OUR profile throughout the stages (Figure 4.5)

Based on the analysis of OUR, it was speculated that the disagreement might have been caused by things related to oxygen utilization. The author thus decided to use the pilot plant data to help solve the problem because OUR data were available in that data set. Again it was found that HIPURE2 had difficulty to fit the OUR data of the pilot plant (Table 4.12).

Table 4.11 Calculated oxygen uptake rate using recommended parameter values

Model	OUR (mg O2/l/hr)				
	Stage 1	Stage 2	Stage 3	Stage 4	Sum
HIPURE2 (with Death-Regeneration)	80.76	23.21	13.59	11.83	129.40
HIPURE2 (without Death-Regeneration)	70.72	11.92	1.83	0.35	84.82
HIPURE	54.99	37.44	35.84	34.01	162.27

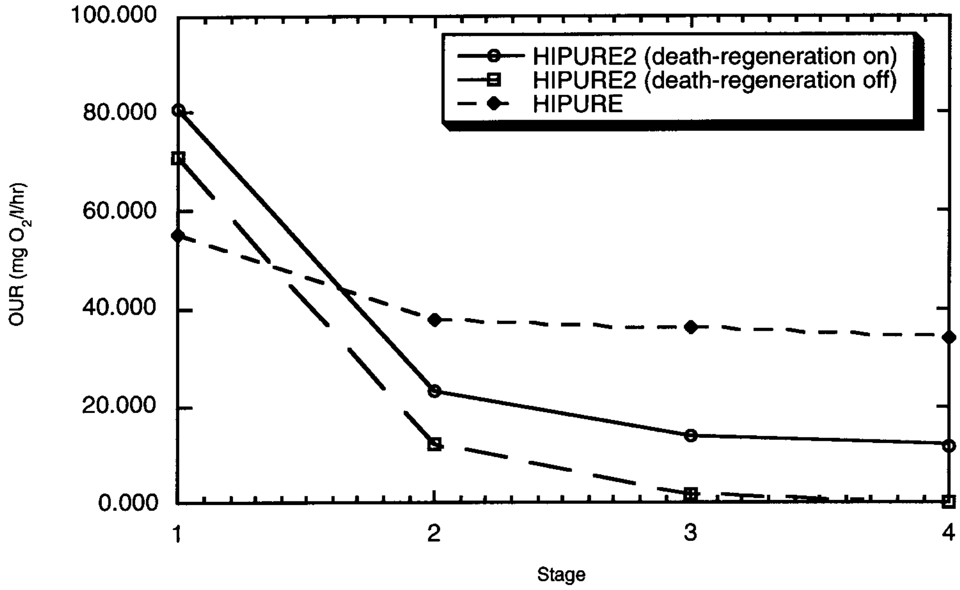


Figure 4.5 Model predicted oxygen uptake rate profiles

Table 4.12 HIPURE2 trial run result

parameters and locations	ppO2 S1	ppO2 S2	ppO2 S3	ppO2 S4	OUR S1	OUR S2	OUR S3	OUR S4
Westpoint Pilot plant	93.7	82.5	71.0	65.6	63	96	48	41
HIPURE2 trial run result	87	81	77	74	56.1	63.0	44.1	32.1

ppO2 = partial pressure of oxygen
S1, ..., S4 = stage 1 through 4

Again, key stoichiometric and kinetic coefficients were adjusted in search for a bit fit but no satisfactory result was obtained. It then became necessary to look into the expression of OUR (Equation 3.23). The OUR expression consist of only one term for HIPURE2 but three terms for HIPURE (see Chapter 5 for details). $\hat{\mu}_H$ and K_S were adjusted in hope of improving the fit but only limited improvements were achieved. It was then the author began to seriously consider if HIPURE2's difficulty of fitting the pilot plant data was caused by the Task Group's adoption of the 'death-regeneration' concept for the description of biomass decay (Dold *et al.* 1980; Henze *et al.* 1987). To verify the hypothesis the death-regeneration was replaced by endogenous respiration which was the most widely approach to describing biomass decay in aerobic systems before the IAWQ Activated Sludge Model No. 1 (Clifft and Andrews, 1981; Stenstrom, 1990). As demonstrated by Dold *et al.* (1980) the two approaches were essentially equivalent under steady-state conditions. The additional advantage of the death-regeneration approach is its ease to describe biomass decay under anoxic condition where the endogenous respiration approach obviously does not apply (see Chapter 5 for detailed discussion). For purely aerobic systems such as the high-purity oxygen activated sludge process this is not necessarily an advantage. It should not be ignored that the decay coefficient and inert mass yield differ significantly in magnitude though they have same notations in both approaches. By reverting the biomass decay to endogenous respiration, the author was able to compare the typical values of biomass decay related parameters with those used previously. The yield coefficient f_P and decay coefficient b_H were converted to their equivalents in the endogenous respiration approach and their values were 0.20 [M(COD)/M(COD)] and 0.24 d^{-1} respectively. Then the author noticed that Clifft (1980) also used 0.20 for f_P, which he denoted as Y_2; but the value of b_H, which he denoted as K_D, was 0.36 d^{-1}. So the author tried $b_H = 0.36$ d^{-1} for HIPURE2 and was surprised to find that the OUR profile matched very well with that observed in the pilot plant (Table 4.13). The relative error is within 10% percent except the fourth stage oxygen uptake rate. It was also found that even a better fit could be achieved by fine-tuning other kinetic coefficients. The result tabulated in Table 4.13, however, suffices for the purpose of this investigation.

Table 4.13 Pilot Plant Data vs. Model Prediction

parameters and locations	ppO2 S1	ppO2 S2	ppO2 S3	ppO2 S4	OUR S1	OUR S2	OUR S3	OUR S4
Pilot plant	93.7	82.5	71.0	65.6	63	96	48	41
Model predictions	83.0	75.0	70.0	66.0	63.7	94.9	51.5	35.8
Relative error (%) [a]	-11.4	-9.1	-1.4	0.6	1.1	-1.1	7.3	-12.7

[a] Relative error (RE) is defined as $RE = \frac{model\,prediction - pilot\,plant}{pilot\,plant} \times 100\%$

It is an important observation that 0.36 day^{-1} instead of 0.24^{-1} day, which is the typical value recommended by the IAWQ Task Group, should be used for decay coefficient in order to fit the oxygen uptake rate data of the pilot high-purity oxygen activated sludge wastewater treatment plant. This finding conforms to the characteristics of the high-purity oxygen activated sludge process reported in the literature. One of the advantages that have been claimed for the high-purity oxygen activated sludge process is less sludge production. There has also been a hypothesis that endogenous respiration is a more prominent process in the high-purity oxygen activated sludge process, particularly in the third and fourth stages. The requirement of a higher decay coefficient value is believed to be a theoretical confirmation to these previous claims and hypotheses.

The new HPO-ASP model was then verified using the August 1990 data of the full-scale high-purity oxygen activated sludge wastewater treatment plant. Monthly averaged input was used for model simulation and results were compared with the monthly averaged outputs. The set of stoichiometric and kinetic coefficients were the same as that used for the pilot plant. The dynamic model was found to reach steady state numerically in less 12 simulated hours under constant input condition. The result of simulation is listed in Table 4.14. The fit was excellent between simulation and field data (Table 4.15). The relations among daily variation, monthly average, and simulated monthly average are illustrated in Figure 4.6 and Figure 4.7.

Table 4.14 Output of simulation of August 1990

```
Stage    Si       Ss      Xi       Xs     Xnv       Xbh      Xp      DO         Snh3      Snd
  1    68.0     51.9    421.     32.    163.     1477.     85.     9.8         12.9     2.7
  2    68.0      7.5    419.     14.    164.     1502.     86.     6.0         11.8     1.2
  3    68.0      1.3    417.      5.    164.     1494.     87.     6.0         12.4      .7
  4    68.0       .3    415.      2.    164.     1480.     89.    12.8         13.2      .5

Stage    Xnd    Salk      pH    ppO2    ppCO2      ppN2    O2up     Kla   MLVSS    MLSS
  1      1.1 158.6088    6.1     .84      .07       .09   146.4     4.2   1362.   1525.
  2       .8 154.7592    6.0     .79      .09       .11    66.7     1.5   1366.   1529.
  3       .6 157.0246    6.0     .76      .10       .12    28.6      .8   1354.   1518.
  4       .5 159.8699    6.0     .73      .11       .14    20.8     1.2   1341.   1506.

Secondary Clarifier Output

x( 1)=       .909474E+03 mg/l
x( 2)=       .903022E+03 mg/l
x( 3)=       .901223E+03 mg/l
x( 4)=       .901484E+03 mg/l
x( 5)=       .903825E+03 mg/l
x( 6)=       .908192E+03 mg/l
x( 7)=       .917854E+03 mg/l
x( 8)=       .916712E+03 mg/l
x( 9)=       .289566E+04 mg/l
x(10)=       .512915E+04 mg/l

trigl=-.500000E+00    pulse= .000000E+00 time=    12.00 delt= .400000E-03
```

Table 4.14 Output of simulation of August 1990 (cont.)

```
Flow (MGD)                     147.90   Influent Ss                    255.
O2 Flow (SCFM/train)           395.09   Influent Xs                     87.
SRT (days)                        2.0   F:M ratio (1/day)              1.45
BOD5 Removed (#/day)          238728.   O2 Consumed (#/day)         193595.
Waste VSS (#/day)              85487.   O2 Cnsd/BOD5 Rmvd(#/#)          .81
Waste VSS/BOD5 Rmvd(#/#)          .36   O2 Utilization (frac)           .58
O2 Cnsumed(bio)               171912.   O2 Cnsd(bio)/BOD5 Rmvd(#/#)     .72
```

Table 4.15 Simulation result vs. SRWTP August 1990 data

	vent gas oxygen %	sec. effluent NH3-N (mg/l)	aeration tank pH	MLSS (mg/l)	return sludge conc. (mg/l)
AUG 90 data	72.12	13.0	6.5	1507	5064
Simulation	73.00	13.2	6.0	1506	5129

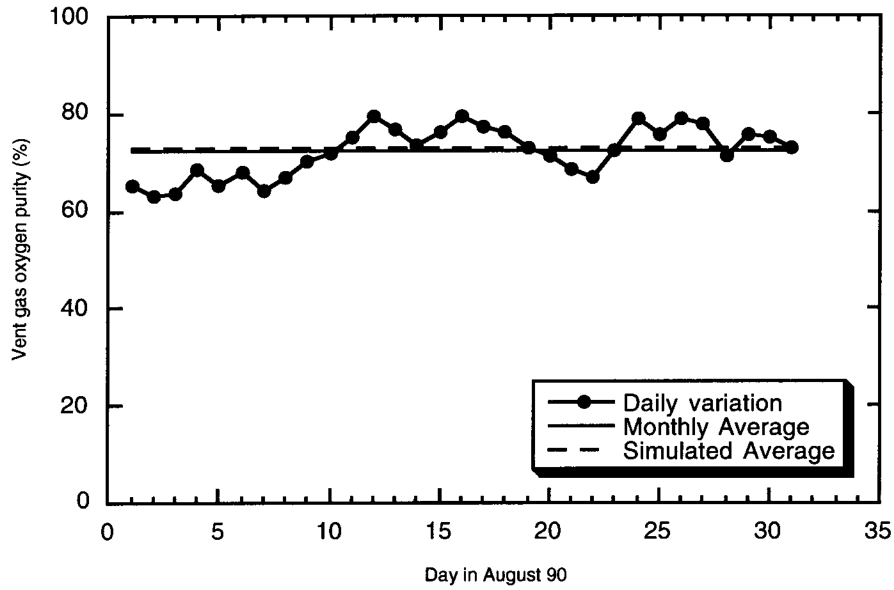


Figure 4.6 Simulated and observed vent gas oxygen purity in the model HPOASP (August 1990)

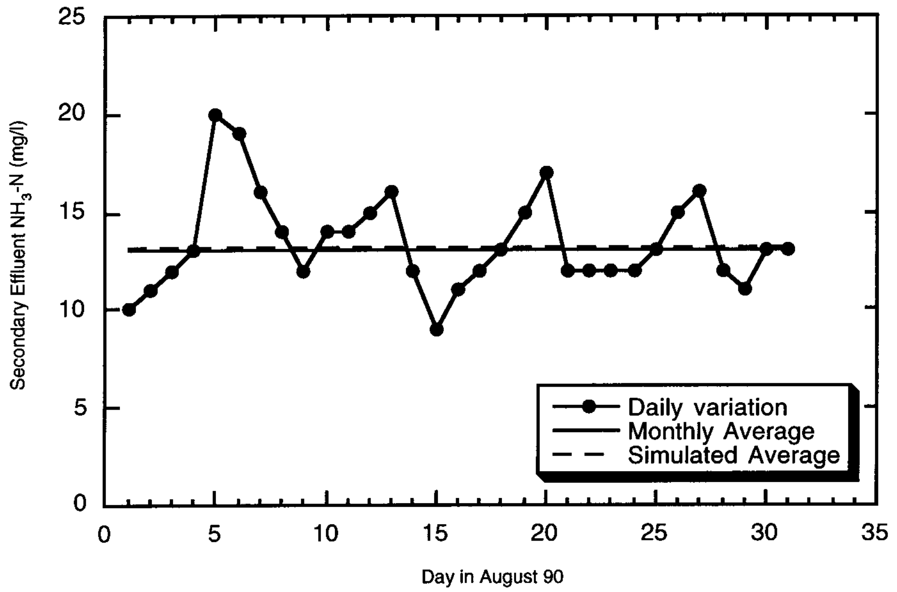


Figure 4.7 Predicted and observed secondary effluent ammonia nitrogen of the model HPOASP (August 1990)

The model was then used to simulate the monthly averaged performance of the full-scale high-purity oxygen activated sludge process in June 1990 (Table 4.16. The same set of stoichiometric and kinetic coefficients was used as that for August 1990. The fit between model simulations and observations was in reasonably good agreement except vent gas oxyen purity (Table 4.17). Small adjustments of stoichiometric and kinetic coefficients resulted in no conspicuous improvement. Based on the knowledge of HIPURE2, the author then adjusted the leakage coefficient. It was found that the vent gas oxygen purity was sensitive to the leakage coefficient. The model fitted June 1990 vent gas oxygen purity data well when K_{leak} was set to 1500. As aforementioned HIPURE2 has the capability of considering gas leakage. The leakage coefficient was set to zero for the pilot plant. Gas leakage has not been demonstrated experimentally in the full-scale high-purity oxygen activated sludge wastewater treatment plant; but as reported in the literature it happens in almost all treatment plants though the degree of leakage is different from place to place. As a result the consideration of gas leakage in the model is not something unacceptable. Clifft and Barnett (1988) also found it necessary to consider gas leakage in order to fit their model to the data from a full-scale oxygen activated sludge treatment plant. It is not clear why gas leakage does not need to be considered for August 1990 simulation. The relation among daily variation, monthly average, and simulated monthly average is illustrated in Figure 4.8 and Figure 4.9.

Table 4.16 Simulation output for June 1990

```
Stage    Si      Ss     Xi      Xs    Xnv     Xbh      Xp      DO       Snh3     Snd
  1    22.0    36.5   538.    19.   174.   1263.    79.     6.0       15.7     1.7
  2    22.0     6.8   534.     9.   174.   1283.    80.     6.0       15.1     1.2
  3    22.0     1.3   530.     4.   175.   1282.    81.     6.0       15.8      .8
  4    22.0      .4   526.     2.   175.   1276.    82.     6.0       16.5      .6

Stage    Xnd    Salk     pH    ppO2    ppCO2     ppN2   O2up    Kla  MLVSS   MLSS
  1     1.8 157.7106   6.2     .84      .06      .08  112.4    3.0  1283.  1458.
  2     1.1 155.5447   6.1     .79      .07      .12   54.3    1.4  1288.  1463.
  3      .7 157.8949   6.1     .74      .08      .16   25.0     .7  1282.  1457.
  4      .5 160.5374   6.1     .64      .08      .26   18.2     .6  1274.  1449.

Secondary Clarifier Output
x( 1)=      .804824E+03 mg/l
x( 2)=      .806716E+03 mg/l
x( 3)=      .803779E+03 mg/l
x( 4)=      .793229E+03 mg/l
x( 5)=      .788503E+03 mg/l
x( 6)=      .788107E+03 mg/l
x( 7)=      .788823E+03 mg/l
x( 8)=      .790448E+03 mg/l
x( 9)=      .281035E+04 mg/l
x(10)=      .523790E+04 mg/l

trig1=-.500000E+00    pulse= .000000E+00 time=   12.00 delt= .400000E-03

Flow (MGD)                    143.20   Influent Ss                    160.
O2 Flow (SCFM/train)          365.67   Influent Xs                     47.
SRT (days)                       2.0   F:M ratio (1/day)              1.20
BOD5 Removed (#/day)         136873.   O2 Consumed (#/day)         116305.
Waste VSS (#/day)             60685.   O2 Cnsd/BOD5 Rmvd(#/#)          .85
Waste VSS/BOD5 Rmvd(#/#)         .44   O2 Utilization (frac)          1.02
O2 Cnsumed(bio)              106611.   O2 Cnsd(bio)/BOD5 Rmvd(#/#)     .78
```

Table 4.17 Simulated and observed June 1990 performance

	vent gas oxyen purity %	sec. eff. NH3-N (mg/l)	aeration tank pH	MLSS (mg/l)	return sludge conc. (mg/l)	F/M ratio (based on BOD_5)
Observed	58.65	16.0	6.6	1449	4732	1.24
Simulated	64.00	16.5	6.1	1448	4994	1.20

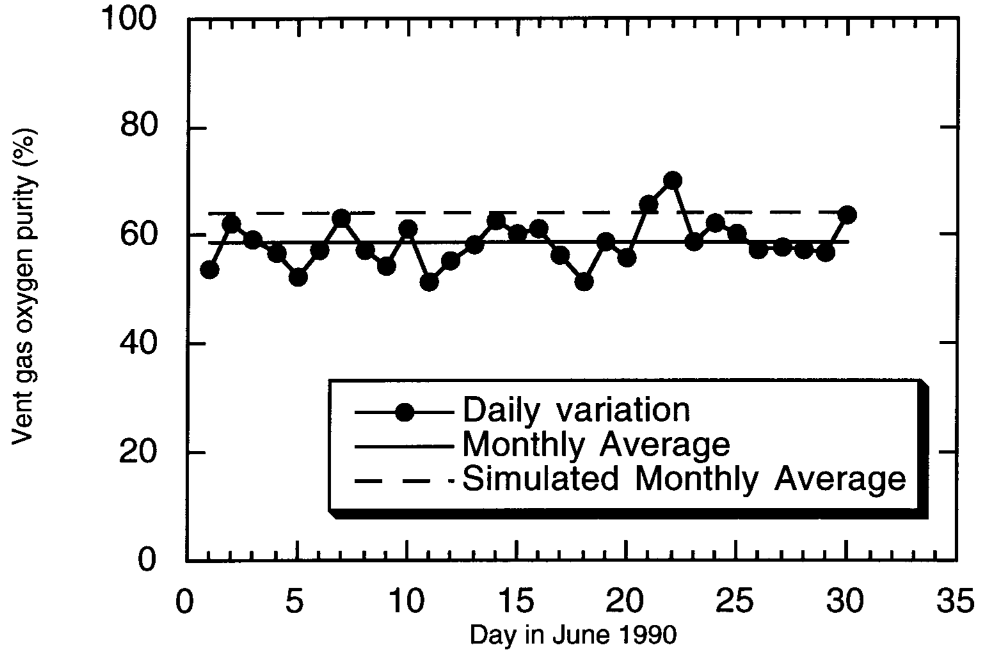


Figure 4.8 Simulated and observed vent gas oxygen purity for June 1990

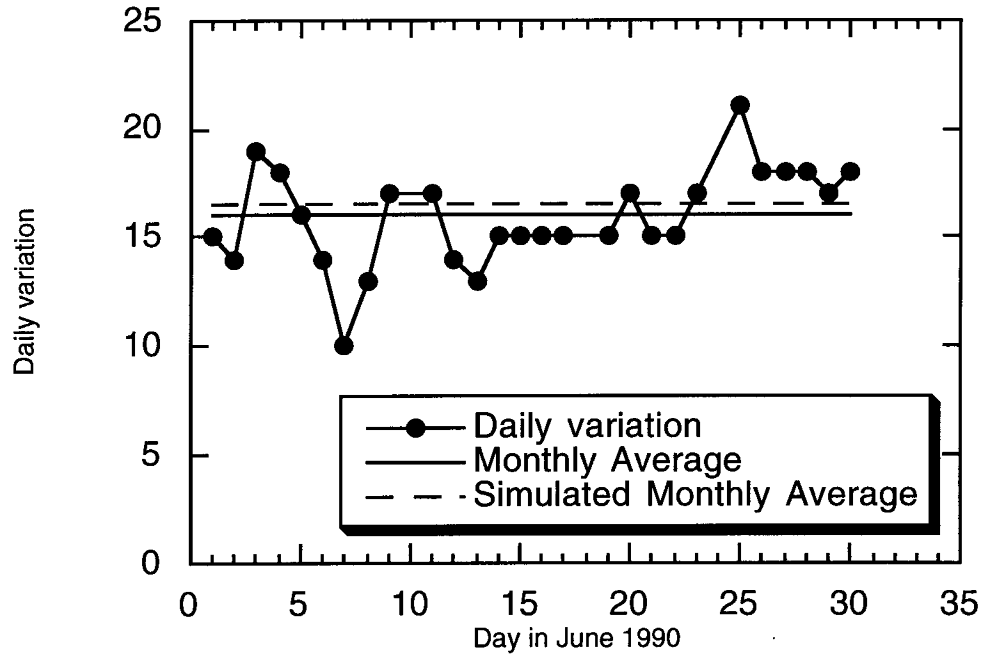


Figure 4.9 Simulated and observed secondary effluent NH_3-N for June 1990

Since the transformation of organic nitrogen is considered in HIPURE2, it was found easy to fit the effluent ammonia data. HIPURE, which did not consider organic nitrogen, tend to underpredict the effluent ammonia concentration though it has little impact on oxygen utilization patters (Tzeng, 1992).

The new process model for the high-purity oxygen activated sludge process was considered as being verified and validated by the previous efforts of matching model predictions to observations. The verification and validation, nevertheless, has been confined to the steady-steady or pseudo steady-stated conditions in this investigation. From the history of activated sludge model (Chapter 2) it is clear that the deficiency of an activated sludge model is often revealed when the model is subject to dynamic conditions. So one should be aware that more verification and validation of the new high-purity oxygen activated sludge process model are necessary for dynamic conditions. This, of course, requires a good data set to be available.

The fit between model predictions and observations is quite satisfactory if one considers that many aspects of the models still need to be better defined. One of these aspects, wastewater characterization, deserves special attention. Organic matters are characterized as soluble substrate, particulate substrate, soluble inert organic matter, and particulate organic matter in the two structured AS models studied in this investigation. The fractions of organic matter should be identified based on the microbial responses, e.g. oxygen uptake rate, of the wastewater-inoculum mixture under batch conditions. In other words, they are determined biologically, not physically. In most wastewater treatment plants, BOD_5 and COD are measured as soluble and total respectively depending on if the sample is filtered (usually through a $0.45\,\mu m$ filter). Both data sets used in this investigation contain measurements on soluble BOD_5, total BOD_5, soluble COD, total COD, suspended solids (SS), and volatile suspended solids (VSS). The characterization of wastewater is done based on these measurements. More specifically, soluble BOD_5 are converted to BOD_u and BOD_u is considered as a good approximation of soluble substrate. The difference between soluble COD and soluble BOD_u is considered as soluble inert organic matter. So on and so forth. It is conceivable that errors might be introduced into predictions by such approximations. It should be noted that the soluble and particulate substrate fractions should be determined biologically, not physically. By biologically, it means that the fractions should be divided based the responses of microorganism. By physically, it might be understood as a division based on 0.45μ filter filtration which is the standard method of measurement adopted in most wastewater treatment plants. Theoretically, the fractions determined by filtration are different from those measured through biological procedures; but the two methods should have good correlations. In this study, the soluble and particulate BOD_5 concentrations are converted to BOD_u and used as inputs to the models. No effort is devoted to adjust the fractions.

The fact that model predictions and observations are in good agreement despite the uncertainties associated with model inputs and parameter values is a strong proof that the model is sound and robust. In other words, one should not expect a model with hidden deficiencies to provide robust performances under the same conditions.

4.3.2 Petroleum Refinery Activated Sludge Process

There is not enough information to perform a rigorous verification of the petroleum refinery activated sludge process model. Organic matter in the model refinery wastewater has been measured as COD while the model requires that organic matter be characterized into soluble inert, readily biodegradable, particulate inert, and slow biodegradable. There is information concerning such characterizations in the model refinery. Consequently the numbers in Table 4.18 was used based on the best available information on refinery wastewater. The same difficulty also exists for determining values for the stoichiometric and kinetic coefficients. The parameter values used in the simulation is listed in Table 4.19. A typical output file is shown in Table 4.20.

Table 4.18 INPUTS used for petroleum refinery activated sludge process simulation

```
40.       Conc. influent Si (mgCOD/L)
80.       Conc. influent Ss (mgCOD/L)
40.       Conc. influent particulate inert Xi (mgCOD/L)
120.      Conc. influent particulate biodegradable Xs (mgCOD/L)
```

Table 4.18 INPUTS used for petroleum refinery activated sludge process simulation (cont.)

13.	Conc. Influent non-volatile solids Xnv (mg/L)
0.	Conc. Influent decay products Xp (mgCOD/L)
0.	Conc. Influent active biomass Xbh(mgCOD/L)
0.	Xban1 - nitrosomonas
0.	Xban2 - nitrobacter
0.	Xbas - sulfur oxidizers
0.001	Conc. influent dissolved oxygen So2 (mgO2/L)
0.44	conc. influent dissolved carbon dioxide Sco2 (mg/L)
180.	Conc. Influent ammonia Snh3 (mg/L)
0.	nitrite
0.	Nitrate
15.	Sulfide
0.	Sulfate
373.	Conc. Influent alkalinity Salk (as CaCO3, mg/L)
7.8	Influent pH
2.	Number of Basins
2.304	Flow rate Q (mgd)
0.40	Recycle Rate (fraction of input flow rate)
12.	SRT (set point, days)
15.7	Temperature (deg C)
1000.	Air flow rate, scfm
.21	Oxygen fraction in air
1.	Input type (1=constant, 2= sinusoidal, 3= actual data)
1.	Percent sinusoidal variation in flow input (input type = 2)
1.	Percent sinusoidal variation in Ss conc. (input type = 2)
1.	Percent sinusoidal variation in Xs conc. (input type = 2)
1.	Percent sinusoidal variation in NH3-N conc. (input type = 2)
1.	Percent sinusoidal variation in H2S-S conc. (input type = 2)

Table 4.19 Parameters used for petroleum refinery activated sludge process simulation

1.0	alpha
0.99	beta
3.0	DO set point
1.0	Proportional gain for DO control (set to zero for no control)
1.0	Reset (integral) gain for DO control (set to zero for no control)
7.5	alkalinity set point
5.0	Proportional gain for pH control (= 0 no control; = 0.05 works)
.0	Reset (integral) gain for pH control (set to zero for no control)
0.67	yh - heterotrophic yield (g cell COD formed/g COD oxidized)
0.05	yan1 - autotrophic yield (g cell COD formed/g N oxidized)
0.05	yan2 - autotrophic yield (g cell COD formed/g N oxidized)
0.24	yas- autotrophic yield (g cell COD formed/g S oxidized)
0.08	fp - fraction of biomass yielding particulate products

Table 4.19 Parameters used for petroleum refinery activated sludge process simulation (cont.)

0.086	ixb - mass N/mass COD in biomass
0.06	ixp - mass N/mass COD in products from biomass decay
1.48	codvss - converting the unit of mlvss from COD to VSS
1.375	co2o2 - mass co2 produced/mass o2 consumed
6.0	uh - maximum specific growth rate of heterotrophs, 1/day
0.7	uan1 - maximum specific growth rate of N-autotrophs, 1/day
1.0	uan2 - maximum specific growth rate of N-autotrophs, 1/day
0.8	uas- maximum specific growth rate of S-autotrophs, 1/day
1.0	knh- saturation coefficient (nitrification)
1.0	khs- saturation coefficient (H2S oxidation)
20.0	ks - saturation coefficient (heterotrophic growth)
0.20	koh - saturation coefficient (DO 'switch' function)
0.40	koa - saturation coefficient (DO 'switch' function)
0.50	bh - decay rate constant (heterotrophs)
0.05	ban1- decay rate constant (N-autotrophs)
0.05	ban2- decay rate constant (N-autotrophs)
0.132	bas- decay rate constant (S-autotrophs)
0.08	ka - l.COD/(mg.day)
3.0	kh - hydrolysis rate constant
0.03	kx - saturation coefficient (hydrolysis)
.0030075	a1 - empirical coefficient in Kla(Qair) function
1.4135	a2 - empirical coefficient in Kla(Qair) function
6360.	areaft - clarifier area (ft^2)
15.	adepth - clarifier depth (ft)
10.	anelem - number of element in clarifier
1.	ameth - flag, uesed for srt calculation
240625.8	aeration tank volume (liquid, ft^3)
0.01	flow rate of NaOH,m3/hr
0.01	conc. of NaOH, M (mole/l)

Table 4.20 Simulated yearly averaged output of the model refinery effluent treatment plant

```
Time   Si     Ss     Xi     Xs     Xnv    Xp     Xbh    Xban1  Xban2
12.00  40.0   2.2    1397.3 3.6    826.2  1512.1 366.4  135.4  45.7


Time   Xbas   Sco2   DO     Qair   Qnaoh  Kla    Snh3   Sno2   Sno3
12.00  15.16  18.92  3.00   216.11 0.00   1.836  0.10   0.14   128.1


Time   Sh2s   Sso4   Salk   pH     rO2    MLVSS  MLSS
12.00  0.30   15.5   348.96 7.6    7.5    2226.0 3052.2


Secondary Clarifier Output
```

Table 4.20 Simulated yearly averaged output of the model refinery effluent treatment plant (cont.)

```
x( 1)=      .281000E+03 mg/l
x( 2)=      .281000E+03 mg/l
x( 3)=      .281500E+03 mg/l
x( 4)=      .281500E+03 mg/l
x( 5)=      .281500E+03 mg/l
x( 6)=      .281500E+03 mg/l
x( 7)=      .282000E+03 mg/l
x( 8)=      .283100E+03 mg/l
x( 9)=      .142110E+04 mg/l
x(10)=      .108770E+05 mg/l
```

The simulation results show that under normal conditions ammonia can be completely nitrified into nitrate, with no nitrite accumulation. The oxidation of hydrogen sulfide into sulfate is also complete and satisfactory. The program has a built-in dissolved oxygen controller which manipulates air flow rate to maintain DO at 3 mg/l. The program also has a PI (proportional-integral) controller for pH control, which manipulates the dosage of sodium hydroxide for pH control. The pH controller, however, constantly overshoots if the pH set point is close to 7.0. From the literature it was found that pH control is extremely challenging because of the severe non-linearity between the manipulated variable (sodium hydroxide dosage) and the controlled variable (pH). In other words sodium hydroxide dosage directly affects the hydrogen ion concentration ($[H^+]$); but it is the minus log of $[H^+]$, the pH, that is to be controlled. When titration approaches the neutral point, OH^- dosage is in the magnitude of 10^{-7}. When pH set point is set to 8.5 the problem is much less pronounced. As a result the controller was turned off in most simulations.

5. MODEL COMPARISON

The objective of this chapter is to compare the new high-purity oxygen activated sludge process model developed in this research with the one developed and applied by Stenstrom (1990) and Tzeng (1992). The corresponding simulation programs of these two models are HIPURE2 and HIPURE. As aforementioned HIPURE2 incorporates the modified IAWQ Activated Sludge Model No. 1 and HIPURE uses the structured Clifft and Andrews Activated Sludge Model (Clifft and Andrews, 1981). A model's ability to correctly predict oxygen utilization patterns is the focus of this comparison. Model comparison is limited to the high-purity oxygen activated sludge process models only since there is no other model available for the petroleum refinery activated sludge process except the one developed in this research.

5.1 Background

The value of OUR determines the capacity of aeration equipment in the activated sludge process. In the design of aerobic biological reactor we frequently use correlation of data more or less approximating the situation of interest to establish whether the slowest process step is the oxygen transfer rate (OTR) or the oxygen uptake rate (OUR). Our ability to accurately and precisely predict the value of OUR determines, to large extent, our ability to control the aeration equipment to minimize the energy requirement of oxygen supply and dissolution while at the same time satisfying the oxygen requirement exerted by the aerobic growth of microorganisms. Since the cost associated with oxygen supply and dissolution accounts for over 80% of the total operation cost in many activated sludge wastewater treatment plants, it is obvious that an improved understanding of OUR will certainly enhance our capability to design and operate activated sludge wastewater treatment plants in a more energy efficient way.

For the purpose of design, if no nitrification occurs, oxygen requirement of an activated sludge process has been traditionally estimated by the following formula:

$$\text{kg O}_2/\text{d} = \frac{Q(S_o - S)\times(10^3 g/kg)^{-1}}{f} - 1.42(P_X) \qquad (5.1)$$

where So, S = five day biochemical oxygen demand (BOD_5) concentration of influent and effluent respectively, g/m^3; Q = influent wastewater flow rate, m^3/d; f = conversion factor for converting BOD_5 to BOD_u (ultimate BOD); P_X = net waste activated sludge produced each day, measured in terms of volatile suspended solids (VSS), kg/d; 1.42 = conversion factor for converting VSS to oxygen equivalent assuming the formula of cells is $C_5H_7NO_2$.

Equation (5.1) is basically an steady state mass balance equation. While it suffices for the purpose of activated sludge process design, it reveals no stoichiometric and kinetic relation between substrate utilization/active mass formation and oxygen utilization; therefore it is not capable of predicting process behaviors under transient conditions.

The modeling of oxygen utilization rate is usually part of an comprehensive activated sludge model which involves all processes (e.g. aerobic growth of heterotrophs and biomass decay) and components (e.g. substrate, biomass, and dissolved oxygen) of the activated sludge. The ability to correctly predict OUR has been considered as a major indicator of excellence for an activated sludge model because of the importance of oxygen for the activated sludge process. Early expressions of OUR differ in notation and format, but all of them represent the following expression (Bryant, 1972; Busby, 1973; Ekama and Marais, 1976):

$$OUR = \frac{1-Y_1}{Y_1}\mu_m\left(\frac{S}{K_S+S}\right)X + (1-Y_2)K_dX \tag{5.2}$$

where S = substrate concentration, [M(COD)L^{-3}]; K_S = half-velocity coefficient, [M(COD)L^{-3}]; X = biomass concentration, [M(COD)L^{-3}]; Y_1 = yield coefficient, biomass synthesized per unit mass of substrate utilized; μ_m = maximum specific growth rate of heterotrophs; Y_2 = yield coefficient, inert mass generated per unit mass of biomass decayed; K_d = decay coefficient of biomass, 1/d. It should be noted that if the unit of biomass is in VSS and/or the unit of substrate is in BOD$_5$, conversion factors will be needed to convert biomass and substrate units from [M(VSS)L^{-3}] and [M(BOD$_5$)L^{-3}] to [M(COD)L^{-3}].

Equation (5.2) has two terms which represent oxygen uptakes originating from aerobic growth and endogenous respiration of heterotrophs. It is evident that the rate of aerobic growth of heterotrophs is described by the Monod kinetics here and oxygen uptake rate is related to the growth rate. Biomass decay is modeled as a first-order reaction with respect to biomass concentration. It should be noted that biomass decay means complete oxidation of biomass into carbon dioxide and water here. Oxygen uptake exerted by biomass decay is equal to the oxygen equivalent of the decayed biomass. Y_2 would equal to zero under such a consideration.

It should also be noted that Equation (5.2) actually represents a conventional activated sludge model, which was found incapable of describing oxygen utilization in the activated sludge process in the early 1970s. A variety of structured activated sludge models were developed to correct the deficiency of the conventional activated sludge model. In this study two representative structured activated sludge models are compared in the high-purity oxygen activated sludge process - the IAWQ Activated Sludge Model No. 1 and the Clifft and Andrews Activated Sludge Model.

The high-purity oxygen activated sludge process is the ideal process for model comparison. If the two models have any difference in predicting oxygen utilization related process performance, the difference would be magnified in the high-purity oxygen activated sludge process. Since there are differences in reaction mechanisms and rate expressions, it is important to find out if both of them are capable of providing realistic predictions. It is perhaps more important to go to the 'micro-level' of OUR to reveal how the oxygen uptake is described both qualitatively and quantitatively within each model. This study will provide insights into oxygen utilization modeling, improve our understanding of the mechanisms, and stimulate new research on this subject.

5.2 Theoretical

The Clifft and Andrews Activated Sludge Model and the IAWQ Activated Sludge Model No. 1 are the two most important activated sludge models for this research. Despite their differences in reaction mechanisms, the two model have some common aspects. Both model divides substrate into two fractions - soluble and particulate. Both models assume that the particulate substrate is instantaneously removed from water upon contact with sludge flocs. Both models assumes that inert organic matter is generated by biomass decay. Differences, however, are much more prominent compared with similarities. The most prominent difference lies in the removal mechanisms of soluble and particulate substrate. For soluble substrate, the Clifft and Andrews Activated Sludge Model assumes it can be either metabolized directly by active heterotrophs or converted into stored mass while in Activated Sludge Model No. 1 the only reaction mechanism for soluble substrate (readily biodegradable substrate) is direct metabolism (aerobic growth of heterotrophs). There is no such a pool of mass called stored mass in the Activated Sludge Model No. 1. For particulate substrate, both the Clifft and Andrews Model and the IAWQ Model assume that it is instantaneously removed from liquid phase upon contact with sludge. This phenomenon is referred to as entrapment or enmeshment, and the entrapped particulate substrate is called stored substrate in Clifft and Andrews Model and entrapped organic matter in Activated Sludge Model No. 1. Subsequent reactions, however, are quite different for these two models. In the Clifft and Andrews Model, stored particulate substrate is transformed into stored mass and stored mass, originated from both soluble and particulate substrate, is then converted into active mass. In Activated Sludge Model No. 1 entrapped organics is hydrolyzed into soluble substrate by extracellular enzymatic activities and then utilized.

Another prominent difference is the modeling of biomass decay. The approach adopted by the Clifft and Andrews Model is endogenous respiration. Activated Sludge Model No. 1, on the other hand, uses the 'death-regeneration' approach. No oxygen is explicitly consumed. Possible oxygen uptake raised form biomass decay is reflected by a generation of slowly biodegradable substrate by biomass decay which is then hydrolyzed into soluble substrate and metabolized. Dold *et al.* (1980) has shown that with careful selection of parameter values the two approaches, endogenous respiration and death-regeneration, could yield the same results in oxygen uptake rate and active mass production under steady state. The major advantage of death-regeneration approach is that it is applicable to anoxic and anaerobic conditions as well as aerobic conditions while the endogenous respiration approach only makes sense under aerobic conditions. For single sludge carbon oxidation, nitrification, and denitrification system, the advantage of death-regeneration approach is obvious. For the high-purity oxygen activated sludge process, endogenous respiration approach might be a better one since the death-regeneration is less direct in pure aerobic systems.

Because of the above differences in reaction mechanisms, the expressions of oxygen uptake rate (OUR) are very different for these two models. For the Clifft and Andrews Model, OUR equals to the opposite of the total reaction rate of dissolved oxygen (Table 2.8):

$$OUR = (1 - Y_1) R_{SD} X_A S_D + \frac{1 - Y_1}{Y_1} R_{XA} X_A f_S + (1 - Y_2) K_D X_A \tag{5.3}$$

Oxygen uptake originates from three sources which are (1) directly metabolism of soluble substrate, (2) metabolism of stored mass by heterotrophs, and (3) endogenous respiration respectively. Of these three oxygen uptake terms, term (2) does not exist in Activated Sludge Model No. 1 since substrate storage is not a reaction mechanism in it. Term (3) does not appear in the OUR expression of the Activated Sludge Model No. 1 either because it replaced the traditional 'endogenous respiration' by 'death-regeneration' to describe biomass decay. Thus the oxygen uptake rate expression of Activated Sludge Model No. 1 only has one term which originates from soluble substrate utilization/aerobic growth of active heterotrophs (Table 2.10):

$$OUR = \frac{1 - Y_H}{Y_H} \mu_H \left(\frac{S_S}{K_S + S_S} \right) \left(\frac{S_O}{K_{OH} + S_O} \right) X_{BH} \tag{5.4}$$

Other differences include the handling of nitrogenous matters. The Clifft and Andrews Activated Sludge Model assumes ammonia nitrogen is the only nitrogen component of importance in wastewater influent, of which a fraction is incorporated into heterotrophic cells as nitrogen nutrient. Nitrogen is assumed to be released back into liquid phase as ammonia nitrogen when biomass decays. In Activated Sludge Model No. 1, soluble and particulate organic nitrogen in influent is considered in nitrogen transformations. Ammonification, the conversion of organic nitrogen to ammonia nitrogen, and hydrolysis of particulate organic nitrogen to soluble nitrogen, are two mechanisms that do not exist in the Clifft and Andrews Model. These differences in modeling nitrogenous components, however, have little impact on the modeling of oxygen utilization in the high-purity oxygen activated sludge process.

The following differences in notation and definition between the Clifft and Andrews Activated Sludge Model and Activated Sludge Model No. 1 should be noted (Table 5.1):

Table 5.1 Notational differences between Clifft and Andrews Activated Sludge Model and the IAWQ Activated Sludge Model No. 1

	Clifft and Andrews AS Model	IAWQ AS Model No. 1
X_P	stored (entrapped) particulate substrate (equivalent to X_S in the IAWQ AS Model No. 1)	particulate products (inert organic matter) arising from biomass decay
X_S	stored mass	particulate substrate (slowly biodegradable)
soluble substrate	S_D	S_S
active biomass	X_A (active mass)	X_{BH} (active heterotrophs)
decay coefficient	K_D	b_H
f_P	fraction of stored particulate substrate in biomass	fraction of biomass leading to particulate inert organic matter (X_P)
mass of inert organic matter produced per unit mass of active biomass decayed	Y_2	f_P
ammonia nitrogen	NH	S_{NH}

mass of ammonia nitrogen utilized per mass of active biomass (in COD) produced	Y_{NS}	i_{XB}
mass of nitrogen released per mass of active biomass (in COD) decayed	Y_{ND} (ammonia nitrogen released)	i_{XP} (particulate organic nitrogen released)
hydrolysis	stored substrate(entrapped particulate substrate) to stored mass	slowly biodegradable (entrapped particulate substrate) to readily biodegradable substrate (soluble substrate)

It should also be noted that R_{SD} was called direct growth rate coefficient by Clifft (1980); it, however, actually is direct substrate utilization rate coefficient. This is obvious if one looks at Table 2.8. The stoichiometric coefficient is 1 for soluble substrate. This means that the rate expression ρ_2 is for substrate utilization.

5.3 Model Comparison

We have compared the theoretical differences of the two structured activated sludge models. Previous research (Stenstrom 1990; Tzeng 1992) and Chapter 4 of this dissertation have concluded that both of these models are capable of predicting oxygen utilization patterns realistically in the high-purity oxygen activated sludge process. The way they did it, however, was very different. It is thus of interest to find out how the two models quantitatively describes oxygen utilization. Such insights will provide useful information regarding the modeling of oxygen related processes. The same inputs were used for HIPURE2 and HIPURE wherever applicable.

The two models' abilities to fit the pilot plant data are about the same (Table 5.2). HIPURE seems to have predicted the gas phase oxygen purity better while HIPURE2 appears to give a better fit of oxygen uptake rates. Overall both models fit the pilot plant data very well.

Table 5.2 Measured and predicted oxygen partial pressures and OURs for the pilot plant

parameters	ppO2 S1	ppO2 S2	ppO2 S3	ppO2 S4	OUR S1	OUR S2	OUR S3	OUR S4
Pilot plant	93.7	82.5	71.0	65.6	63	96	48	41
Activated Sludge Model No. 1 (Relative error % [a])	83.0 (11.4)	75.0 (-9.1)	70.0 (-1.4)	66.0 (0.6)	63.7 (1.1)	94.9 (-1.1)	51.5 (7.3)	35.8 (-12.7)
Clifft and Andrews (Relative error % [a])	85 (-9.3)	78 (-5.8)	73 (2.8)	69 (5.2)	65 (3.2)	92 (4.2)	51 (6.3)	36 (12.2)

[a] Relative error (RE) is defined as $RE = \frac{model\ prediction - pilot\ plant}{pilot\ plant} \times 100\%$

The profiles of the three OUR terms in Clifft and Andrews Model are shown in Table 5.3. It is obvious that oxygen uptake by soluble substrate utilization (OUR1) is only important in the first stage to which the influent is fed. OUR1 sharply decreases to zero from stage 2 to stage 4. Oxygen uptake by the utilization of stored mass (OUR2) is relatively stable though it declines from 10.66 to 7.27 from stage 1 to stage 4. Oxygen uptake resulting from biomass decay is very stable throughout the stages. It accounts for at least 50% of the total OUR and becomes the dominant oxygen uptake mechanism in the last two stages. As discussed in Chapter 4, sludge decay is very important in terms of oxygen utilization patterns in the high-purity oxygen activated sludge process. Results in Table 5.3 again confirm the conclusion. If sludge decay had been ignored the model would have had tremendous difficulty to fit the pilot plant oxygen uptake rate data. The finding also lead to the conclusion that the death-regeneration is a less preferred approach for describing sludge decay in the high-purity oxygen activated sludge process.

Table 5.3 Profiles of the three OUR terms in Clifft and Andrews Activated Sludge Model (SRWTP)

Clifft and Andrews	OUR 1 (mg/l/hr)	OUR 2 (mg/l/hr)	OUR 3 (mg/l/hr)	OUR* (mg/l/hr)
Stage 1	19.08	10.66	25.07	54.82
Stage 2	0.42	10.12	26.68	37.23
Stage 3	0.01	8.71	26.92	35.64
Stage 4	0.00	7.27	26.56	33.83
				161.52

* data corresponds to June 1990 SRWTP data

The profiles of the two oxygen uptake rate terms in the modified Activated Sludge Model No. 1 are shown in Table 5.4. The model was calibrated to the data set of the Westpoint pilot plant, which was operated in reaeration mode (wastewater was fed to the second stage). It can be seen that oxygen uptake from the utilization of soluble substrate (OUR1) was dominant in the second stage. OUR1 is still important in stage 2, 3, and 4. Oxygen uptake from the endogenous respiration (OUR2) accounted for two thirds of the total oxygen uptake. OUR2 was at about the same level of OUR in the fourth stage.

The Clifft and Andrews Model, however, exhibits a different pattern (Table 5.5). Oxygen uptake from the utilization of soluble substrate (OUR1) manifests the same pattern as it does in the modified Activated Sludge Model No. 1 but the magnitude is generally lower. Oxygen uptake from the conversion of stored mass to active mass (OUR2) and oxygen uptake from endogenous respiration (OUR3) again display flat patterns except in stage 1. It is obvious that stored mass utilization and endogenous respiration are the governing mechanisms of oxygen utilization.

Table 5.4 Profiles of the two OUR terms in the modified Activated Sludge Model No. 1 (Westpoint)

Modified Activated Sludge Model No. 1	OUR1, mg/l/hr (soluble substrate utilization)	OUR2, mg/l/hr (endogenous respiration)	total OUR (mg/l/hr)
Stage 1	23.40	41.09	64.49
Stage 2	77.17	14.40	91.57
Stage 3	36.53	14.54	51.07
Stage 4	21.05	14.60	35.65

Table 5.5 Profiles of the three OUR terms of the Clifft and Andrews Model (Westpoint)

Clifft and Andrews	OUR1 (soluble substrate utilization)	OUR2 (stored mass to active mass)	OUR3 (endogenous respiration)	Total OUR (mg/l/hr)
Stage 1	0.92	48.81	13.08	62.82
Stage 2	64.26	25.36	4.59	94.20
Stage 3	20.36	26.75	4.65	51.76
Stage 4	6.38	24.94	4.69	36.01

5.5 Summary and Conclusions

The theoretical differences of two structured activated sludge models, the Clifft and Andrews Activated Sludge Model and the modified Activated Sludge Model No. 1, are critiqued with special emphasis on the description of oxygen uptake rates. The two models are then compared in the high-purity oxygen activated sludge process for their abilities to accurately predict oxygen uptake rates. The profiles of OUR terms are determined to reveal micro-scale information on how the models fit the OUR data.

It is evident the both the modified Activated Sludge Model No. 1 and the Clifft and Andrews Activated Sludge Model are capable of realistically describing the oxygen utilization patterns in the high-purity oxygen activated sludge process in spite of their differences in reaction mechanisms.. The Clifft and Andrews Activated Sludge Model tend to predict a more smoother OUR profile because of the incorporation of stored mass. Soluble substrate is of less importance. The modified Activated Sludge Model No. 1, on the other hand, tend to predict a steeper OUR profile which decreases from stage 1 to stage 4. Soluble substrate, which also includes those hydrolyzed from particulate substrate, plays an much more important role in the modified Activated Sludge Model No. 1. Endogenous respiration is important in both models.

It appears that substrate characterization might be different for these two models, as suggested by Grady (1989). This hypothesis, however, has never been confirmed. The same substrate fractions are used for both models in this study. The fact that both of the models fit the data well using the same inputs indicates that substrate characterization has not been a limiting factor here. A better understanding of substrate characterization for these two models, nevertheless, will definitely improved the precision and accuracy of these two models.

6. EXPERT SYSTEM DEVELOPMENT

The effort of expert system development was limited to the petroleum refinery activated sludge process only in this dissertation. Development of an expert system for the high-purity oxygen activated sludge process is currently being undertaken as another independent research.

This chapter documents the development of an expert system to improve operation and control for the petroleum refinery activated sludge process, as reported, in part, by Yuan, *et al.* (1993a).

6.1 Introduction

In the past decade, research in the field of Artificial Intelligence (AI) has had many important successes. Among the most significant of these has been the development of powerful computer systems known as "expert" or "knowledge-based" systems. These computer systems are designed to represent and apply factual knowledge of specific areas of expertise to solve problems. The potential power of expert systems which can replicate expensive or rare human knowledge has led to a worldwide effort to extend and apply this technology.

An expert system is a computer program that has a wide base of knowledge in a restricted domain, and uses complex inferential reasoning to perform tasks which a human expert could do. The process of building an expert system (often called knowledge engineering) involves the acquisition, representation, and updating of the domain knowledge. Through a special form of interaction between the expert system builder, called the knowledge engineer, and one or more human experts in the problem domain, the knowledge engineer extracts from the human experts their procedures, strategies, and rules of thumb for problem solving, and builds this knowledge into an expert system shell.

An expert system differs from more conventional computer programs in several important respects. In a knowledge-based expert system, there is a clear separation of the domain knowledge and the methods used for performing reasoning. However, in a conventional computer program, they are all intermixed, making it difficult to change the program. Another feature is that beyond simply reaching a conclusion when faced with a complex problem, an expert system is capable of explaining, to some extent, the reasoning that led to the conclusion. The explanation typically consists of an identification of the steps in the reasoning process and justification for each step. The explanation system accesses a record of the knowledge that was used in the processing, based on the representation scheme of the knowledge base (such as heuristic rules), and translates it into a form that is palatable to the user. This is an important feature that is generally missing from traditional computer programs.

Although it is difficult to develop an expert system, there are many important reasons why expert systems are desirable. First, human experts, especially the most experienced ones, are very scarce, and hence very expensive. Expert systems, by contrast, are relatively inexpensive. They are costly to develop but cheap to operate. Second, it is easy to transfer or reproduce expert systems. However, transferring knowledge from one human expert to another is laborious, lengthy, and expensive. Third, expert systems give more consistent, reproducible results than human experts. A human expert may make different decisions in identical situations because of emotional factors. For example, a human expert may forget to use an important rule in a crisis situation because of time pressures or stress. An expert system is not susceptible to these distractions. Fourth, but by no means last, expert systems allow automation of many tasks that could not be effectively handled by human experts (Yang and Okrent, 1991).

Much research has been devoted to the development and application of expert system technology to various environmental engineering fields. Kim *et al.* (1988) investigated the feasibility of applying Artificial Intelligence to help the operation and maintenance of U.S. Army wastewater treatment plants. Koskinen (1989) reported the use of an expert system as a top level controller for an activated sludge wastewater treatment plant. Lai and Berthouex (1990) tested an activated sludge expert system, which is a component of an information system for a entire treatment plant. The expert system consistently reproduced the expert operator's decisions and performed better than nonexperienced operators. Collins, *et al.* (1991) documented some important aspects of the intelligent tutoring component of an expert system for small wastewater treatment plants. The expert system was designed to be capable of diagnosing and explaining common problems associated with five major unit operations—chemical addition, flocculation, sedimentation, filtration, and chlorination. The tutorial component focuses on the jar test for chemical dosage. Barnwell, *et al.* (1989) reviews the use and evaluated the potential of expert system technology in water quality modeling and described the elements of an expert advisor for the stream water quality model QUAL2E. Cross, *et al.* (1990) described the design and implementation of an expert system which can help environmental engineers and consultants in the selection of the appropriate techniques for the management and control of hazardous waste sites. Lapointe, *et al.* (1989) presented a prototype of an expert system, name BIOEXPERT, to control a Upflow Anaerobic Sludge Blanket (UASB) wastewater treatment process with applications to failure detection and diagnosis. Gall and Patry (1989) presented a knowledge-based system for the diagnosis of an activated sludge plant. Yang and Okrent (1991) presented a diagnostic expert system for helping the operation of hazardous waste incinerators. Davies and Emery (1992) reported the application of Gensym's G2 real-time expert system in plant monitoring of a product container system, whereby membrane bags are used within existing tanks to contain hydrocarbon fuels so that no product liquid or vapor escapes to the environment. A system of sensors monitors the spaces over the bags to ensure the integrity of the product container system; it also monitors for leaks and emissions at potentially susceptible locations at petroleum product terminals and retail sites. The expert system manages the sensor data, along with information from other plant sensors (tank level sensors, etc.) and uses this information to advise operators of corrective actions. Yuan, *et al.* (1992) proposed the idea of an integrated expert system by integrating an expert system with a process simulator for a refinery activated sludge process. The additional benefits that can be derived from such an integration are many fold. While a process simulation program is not capable of describing such poorly understood phenomena as sludge bulking and foaming, it provides quantitative information about the effluent quality, oxygen utilization, interactions among state variables and manipulated variables, etc. which are much needed for process operational control. Parker and Parker (1989) presented an expert system that handles sludge settling problems in the activated sludge process —filamentous bulking, sludge floating, ashing, various flocculation problems, and possible combination of these problems.

The major areas of concern that could potentially be addressed through the application of expert systems to the operation and maintenance of wastewater treatment plants are (Kim, *et al.*, 1988):

- operator training

- Proper operation and control techniques to meet NPDES permit limitations
- Efficient operation to minimize the operating costs (i.e., manpower, energy, and chemicals)
- Plant operation and laboratory records management
- Reporting as required by in-house management and the regulatory agencies

Few expert systems that have been developed have been actually applied to wastewater treatment systems. Most of them are prototype expert systems and were mainly used to demonstrate concepts, show potentials, develop knowledge acquisition and representation methodologies, etc. It is clear that there is gap between research and real-world requirements so far as the applicability of expert systems is concerned. Many factors attribute to the existence of the gap: poor interface, few abilities to collect and use information in a real-time manner, little or no process schematics, especially dynamic schematics, to name a few . It is now clear that expert systems will not play an important role in the real world unless the gap is shrunk and eventually eliminated.

Easy modification is necessary for maintaining an expert system. The structuring of the code should minimize the risk of hidden side-effects when adding new rules (Laukkanen and Pursiainen, 1991). Ozgur and Stenstrom (1994) and Ozgur (1991) developed a window-style, user-friendly interface using TURBO Pascal for IBM PCs and compatibles. The interface, however, does not permit easy modification and updating.

User interface is crucial for the acceptance of the system. Small faults, or poor screen layouts, have a disproportionate effect on a user's appreciation of the system. The choice of the expert system shell has a prominent influence on the user interface.

This research attempts to close the gap by developing an user-friendly interface, incorporating process schematics into knowledge base, and integrating data management into the program. In addition, the knowledge base is formulated as generic as possible and structured in such a way that it can be readily updated in the future with little possibility of reducing the integrity of the program.

The model activated sludge wastewater treatment system used in this investigation is in the Effluent Treatment Plant (ETP) of an integrated west coast petroleum refinery. Some information of the refinery and its ETP has been previously reported (Ozgur and Stenstrom, 1994; Yuan, *et al.*, 1992; Ozgur, 1991). The refinery has a production capacity of approximately 400,000 barrels per day. The average daily dry-weather flow of about 4.4 million gallons/day (MGD) comprises non-contact cooling water bleedoff, petroleum processing wastewaters, water treatment/conditioning system blowdown, and shallow recovery well groundwaters. The petroleum processing wastewaters and shallow recovery groundwater are treated in the refinery's ETP before discharge. The treatment plant consists of dissolved air flotation units, an equalization basin, and activated sludge units. Figure 6.1 is the process schematics of the ETP.

The feed of ETP is a complex mixture of many chemical compounds. Table 1 is a summary of concentration ranges from November 1992 to February 1993. The two parallel activated sludge units are single sludge systems which are operated to perform carbon oxidation and nitrification. In case there exist excessive suspended solids in secondary clarifier effluent, the secondary effluent is polished in an induced air flotation (IAF) unit before discharge. In case of a process failure, the secondary effluent is diverted to the storage tank and will be recycled to ASUs as influent.

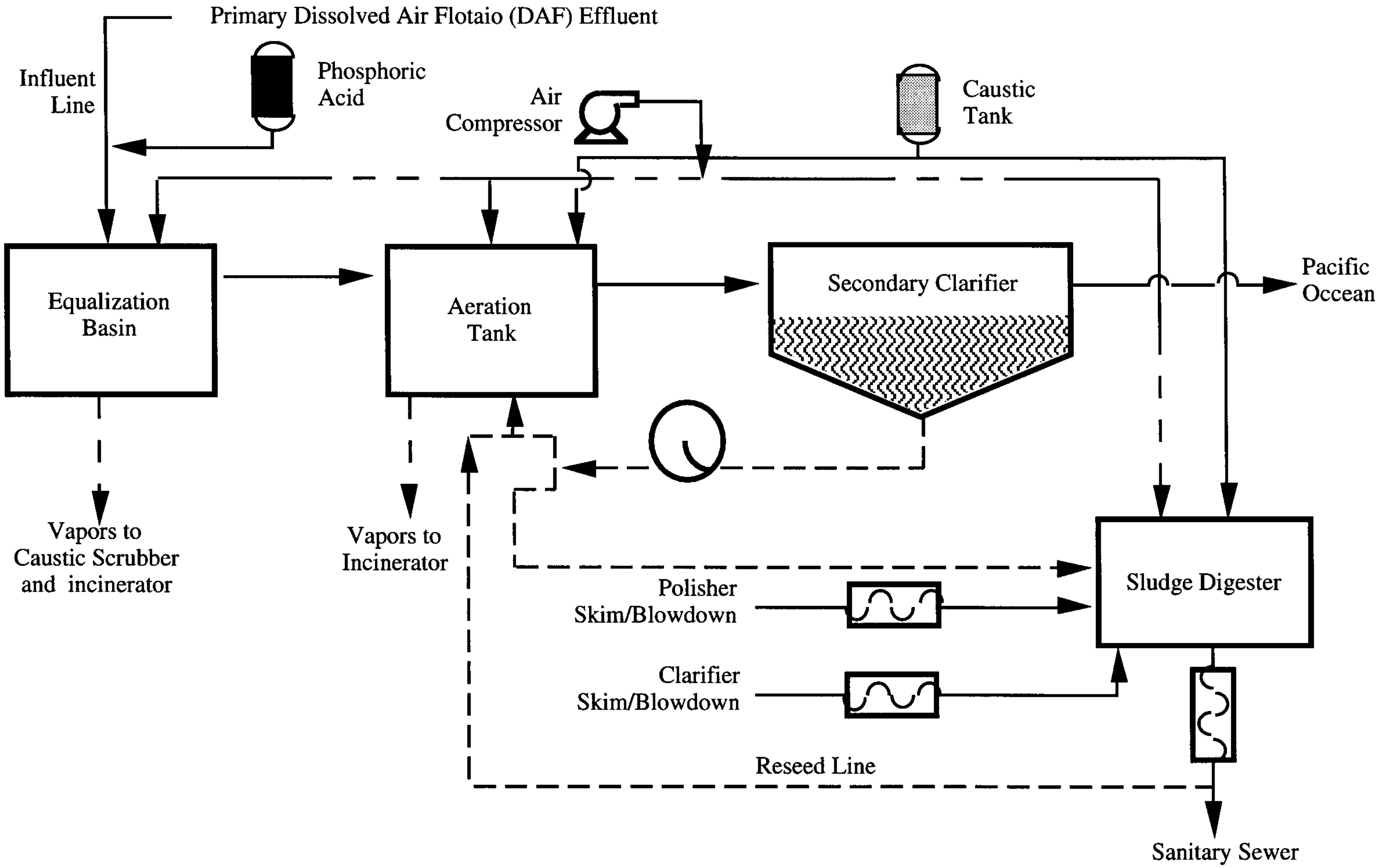


Figure 6.1 Schematic diagram of the model activated sludge system

The model activated sludge system suffers from occurrences of process upsets, transients, such as intermittent and shock loadings, sludge bulking, foaming, and loss of nitrification. The complex composition of refinery wastewater and the complexity of the single sludge system have made process operation and control extremely challenging.

Table 1 Characteristics of the influent to activated sludge units

parameter	range	note
TSS	50 - 400 mg/l	
COD	500 - 3500 mg/l	
Oil and Grease	20 - 600 mg/l	20 - 300 mg/l 11/29/92 to 2/12/93
pH	7.25 - 10.25	
Temperature	80 - 105 °F	
ammonia nitrogen	50 - 250 mg N/l	
sulfide sulfur	0 - 100 mg S/l	
Sulfite	0 - 100 mg/l	

The potentials of an expert system in improving operation and enhancing performance of model refinery activated sludge process have been demonstrated by Ozgur and Stenstrom (1994), Ozgur (1991), and Yuan, *et al.* (1992). This research is an extension of the previous work.

The objectives of this research is to develop an expert system that will do the following:

- improve data management and make better use of data for process operation and control;
- provide complete process schematics and dynamic indications of operational problem locations on schematics;

- alert operators to departures from normal operating ranges and provide diagnoses and qualitative/semi-quantitative suggestions to operators for steps to improve a deteriorating situation;
- facilitate the preparation of turnovers for ETP operation personnel;
- help in the training of newer, less-experienced operators.

6.2 Methodology

The shell used for expert system development is G2® (G2 the Real-Time Expert System®) (Gensym Corporation, 1992). The computer being used is an IBM RISC/6000 POWERstation (Model 520).

At the heart of G2 is its ability to do the following (Gensym Corporation, 1992):

- Scan an application, such as an human operator would, and focus on key areas when it detects potential problems.
- Reason about and control events in a continuously changing environment.
- Respond to events when they occur.
- Apply both procedural knowledge and rule-based heuristics.
- Represent the permanent and transient aspects of an application.
- Express and make use of relationships between objects.
- Acquire information from any number of data sources, both local and remote.
- Provide information to and respond to requests form users, both locally and at remote windows.

- Communicate with other G2 based expert systems and applications (e.g. process simulation program).

The implementation of the expert system has taken full advantage of the shell. All features and functions of the expert system has been developed using the shell's built-in tools.

6.3 Results and Discussion

The features and functions of the current version of the expert system are presented in this section.

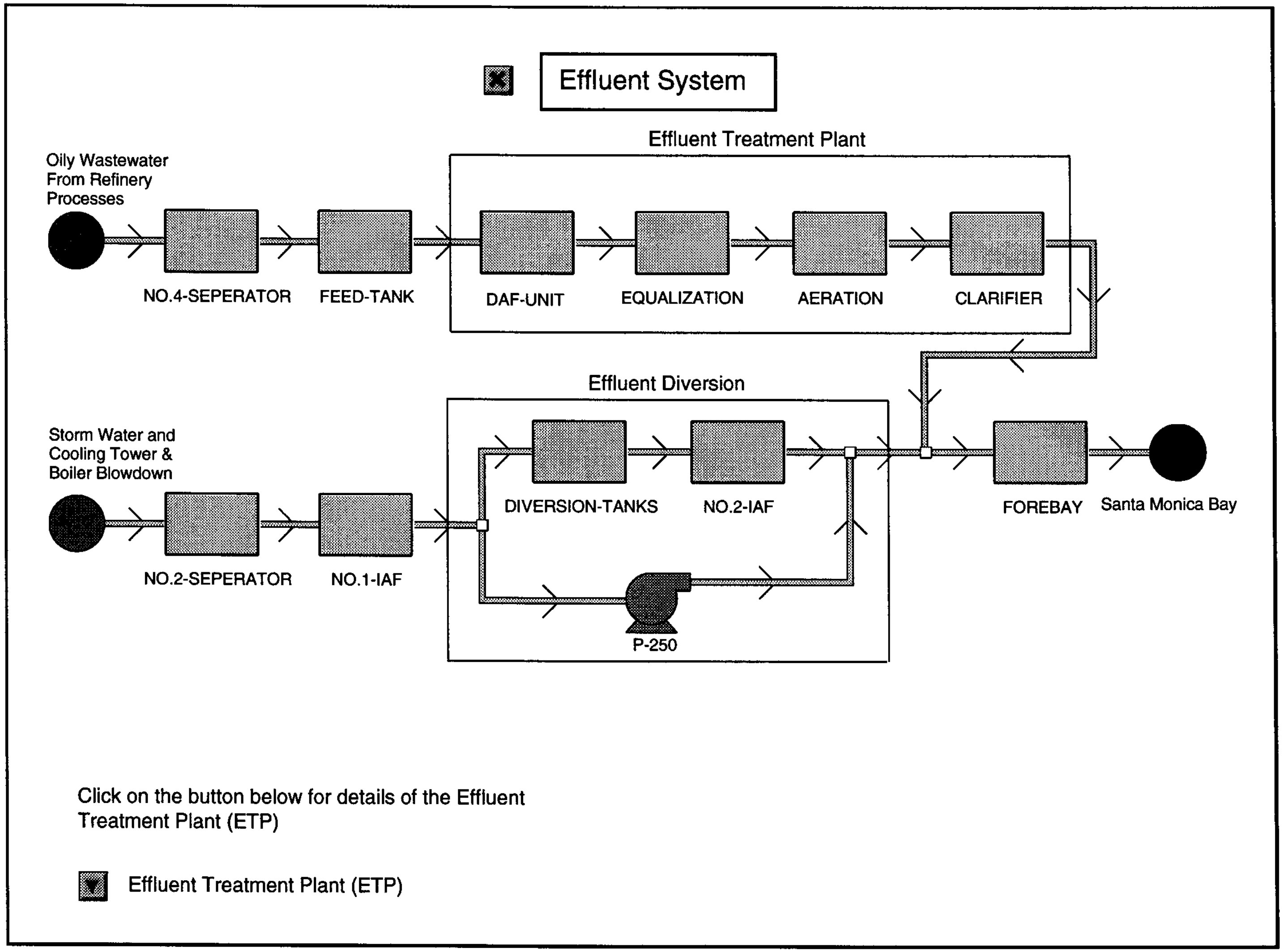
6.3.1 Process schematics

One distinct superiority of the expert system is the inclusion of process schematics into the knowledge base. Process schematics not only provide on-screen display of process equipment layout, flow diagram, but are also capable of indicating process dynamics. The icon of every tank, for example, has an alarm layer. When a problem is detected for that particular tank, the expert system fires the alarm by changing the color of the alarm, which is transparent in normal conditions, to red, and flashing it until the alarm is acknowledged by the operator. Figure 6.2 through Figure 6.5 show some of the process schematics of the knowledge base.

6.3.2 Data Entry

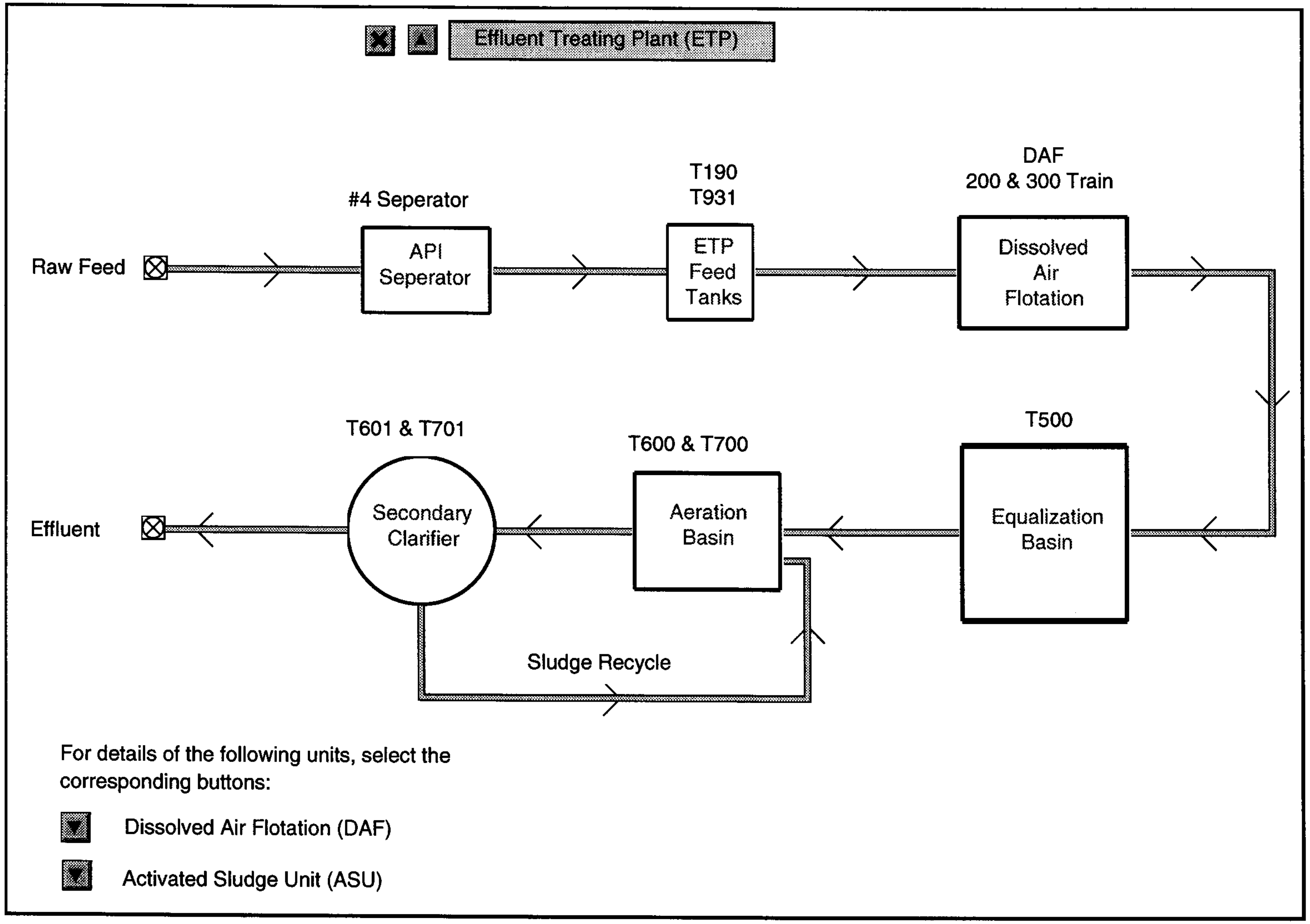
Operators can type data collected from sensors and laboratories into the expert system. The data entry workspace in the form of a spreadsheet and is as user-friendly as a spreadsheet program, such as EXCEL® on Macintosh® (Figure 6.6). To enter data into a cell, just click the cell to select it, then enter the data, and hit return. If a cell has not been selected, there are three asterisks in the cell. The expert system is also capable of detecting certain typing errors. For example, if the pH in the aeration tank in entered as 80 when it is actually 8.0, the expert system informs the operator that pH=80 is not likely (Figure 6.7). The data typed in by the operator is automatically saved into a data file and can also be retrieved when requested. The data file can also be transferred to an IBM PC or compatible or to a Macintosh for importing into a spreadsheet or other program.

Each cell in the template spreadsheet is a type-in box, which is one kind of buttons in G2. One attribute of a type-in box is variable-or-parameter, which indicates which variable or parameter receives a value when a value is typed into the box. Once this variable receives a new value through type-in box, it can be used for other purposes within G2, e.g. trending data and triggering rules, because variables are "global" in G2. The offers obvious advantage since G2 is capable of receiving new values in several different way. Values received from any channel will become immediately available to all other components of G2. This guarantees that most updated values are used as soon as they become available.



Click on the button below for details of the Effluent Treatment Plant (ETP)

Figure 6.2 Effluent Treatment System



For details of the following units, select the corresponding buttons:

▼ Dissolved Air Flotation (DAF)

▼ Activated Sludge Unit (ASU)

Figure 6.3 Effluent Treatment Plant

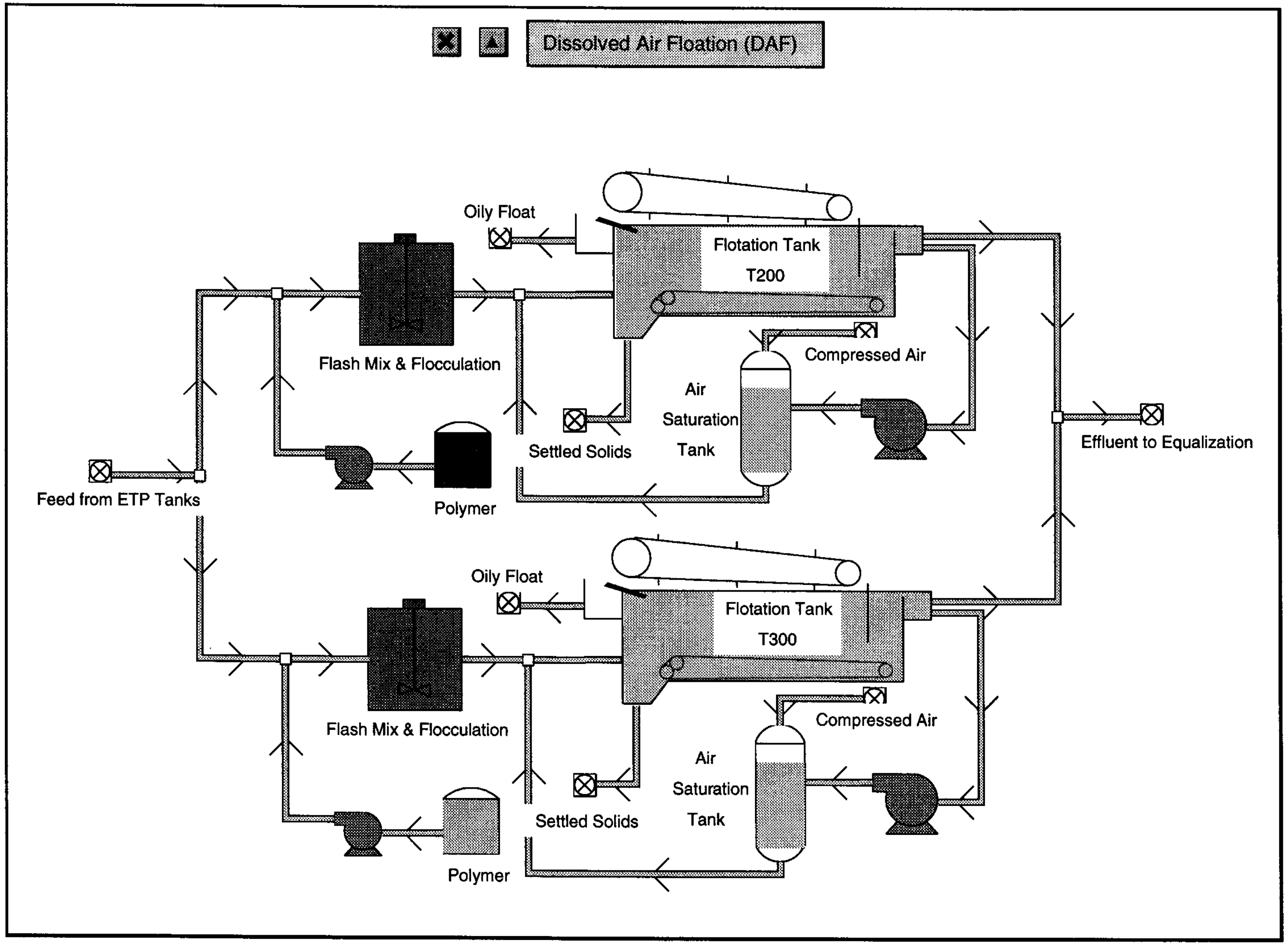


Figure 6.4 Schematics of the dissolved air flotation unit

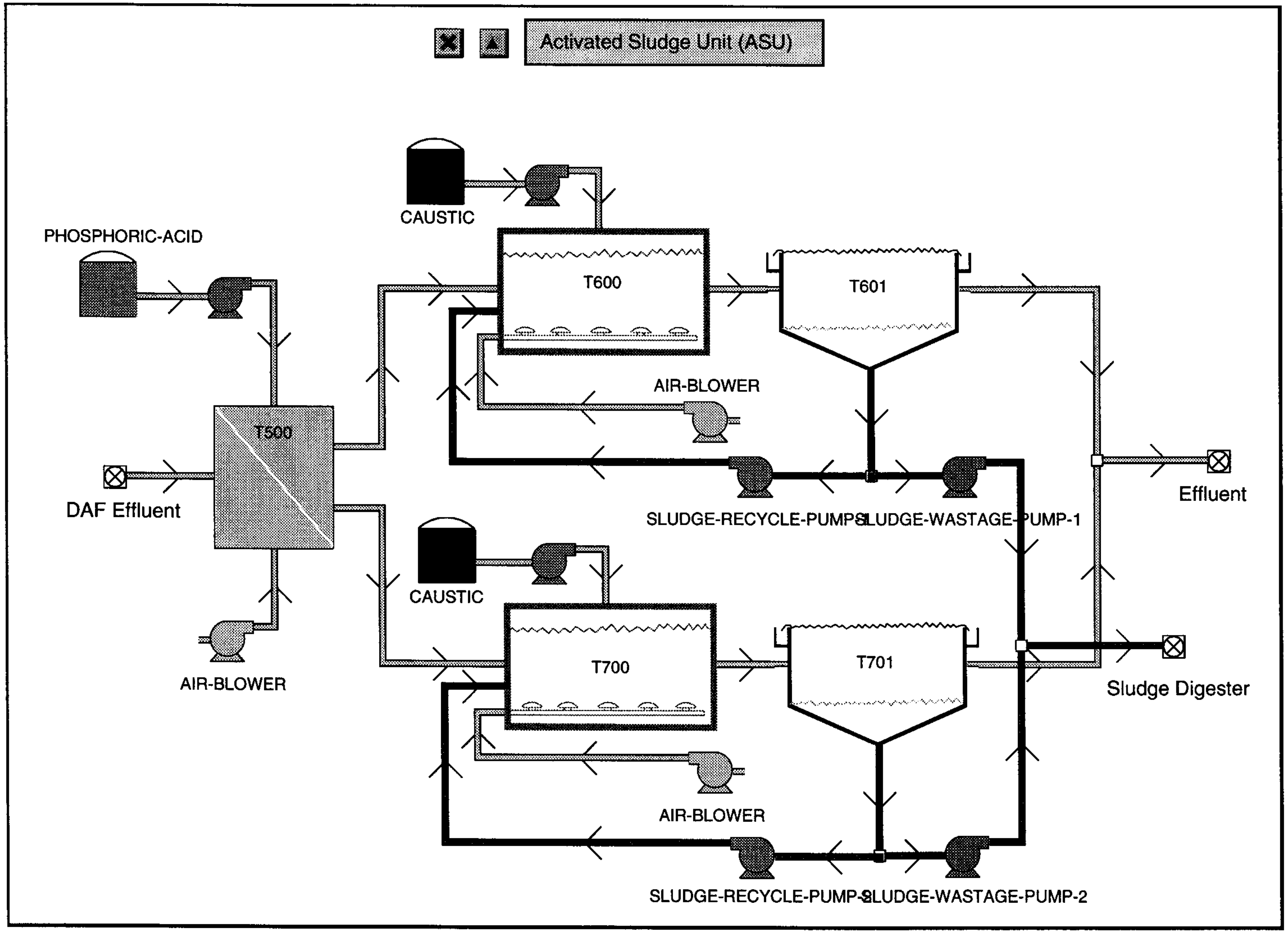
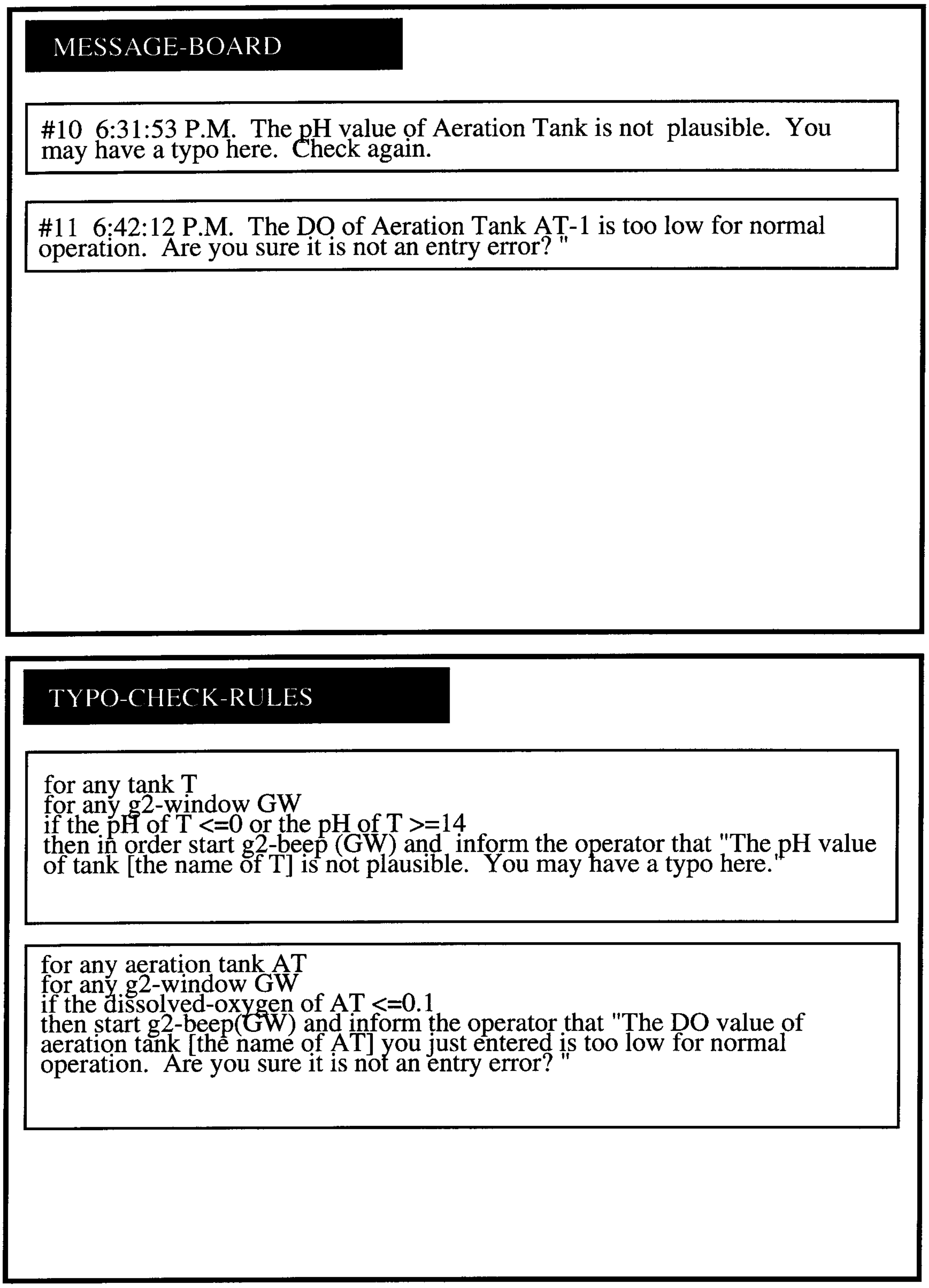


Figure 6.5 Schematics of the activated sludge unit



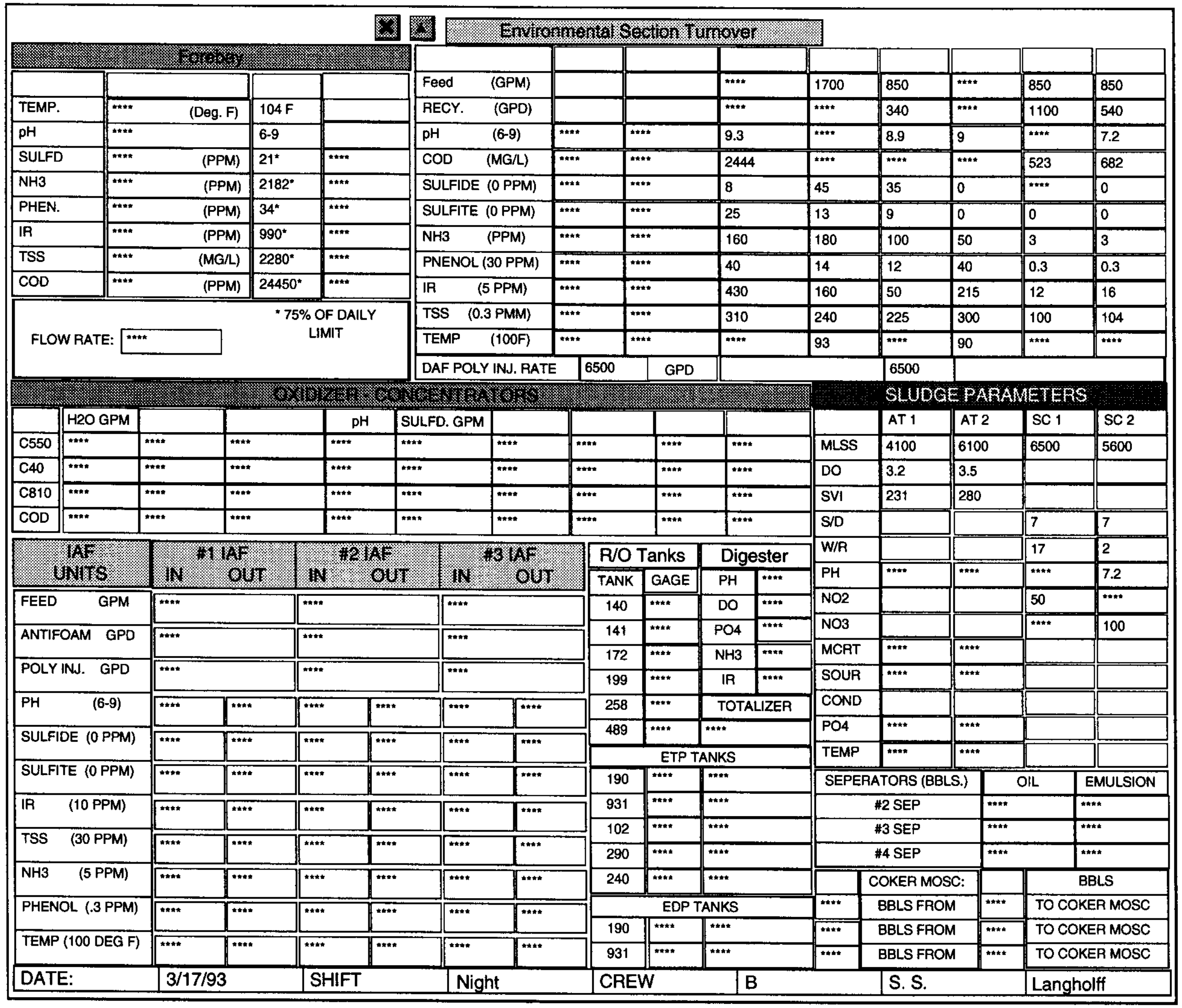
#10 6:31:53 P.M. The pH value of Aeration Tank is not plausible. You may have a typo here. Check again.

#11 6:42:12 P.M. The DO of Aeration Tank AT-1 is too low for normal operation. Are you sure it is not an entry error? "

```
for any tank T
for any g2-window GW
if the pH of T <=0 or the pH of T >=14
then in order start g2-beep (GW) and  inform the operator that "The pH value
of tank [the name of T] is not plausible.  You may have a typo here."
```

```
for any aeration tank AT
for any g2-window GW
if the dissolved-oxygen of AT <=0.1
then start g2-beep(GW) and inform the operator that "The DO value of
aeration tank [the name of AT] you just entered is too low for normal
operation.  Are you sure it is not an entry error? "
```

Figure 6.6 Messages displayed on message board when typo-check rules are fired



Environmental Section Turnover

Forebay

TEMP.	**** (Deg. F)	104 F	
pH	****	6-9	
SULFD	**** (PPM)	21*	****
NH3	**** (PPM)	2182*	****
PHEN.	**** (PPM)	34*	****
IR	**** (PPM)	990*	****
TSS	**** (MG/L)	2280*	****
COD	**** (PPM)	24450*	****

FLOW RATE: ****

* 75% OF DAILY LIMIT

Feed (GPM)			****	1700	850	****	850	850
RECY. (GPD)			****	****	340	****	1100	540
pH (6-9)	****	****	9.3	****	8.9	9	****	7.2
COD (MG/L)	****	****	2444	****	****	****	523	682
SULFIDE (0 PPM)	****	****	8	45	35	0	****	0
SULFITE (0 PPM)	****	****	25	13	9	0	0	0
NH3 (PPM)	****	****	160	180	100	50	3	3
PNENOL (30 PPM)	****	****	40	14	12	40	0.3	0.3
IR (5 PPM)	****	****	430	160	50	215	12	16
TSS (0.3 PMM)	****	****	310	240	225	300	100	104
TEMP (100F)	****	****	****	93	****	90	****	****

DAF POLY INJ. RATE 6500 GPD | 6500

OXIDIZER - CONCENTRATORS

	H2O GPM			pH	SULFD. GPM				
C550	****	****	****	****	****	****	****	****	****
C40	****	****	****	****	****	****	****	****	****
C810	****	****	****	****	****	****	****	****	****
COD	****	****	****	****	****	****	****	****	****

SLUDGE PARAMETERS

	AT 1	AT 2	SC 1	SC 2
MLSS	4100	6100	6500	5600
DO	3.2	3.5		
SVI	231	280		
S/D			7	7
W/R			17	2
PH	****	****	****	7.2
NO2			50	****
NO3			****	100
MCRT	****	****		
SOUR	****	****		
COND				
PO4	****	****		
TEMP	****	****		

IAF UNITS	#1 IAF IN	#1 IAF OUT	#2 IAF IN	#2 IAF OUT	#3 IAF IN	#3 IAF OUT
FEED GPM	****		****		****	
ANTIFOAM GPD	****		****		****	
POLY INJ. GPD	****		****		****	
PH (6-9)	****	****	****	****	****	****
SULFIDE (0 PPM)	****	****	****	****	****	****
SULFITE (0 PPM)	****	****	****	****	****	****
IR (10 PPM)	****	****	****	****	****	****
TSS (30 PPM)	****	****	****	****	****	****
NH3 (5 PPM)	****	****	****	****	****	****
PHENOL (.3 PPM)	****	****	****	****	****	****
TEMP (100 DEG F)	****	****	****	****	****	****

R/O Tanks

TANK	GAGE
140	****
141	****
172	****
199	****
258	****
489	****

Digester

PH	****
DO	****
PO4	****
NH3	****
IR	****

TOTALIZER

****

ETP TANKS

190	****	****
931	****	****
102	****	****
290	****	****
240	****	****

EDP TANKS

190	****	****
931	****	****

SEPERATORS (BBLS.)	OIL	EMULSION
#2 SEP	****	****
#3 SEP	****	****
#4 SEP	****	****

	COKER MOSC:		BBLS
****	BBLS FROM	****	TO COKER MOSC
****	BBLS FROM	****	TO COKER MOSC
****	BBLS FROM	****	TO COKER MOSC

DATE:	3/17/93	SHIFT	Night	CREW	B	S. S.	Langholff

Figure 6.7 Environmental Turnover Sheet

6.3.3 Report generation

Figure 6.7 depicts one of the three turnover sheets that the operation personnel at the model refinery activated sludge process needs to prepare. The spreadsheet-like workspace serves as a template for data entry and the template itself matches exactly the format requirements of the turnover sheets. Once all entries have been entered the user can select print from the menu of the workspace that bears the template to generate a hardcopy of the spreadsheet.

6.3.4 Read and Write Data

The expert system is capable of reading historical data in and writing newly acquired data out. The read and write functions are implemented by using G2 File Interface (GFI).

6.3.5 Trending

The expert system displays the trend charts of major process variables. The interval of display is set to one week in the current version of the program, but it can be easily changed to other values.

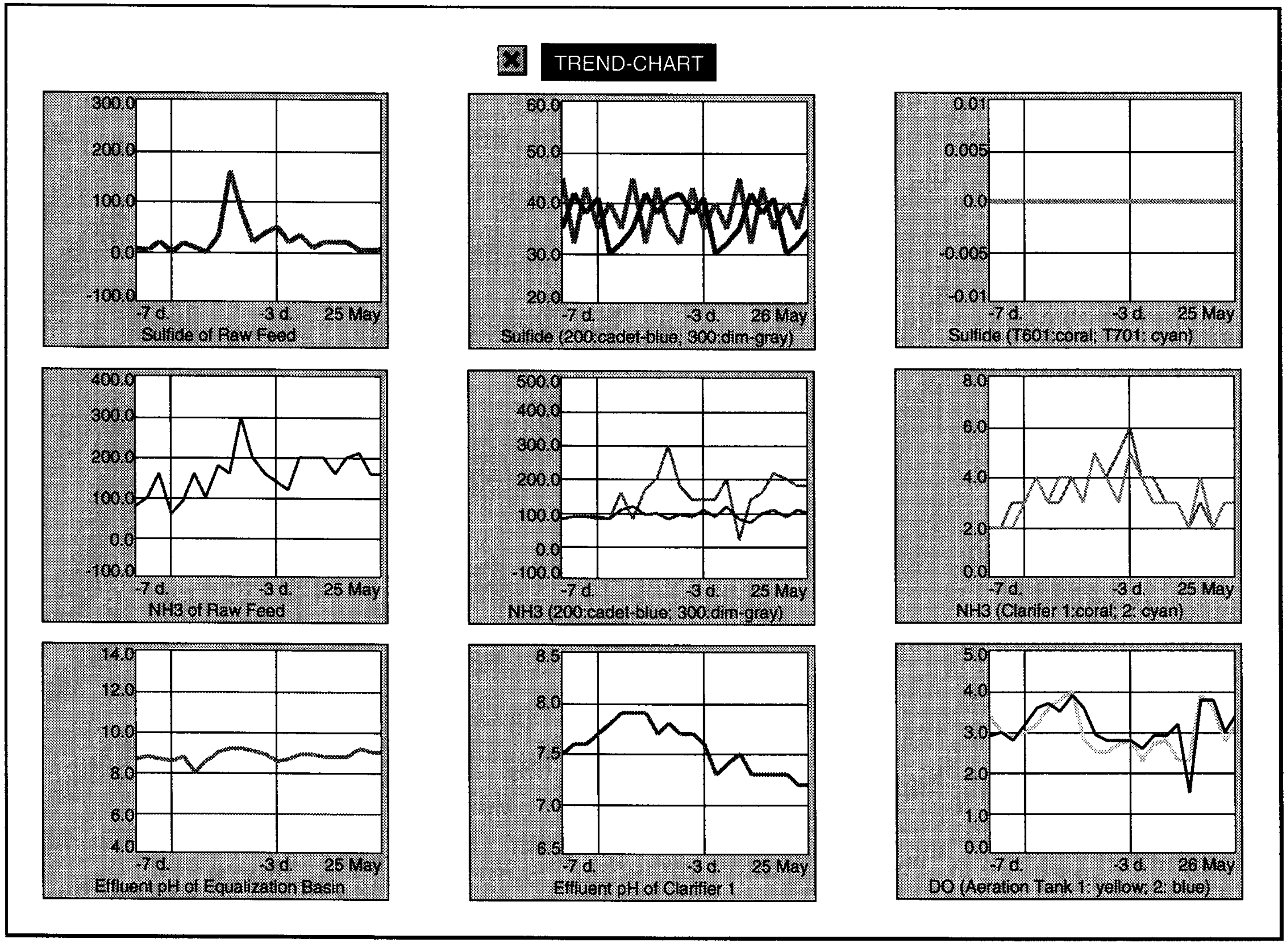


Figure 6.8 Trend Charts

6.3.6 Diagnosis

The diagnosis function of the expert system is to detect actual operation problems, or potential problems, of the treatment plant, alert the operator of the departure of treatment system from normal operation, perform diagnoses, and provide qualitative/semi-quantitative suggestions for steps to alleviate a deteriorating situation.

The knowledge base for diagnosis is based on the work of Ozgur and Stenstrom (1994) and Ozgur (1991), which includes sophisticated logic trees for nitrification control in the refinery activated sludge process. Figure 6.9 is one example of the logic that controls the inference on pH control.

6.4 Summary and Conclusions

The following is a summary of the features that the current version of the expert system has:

- Prepare Turnover sheets. The expert system allows direct data entry into spreadsheet like turnover sheet templates and provides WYSIWYG (what you see is what you get) printouts.
- Read and Write Data. The expert system reads data from historical data files and saves new data into data files.
- Display Trend Charts. The expert system displays the trend charts of all important variables. The charts are automatically updated when new values are received for displayed variables.

- Show Process Schematics. The expert system shows the ETP process schematics on screen. Process schematics not only help the operators understand the process better but also permit indication of the location of an operational problem by light a flashing on the faulty equipment.
- Alert the Operator of Operational Problems. The expert system alerts the operator of operational problems by alarming and messaging.
- Prevent Data Entry Errors. The expert system checks the entered value of a variable. If the value if out of the reasonable range, the operator will receive a message that warns the operator of possible typos.
- Program Security. The expert system can be secured, so that every user is required to have a password in order to use it. The privileges of every class of users are restricted respectively.
- The primary disadvantage of the expert system is the high cost of the basic program.

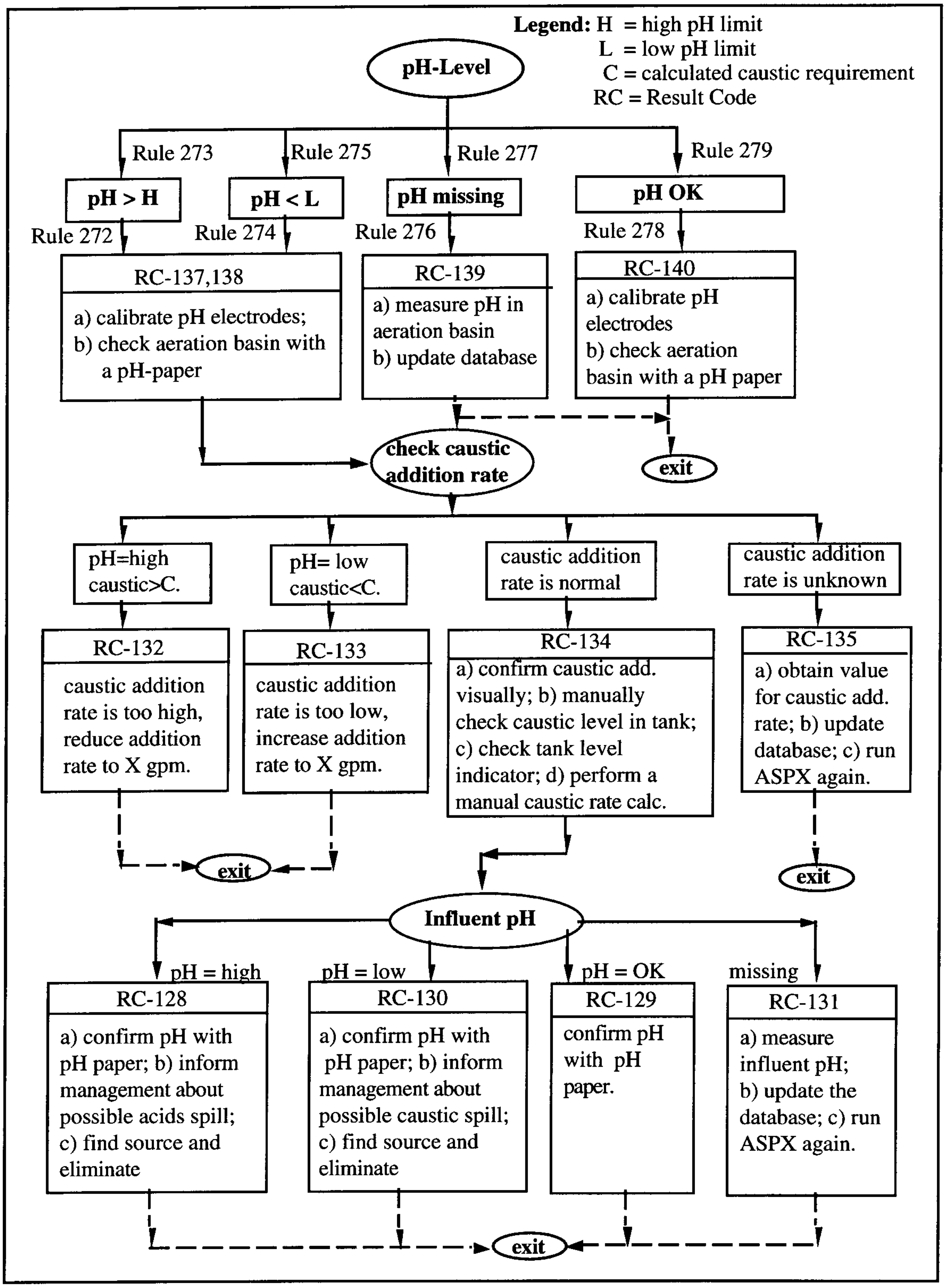


Figure 6.9 Logic tree for pH control (after Ozgur 1991)

7. INTEGRATED EXPERT SYSTEM

The Chapter presents the integrated expert system concept and demonstrates the advantages to be derived from integrating process model and the expert system for the effluent treatment plant in the refinery (Yuan *et al.* 1992).

7.1 Introduction

A complex combination of many different unit petrochemical processes are used in a modern petroleum refinery to change crude oil physically and chemically in order to produce the various products in desired qualities and quantities. Various wastewaters are generated during the refining process. It is typical practice in most refineries to collect all process wastewaters and to combine them into a single wastewater stream which is then treated in a central facility - often called "end-of-pipe" treatment. The end-of-pipe treatment technology in the petroleum refining industry relies heavily upon the use of biological treatment methods. Of all the biological wastewater treatment methods, the activated sludge process is the most cost-effective and widely used secondary treatment technique. The flow diagram of a typical petroleum refinery activated sludge wastewater treatment plant is depicted in Figure 7.1.

One of the biggest challenges faced by activated sludge wastewater treatment plants arises from their operation and control problems. Many refineries fail to satisfy their NPDES (National Pollutant Discharge Elimination System) discharge permits because of their operation and control problems.

Process upsets, transients, such as intermittent and shock loadings, sludge bulking, foaming, loss of nitrification, etc., are intrinsic parts of activated sludge process operation.

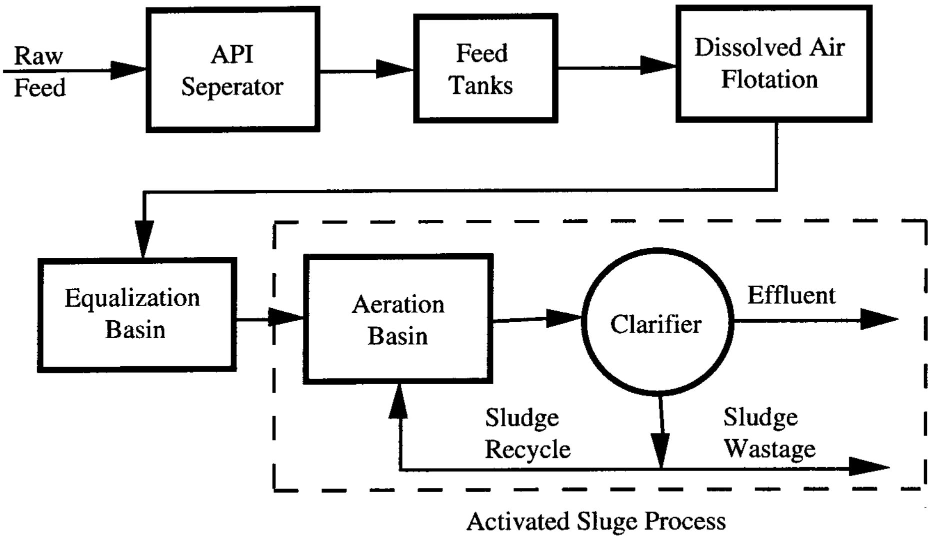


Figure 7.1 Flow diagram of a Typical Petroleum Refinery Effluent Treatment Plant

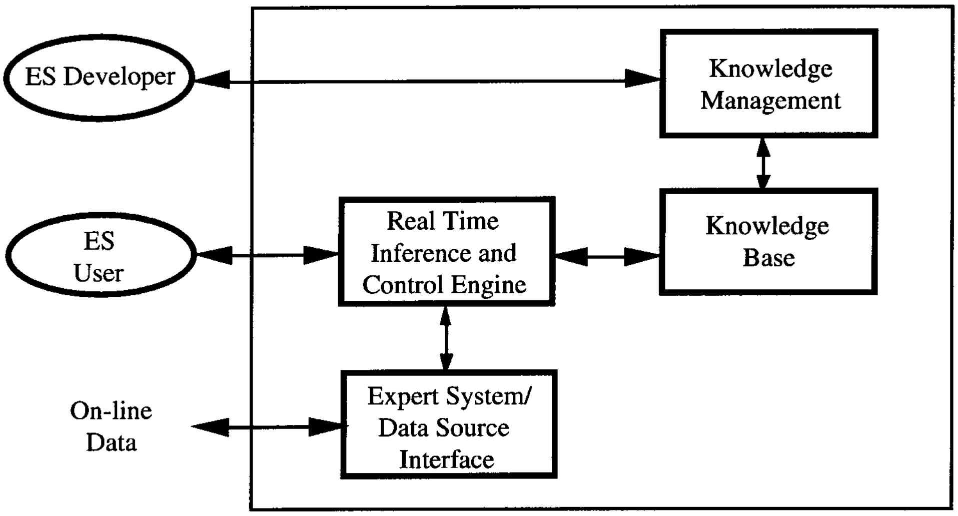


Figure 7.2 Expert System Architecture

In practice, the operators rely heavily on their operating experience to operate and trouble shoot their activated sludge processes. Experienced operators are limited, and their experience is highly personal. When an experienced operator leaves, his experience leaves with him. Obviously, development of a methodology that is capable of representing human knowledge and thus makes it practical to share the valuable human knowledge, is of significant importance.

In recent years, research in the field of Artificial Intelligence (AI) has had many important successes. Among the most significant of these has been the development of powerful computer systems known as "expert" or "knowledge-base" systems. These computer systems are designed to represent and apply factual knowledge of specific areas of expertise to solve problems. The potential power of expert systems which can replicate expensive or rare human knowledge has led to a worldwide effort to apply and extend this technology.

It has been widely recognized that expert systems are capable of helping improve the operation and control of activated sludge processes. Several expert systems have been built for the activated sludge process; but none of them was developed for a petroleum refinery activated sludge process.

The objective of this research is to develop an user-friendly expert system for a refinery activated sludge wastewater treatment plant which constantly suffers from various operation problems. The methodology demonstrated here, however, is applicable to any petroleum refinery which uses activated sludge as its secondary treatment method.

7.2 Integrated Expert System Concept

The most important part of an expert system is its knowledge base (Figure 7.2). The knowledge base of our integrated expert system comes from the following three categories - knowledge from operators' experience, knowledge from statistical analysis, and knowledge from process simulation. Interactive database and process schematics/graphics are also part of the knowledge base (Figure 7.3).

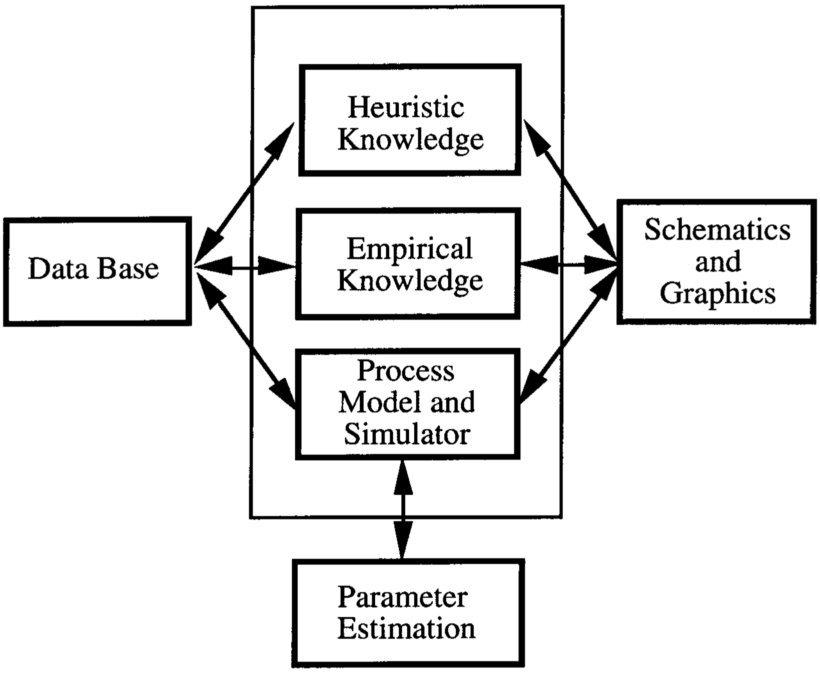


Figure 7.3 Knowledge Base of the Integrated Expert System

Operators' experience is often called heuristic knowledge. The following rules are examples of heuristic knowledge which were acquired through interviews with experienced operators and a literature review:

Rule 01 (Dissolved Oxygen)

IF 1) DO is decreasing, and
2) Air blower is on, and
3) Surface turbulence is normal.
THEN There is a shock loading.

Rule 02 (Sludge Bulking)

IF 1) SVI >= 400, and
2) Microscopic observation shows excessive filamentous microorganism growth.
THEN The problem is filamentous sludge bulking.

Rule 03 (Foaming)

IF Dark brown foams exist on the surface of the aeration tank.
THEN 1) Sludge is "too old", and
2) Decrease the sludge age.

Rule 04 (Nitrification)

IF 1) Ammonia concentration in effluent exceeds the discharge standard, and
2) pH of mixed liquor is less than 6.
THEN 1) Loss of nitrification is due to low pH, and
2) Add caustic soda solution into aeration tank.

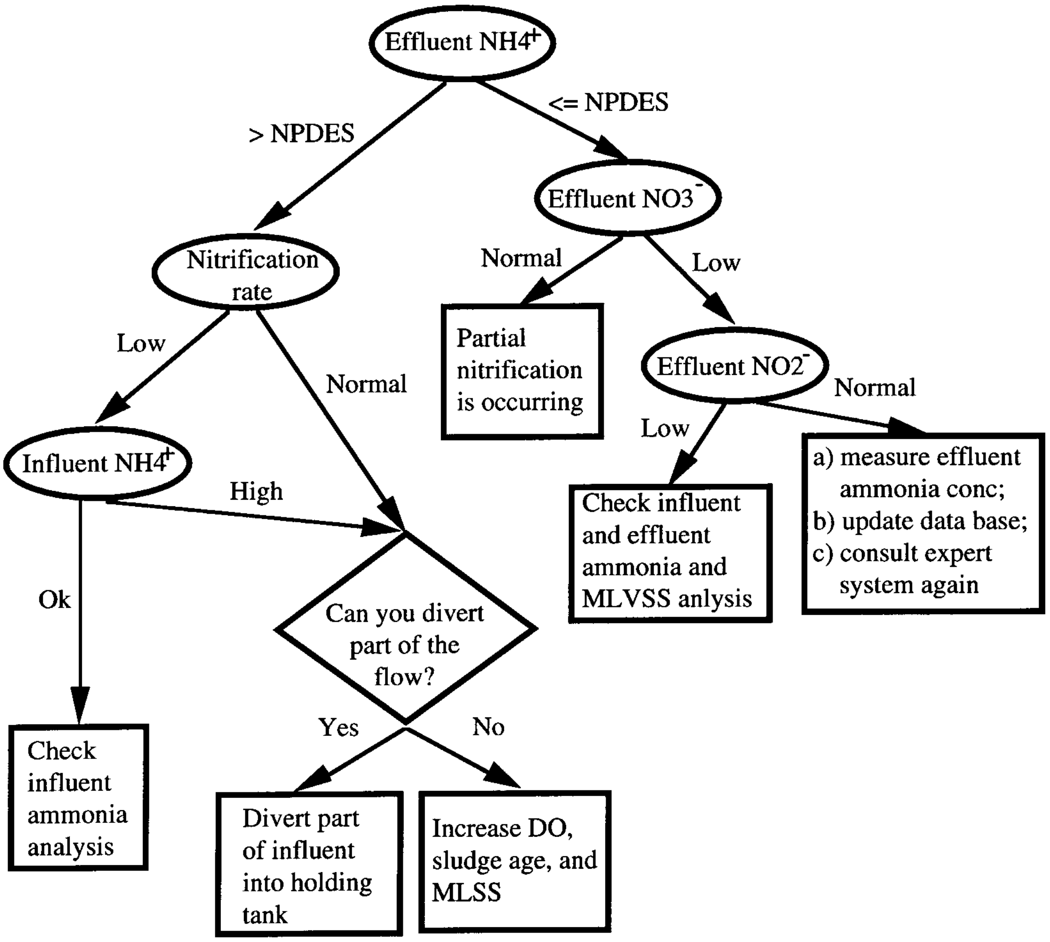


Figure 7.4 The logic tree for nitrification control in the integrated expert system

Another important source of knowledge comes from the statistical analysis of the monitoring data. It is often called statistically/empirically-based knowledge.

Heuristic knowledge, however, is qualitative. It provides no information beyond the operators' experience. The statistical knowledge is quantitative, but plant-specific. The knowledge acquired from data analysis of one plant usually can not be applied to another plant. Often quite different patterns are applicable for another plant.

Process simulation is based on deterministic mathematical models of the activated sludge process, and provides quantitative predictions of the process. A mathematical model was developed for the refinery activated sludge process. The computer simulation program, implemented based on the mathematical model, can simulate the major process dynamics of the petroleum refinery activated sludge process. The mathematical model is a modification of the IAWPRC Activated Sludge Model No. 1 (Henze, *et al.*, 1987).

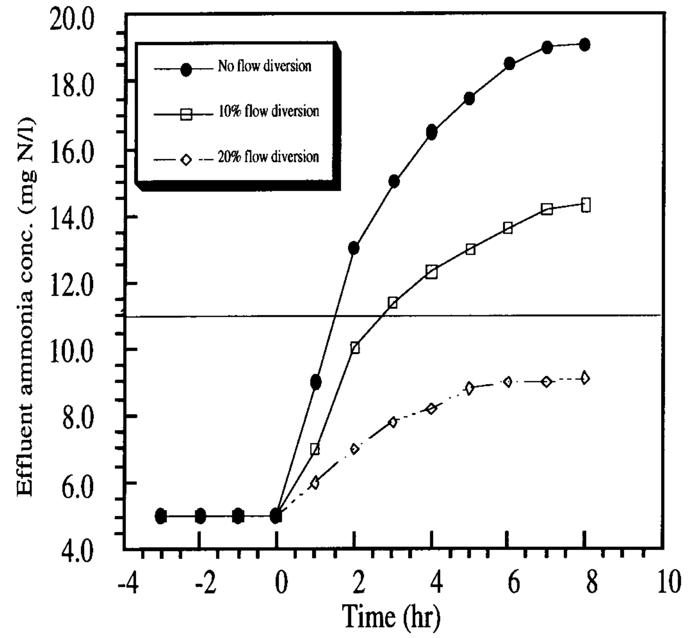


Figure 7.5 Effluent ammonia concentration vs. time for different percentage of influent diversion (shock loading occurred at time t=0).

7.3 Results

The integrated expert system is tested by its developers and some operators to verify its validity. The expert system is in good agreement with the human experts in most cases. The following are the responses of the integrated expert system for a typical problem of the selected refinery activated sludge process - loss of nitrification.

The logic tree that the integrated expert system used for the inference is shown in Figure 7.4. The expert system retrieves data from the database through the expert system/database interface. The data are analyzed to detect operation and control problems. When the effluent ammonia of ammonia is found to be higher than the NPDES limitation, loss of nitrification is determined to be the problem. The expert system then begins to diagnose the process to find the causes of the failure. It first calculates the rate of nitrification. If the nitrification rate is normal, the expert system finds that the process failure was due to excessive process load. Diversion of part of the influent to the holding tank is suggested as the corrective measure.

The simulation program is then used to estimate what percent of the influent should be diverted. This quantitative estimation overcomes the shortcomings of the expert system, which can only provide qualitative advice. As demonstrated in Figure 7.5, a 20% diversion will assure that the effluent ammonia concentration does not exceed 15 mg N/l in this example. The simulation program also provides quantitative advice concerning the adjustment of air flow rate in order to maintain dissolved oxygen at its set point (Figure 7.6).

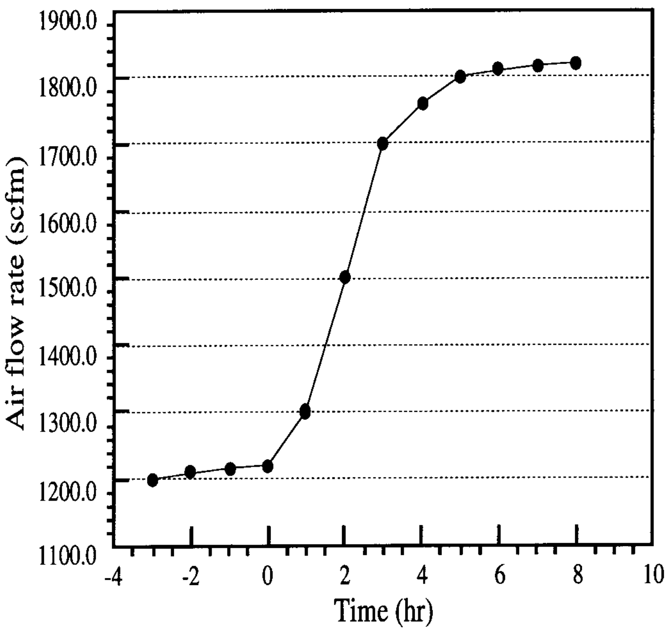


Figure 7.6 Adjustment of airflow rate to keep DO at 3 mg/l after ammonia concentration was increased from 150 mg N/l to 250 mg/l at time t=0.

7.4 Summary and Conclusions

An integrated expert system was developed to help the operation and control of a petroleum refinery activated sludge process. The knowledge base of the expert system consists of heuristic knowledge, empirical/statistical knowledge, and knowledge from process modeling and simulation. It is demonstrated that the expert system can detect process problems, diagnose the causes of process upsets and/or failures, and provide both qualitative and quantitative control advice to the users. Process efficiency and reliability are expected to be enhanced substantially with use of the expert system.

8. SUMMARY AND CONCLUSIONS

This research focuses on the development of dynamic models and expert systems for two important types of activated sludge processes - the high-purity oxygen activated sludge process and the petroleum refinery activated sludge process.

Activated sludge models have evolved from single substrate conventional models to bi-substrate structured models. The major driving force of model development has been the requirement of realistically predicting oxygen utilization patterns in the activated sludge process. The structured activated sludge models developed by two research groups, the Andrews Group and the UCT (University of Cape Town) Group, were reviewed in this dissertation. All these previous models were reformulated into the matrix form which would significantly reduce the difficulty in following and understanding them.

The IAWQ Activated Sludge Model No. 1 was modified for the high-purity oxygen activated sludge process by eliminating nitrification and denitrification related components and processes. Biomass decay was described by endogenous respiration instead of death-regeneration. A new process model was developed for the high-purity oxygen activated sludge process using the modified Activated Sludge Model No. 1. The new model is the first high-purity oxygen activated sludge process model that is based on Activated Sludge Model No. 1. The new high-purity oxygen activated sludge process model consists of an aeration tank model and a secondary clarifier model. The aeration tank model further consists of a gas phase model, a gas transfer model, and a liquid phase model. The modified Activated Sludge Model No. 1 becomes part of the liquid phase mode.

A model calibration algorithm was developed and evaluated for the high-purity oxygen activated sludge process. Synthetic data were used in this study, which was numerically generated by corrupting model predictions with Gaussian noise. The objective was to find out if the poor fit was due to poor data quality, model deficiency, or poor calibration algorithm. In addition the study provides useful information on important calibration issues - effects of the following factors: data quality, number of observations, number of measured variables, and sampling frequency. The results showed that the calibration algorithm, which solves a nonlinear constrained optimization problem using the Complex Method, is robust and performs reliably. As long as the errors are random (no systematic errors), the algorithm is capable of estimating the parameters to a acceptable accuracy. The study also found that the accuracy of calibration improves as the number of observations increases. However, the improvement slows down as the number of observations increases. No significant improvement is observed beyond n=96 (hourly observations of 4 days). In this study twenty four points (hourly data of 1 day) is able to estimate the yield coefficient and the maximum specific growth rate coefficient within 10% of their true values. For applications in which 10% is an acceptable estimation error, hourly sampling for 24 hours should be an adequate sampling scheme. Another important finding is that only a certain number of parameters can be reliably estimated using a given set of observations. Sensitivity analysis is helpful in determining what parameters are to be estimated. If additional variables are to be measured and used for calibration, the potential benefits resulted from the addition should be quantitatively evaluated in advance.

The new high-purity oxygen activated sludge process model was verified and validated using the two data sets - the West Point Pilot Plant data and the Sacramento Regional Wastewater Treatment Plant data. The model had difficulty to fit the data using the typical parameter values of Activated Sludge Model No. 1. It was found that a higher value (0.36 day^{-1} instead of 0.24 day^{-1}) needed to be used for sludge coefficient in order for the model to fit the observed oxygen uptake rates at the pilot plant. This confirms that sludge does decay faster in the high-purity oxygen activated sludge system than it does in the air system. Excellent fits were achieved when the same set of stoichiometric and kinetic coefficients was used for the simulation of both pilot and full-scale plants.

Model comparison shows that oxygen uptake from soluble substrate utilization (OUR1) is only important in the feeding stage for Clifft and Andrews Activated Sludge Model. OUR1 sharply decreases to zero from stage 2 to stage 4. Oxygen uptake by stored mass utilization (OUR2) is relatively stable, and declines from 10.66 to 7.27 from stage 1 to stage 4. Oxygen uptake from biomass decay is very stable throughout the stages. It accounts for at least 50% of the total OUR and becomes the dominant oxygen uptake mechanism in the last two stages. For the modified Activated Sludge Model No. 1, oxygen uptake from soluble substrate utilization is high in the first stage, medium in the second stage and low in the third and fourth stages. Oxygen uptake from biomass decay is stable throughout the stages and becomes the dominant mechanism in the last two stages.

An activated sludge model was developed for a petroleum refinery activated sludge process which performs carbon oxidation and nitrification. Nitrification is modeled as a two-step reaction. The oxidation of sulfide is modeled as a step reaction with sulfate as the end product. Special pH and temperature functions are developed that are capable of modeling the effects of pH and temperature fluctuations in wide ranges. The model is capable of predicting effluent concentrations of COD, ammonia, nitrite, nitrate, sulfide, and sulfate. It also provides information on air flow (aeration) and sodium hydroxide dosage (pH control).

An expert system was developed for the effluent treatment plant in the model refinery. The expert system allows direct entry of process data into spreadsheet-like templates and provides WYSIWYG (what you see is what you get) printouts. It reads data from historical data files and saves new data into data files. It displays trend charts of all important variables. The charts are automatically updated when new values are received for displayed variables. It shows the process schematics on screen, which not only help the operators understand the process better but also permit indication of the location of an operational problem by light a flashing on the faulty equipment. It alerts the operator of operational problems by alarming and messaging. The expert system checks the entered value of a variable. If the value is out of the reasonable range, the operator will receive a message that warns the operator of possible typos. The expert system can be secured, so that every user is required to have a password in order to use it. The privileges of every class of users are restricted respectively.

The concept of an integrated expert system was proposed for the petroleum refinery activated sludge wastewater treatment plant. The structure of the integrated expert system was developed and additional benefits to be derived from such an integration were illustrated. The knowledge base of the expert system consists of heuristic knowledge, empirical/statistical knowledge, and knowledge from process modeling and simulation. It is demonstrated that the expert system can detect process problems, diagnose the causes of process upsets and/or failures, and provide both qualitative and quantitative control advice to the users. Process efficiency and reliability are expected to be enhanced substantially with the integration of expert system and process model.

9. FURTHER RESEARCH

The work presented in this dissertation was the documentation of the development of dynamic models and expert systems for the activated sludge process. Much research needs to be conducted when the models and expert systems are fully applied to engineering applications.

The validity of the dynamic models developed in this dissertation, especially the high-purity oxygen activated sludge process model, have been verified thoroughly under steady-state conditions. For successful applications, additional research is imperative.

Firstly, the performance of the models under dynamic conditions needs to be evaluated. Theoretically the models have incorporated all the mechanisms necessary for realistic predictions of dynamic process behavior ; this, however, needs to be confirmed and tested.

Secondly, wastewater characterization needs to be performed in accordance to the procedures recommended by the IAWQ Task Group. Wastewater is plant-specific. The information on substrate characterization is critical to the success of a modeling effort.

Thirdly, stoichiometric and kinetic coefficients need to be determined for a given wastewater and treatment process under a given conditions. The values of these coefficients dictate the outcome of the modeling to large extent.

For expert systems developed in this research, future research should emphasize their testing under process conditions. Testing should reveal problems and create the need for new functions and features. The expert systems can then be modified and expanded accordingly.

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APPENDIX A Source Code of HIPURE2 - the simulation program for the high-purity oxygen activated sludge process using the IAWQ Activated Sludge Model No. 1

Main Program

```
c***********************************************************************
c***********************************************************************
c.. main simulation program
c***********************************************************************
c***********************************************************************
c.. the following dimension statement is for the secondary clarifier
      dimension vs(10),tflux(10),xdot(10),x(10),setflx(10),ax(5,10)
c.. the following dimension statement is for the integrators. They
c   define the storage that each intergrator needs.  The storage
c   is used to save the initial conditions and the intermediate values.
      dimension dsi(0:5),    si(0:5),      asi(5,0:5),
     1dss(0:5),              ss(0:5),      ass(5,0:5),
     2dxi(0:5),              xi(0:5),      axi(5,0:5),
     3dxs(0:5),              xs(0:5),      axs(5,0:5),
     4dxnv(0:5),             xnv(0:5),     axnv(5,0:5),
     5dxbh(0:5),             xbh(0:5),     axbh(5,0:5),
     6dxp(0:5),              xp(0:5),      axp(5,0:5),
     7dso2(0:5),             so2(0:5),     aso2(5,0:5)
      dimension dsnh3(0:5),  snh3(0:5),    asnh3(5,0:5),
     1dsnd(0:5),             snd(0:5),     asnd(5,0:5),
     2dxnd(0:5),             xnd(0:5),     axnd(5,0:5),
     3dsalk(0:5),            salk(0:5),    asalk(5,0:5),
     4dsn2(0:5),             sn2(0:5),     asn2(5,0:5),
     5dsco2(0:5),            sco2(0:5),    asco2(5,0:5),
     6co2dot(0:5),           co2(0:5),     aco2(5,0:5),
     7o2dot(0:5),            o2(0:5),      ao2(5,0:5)
      real*4 n2dot(0:5),     n2(0:5),      an2(5,0:5)
      dimension              as4po2(5),    as1tp(5)
c   DO control system dimensions
      dimension drsetdo(4),  rsetdo(4),    arsetdo(5,4),
     1dosp(4)
c.. other dimensions
      dimension alpha(4),effd(4),q(4),qr(4),qt(0:4),tpres(0:4),
     1vli(4),vgi(4),vlf(4),vgf(4),ssco2(4),sso2(4),ssn2(4),
     2pco2(4),pn2(4),po2(4),qgt(0:5),qg(4),co2kla(4),akla(4),hi(4),
     3ph(4),qleak(4),o2uptr(4),fstep(4),aqfun(5),qfun(2,200),
     4assfun(5),ssfun(2,200),axsfun(5),xsfun(2,200)
      real*4 kla(4),klai(4),klalim(4,2),kflow,ks,koh,kx,kh,ka,ixb,ixp,
     1kleak,mlss,mlvss,n2mw,n2kla(4),mod
c.. the following real, dimension, and common are for the internal
c   workings of the program and should not be changed. they
c   communicate the values of time and other keys for program control.
      real*4 impuls,limit
c.. comment out the following line to avoid warning messages
c     real*4 impuls,insw,ior,limit,modint,nand,nor,not
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
c.. specifiy the maximum number of elements in the clarifier
c   and the nubmer of aeration stages in series.  they must be
c   integer constants.
      max=10
```

```
      nstage=4
      nstag1=nstage+1
c.. open this file for debugging
      open(unit=27,file='forglen',status='unknown')
c.. set the number of allowable pairs of data for afgen. It must be a an
c   integer constant, and match arrays, qfun...
      maxaf=200
c***********************************************************************
c***********************************************************************
c.. initial section of the model
c***********************************************************************
c***********************************************************************
c.. read the integration and print control parameters.
c       delt   = integration interval
c       method = integration method
c              1 = euler;
c              2 = modified euler;
c              3 = fourth-order  runge-kutta;
c              4 = fourth-order runge-kutta, variable step.
c       prdel  = print interval;
c       outdel = plot interval;
c       fintim = finish time;
c       keep   = counter for integration step (automatically set).
c       key(i) = program control counters (see documentation)
c
c.. Open the file and leave it open for later use in the
c   centra routine for variable step information.
      open(unit=8,file='timers',status='old')
      rewind 8
      read(8,*) method
      read(8,*) delt
      read(8,*) prdel
      read(8,*) outdel
      read(8,*) fintim
c.. intialize the counters which control printing, plotting and
c.. program management. never change the statements in the following
c.. section
      ptime=prdel
      pltime=0.
      iplot=0
      iprint=1
      time=0.
      last=1
c***********************************************************************
c.. specify the model parameters
c***********************************************************************
      open(unit=9,file='params',status='old')
      rewind 9
      read(9,1000) alpha(1),alpha(2),alpha(3),alpha(4),beta,
     1klai(1),klai(2),klai(3),klai(4),
     2klalim(1,1),klalim(2,1),klalim(3,1),klalim(4,1),
     3klalim(1,2),klalim(2,2),klalim(3,2),klalim(4,2),
     4dosp(1),dosp(2),dosp(3),dosp(4),pgaindo,rgaindo,
     5s4po2sp,pgano2,rgano2,pgs4po2,rgs4po2,s1tpsp,pgtpc,rgtpc,
     6yh,fp,ixb,ixp,uh,ks,koh,bh,ka,kh,kx,co2o2,codvss,b5tobus,b5tobup,
     7areaft,adepth,anelem,ameth,
     8vgf(1),vgf(2),vgf(3),vgf(4),vlf(1),vlf(2),vlf(3),vlf(4),
     9kflow
1000  format(f10.0)
      close (9)
c.. check to see if both 1st stage total pressure control and oxygen
```

```
c   feed rate control have been specified. if so end with an error
c   message.
      if(abs(pgano2).gt.0..or.abs(rgano2).gt.0.) then
        if(abs(pgtpc).gt.0..or.abs(rgtpc).gt.0.) then
          write(6,*) ' You can not use pressure control and oxygen'
          write(6,*) ' feed rate control at the same time'
          write(6,1010) pgano2,rgano2,pgtpc,rgtpc
1010      format(
     1' Proportional gain for oxygen feed (pgano2)        ',f10.3,/,
     2' Reset (integral) gain for oxygen feed (rgano2)    ',f10.3,/,
     3' Proportional gain for pressure control (pgtpc)    ',f10.3,/,
     4' Reset (integral) gain for pressure control (rgtpc)',f10.4)
          stop 3
        endif
      endif
c.. check to see if DO control is being used. If not, set a flag to skip
c   the controller calculations in the dynamic section to save time.
      if(abs(pgaindo).gt.0..or.abs(rgaindo).gt.0.) then
        idoctrl=1
      else
        idoctrl=0
      endif
      nelem=anelem+0.5
      meth=ameth+0.5
      if(nelem.gt.max) then
        write(6,*) 'The number of clarifier elements has been specified'
        write(6,*) 'greater than the maximum possible. The maximum'
        write(6,*) 'is being used (',max,')'
        nelem=max
      endif
      nelem1=nelem-1
c*********************************************************************
c.. specify all the initial conditions here
c*********************************************************************
      open(unit=10,file='inits',status='old')
      rewind (10)
c.. the initial conditions are stored in the first position of
c   the storage array
      read(10,*) (si(ij),    ij=0,nstage)
      read(10,*) (ss(ij),    ij=0,nstage)
      read(10,*) (xi(ij),    ij=0,nstage)
      read(10,*) (xs(ij),    ij=0,nstage)
      read(10,*) (xnv(ij),   ij=0,nstage)
      read(10,*) (xbh(ij),   ij=0,nstage)
      read(10,*) (xp(ij),    ij=0,nstage)
      read(10,*) (so2(ij),   ij=0,nstage)
      read(10,*) (snh3(ij),  ij=0,nstage)
      read(10,*) (snd(ij),   ij=0,nstage)
      read(10,*) (xnd(ij),   ij=0,nstage)
      read(10,*) (salk(ij),  ij=0,nstage)
      read(10,*) (pco2(ij),  ij=1,nstage)
      read(10,*) (po2(ij),   ij=1,nstage)
      read(10,*) (ph(ij),    ij=1,nstage)
      read(10,*) (x(ij),     ij=1,nelem)
      close(10)
c.. convert alkalinity unit from mgCaCO3/l to mol/l.
      do 5 i=1,nstage
5     salk(i)=salk(i)/50.e+03
c.. set the initial conditions for controllers
      do 10 i=1,nstage
      drsetdo(i)=0.
```

```
10    rsetdo(i)=0.
c.. stage 4 purity
      ds4po2=0.
      s4po2=0.
c.. stage 1 total pressure
      ds1tp=0.
      s1tp=0.
      s1tpsp1=s1tpsp
c.. o2 utilization
      o2util=0.9
c**********************************************************************
c.. specify the model inputs here.
c**********************************************************************
      open(unit=11,file='inputs',status='old')
      rewind (11)
      read(11,1020) sio,sso,xio,xso,xnvo,xbho,xpo,so2o,snh3o,sndo,xndo,
     1salkao,pho,kleak,abasin,qmgd,fstep(1),fstep(2),fstep(3),fstep(4),
     2qrrat,srtsp,temp,tgasm,fpuro2,ainput,flowamp,ssamp,xsamp
1020  format(f10.0)
      close(11)
      qmgdt=qmgd
c.. convert amplitudes from percents to fractions
      flowamp=flowamp/100.
      ssamp=ssamp/100.
      xsamp=xsamp/100.
      input=ainput+0.5
      if(input.eq.3) then
c.. read the diurnal flow rate data
        open(unit=13,file='diurnal',status='old')
        rewind 13
c.. first read the number of data points
        read(13,*,end=20000) anqfun
        nqfun=anqfun+0.5
          if(nqfun.gt.maxaf) then
            write(6,*) ' Number of flow input datapairs exceeds',maxaf
            write(6,*) ' Number specified =',nqfun
           write(6,*) ' Execution terminating'
           stop 1
          else
           do 11 ij=1,nqfun
11          read(13,1030) qfun(1,ij),qfun(2,ij)
           read(13,*) anssfun
            nssfun=anssfun+0.5
           do 12 ij=1,nssfun
12          read(13,1030) ssfun(1,ij),ssfun(2,ij)
           read(13,*) anxsfun
            nxsfun=anxsfun+0.5
            do 13 ij=1,nxsfun
13          read(13,1030) xsfun(1,ij),xsfun(2,ij)
1030      format(2f10.0)
         endif
      endif
      close(13)
c.. convert the number of parallel basins to integer
      nbasin=abasin+0.5
      nbasn1=nbasin+1
c.. convert the units from English to Metric.  Set the flows all to
c   zero to initialize.  They may be controlled later.
      hclar=adepth*0.3048
c.. convert the flow rate from mgd to m3/hr
      qm3hr=qmgd*3785./(24.*nbasin)
```

```
c.. calculate the recycle flow rate. assume that it all goes to stage 1
      qr(1)=qm3hr*qrrat
c.. set the other recycle rates to zero.
      do 32 i=2,nstage
32    qr(i)=0.
c.. set the zeroth influent flow rate to zero
      qt(0)=0.
      qgt(0)=0.
c.. calculate all the other flow rates. this is necessary for
c   calculating
c   the initial conditions. these calculations are repeated in the
c   dynamic section.
      do 35 ij=1,nstage
c.. convert fstep from percent to fraction
      fstep(ij)=fstep(ij)/100.
c.. convert tank volume from cubic foot to cubic meter
      vli(ij)=1./(vlf(ij)*0.02831685)
      vgi(ij)=1./(vgf(ij)*0.02831685)
c   flow rates
      q(ij)=qm3hr*fstep(ij)
      qt(ij)=q(ij)+qr(ij)+qt(ij-1)
      qg(ij)=0.
      qgt(ij)=0.
35    continue
c.. calculate the total reactor volume
      vti=1./((vlf(1)+vlf(2)+vlf(3)+vlf(4))*0.02831685)
c.. open this file for the plot dataset.
      open(unit=12,file='output.dat')
c.. open this file for the additional plotting dataset. it is provided
c   in order to write and save things as required for special purposes.
c   the writes are added at the end of the pr subroutine.
c*********************************************************************
c.. specify the physical constants that never change
c*********************************************************************
c.. Theta factor for aeration
      theta=1.024
c.. Molecular Weights
      co2mw=44.009
      n2mw=28.013
      o2mw=31.998
c.. ratios of n2 and co2 klas to o2
      fklan2=0.943
      fklaco2=0.836
c.. Ideal gas constant (m3.atm)/(K.Mole)
      r=8.2056e-05
      rt=r*(temp+273.15)
c.. The following relations are empirical fits of handbook data
c   for various physical/chemical constants. This avoids "table
c   look up"
c.. pkW of water
      pkw=14.943-4.2467e-02*temp+1.8234e-04*temp**2
      ckw=10**(-pkw)
c.. pk NH3
      pknh3=pkw-10.059-3.1956e-02*temp
      cknh3=10**(-pknh3)
c.. pk1 and pk2 of H2CO3
      pk1=6.5793-1.3525e-02*temp+1.8126e-04*temp**2
      pk2=10.629-1.5054e-02*temp+1.2074e-04*temp**2
      ck1=10**(-pk1)
      ck2=10**(-pk2)
c.. vapor press H2O (atms)
```

```fortran
      vph2o=(5.0538-2.1092e-02*temp+3.0783e-02*temp**2)/760.
c.. Henry's constants for O2, N2, and CO2. Include beta and
c   convert units.
      heo2=(2.5001+8.453e-02*temp-3.0576e-04*temp**2)/(55555.*
     +o2mw*1.e-04*beta)
      hen2=(5.2726+0.14661*temp-4.5931e-04*temp**2)/(55555.*
     +n2mw*1.e-04*beta)
      heco2=(0.72206+2.9690e-02*temp+2.6693e-04*temp**2)/(55555.*
     +co2mw*1.e-03*beta)
c.. convert the influent alkalinity from mgCaCO3/L to mole/l
      salko=salkao/50.e+03
c.. calculate stage-wise initial conditions and other inputs
c.. tpres(0) is the atmospheric pressure which changes with altitude.
      tpres(0)=1.000
      co2(0)=0.
      n2(0)=0.
      o2(0)=0.
c.. calculate initial pressures in each stage. they are used to
c   calculate the initial n2 partial pressure. assume that each
c   stage has an equal pressure drop.
      do 40 i=1,4
      tpres(i)=s1tpsp-(s1tpsp-tpres(0))*(i-1)/nstage
c..   leak gas flow rates
      qleak(i)=kleak*(tpres(i)-tpres(0))**0.5
c.. set the effective depth for aeration tank (=1.0 for surface aerator;
c   >1 for submerged aerator)
      effd(i)=1.32
c.. hydrogen ion concentration
      hi(i)=10**(-ph(i))
c     salk(i)=salko
c.. initial concentrations for dissolved co2 and n2--assume
c   equilibrium.
      pn2(i)=tpres(i)-po2(i)-pco2(i)-vph2o
      n2(i)=pn2(i)/rt
      o2(i)=po2(i)/rt
      co2(i)=pco2(i)/rt
c.. CO2 here is total carbonate concentration
      sco2(i)=pco2(i)/(heco2*fco2(hi(i),ck1,ck2))
      sn2(i)=pn2(i)/hen2
c.. calculate the kla's for n2 and co2 as a function of the o2
c   klas.  copy this to the dynamic section if klas change.
      kla(i)=klai(i)
      akla(i)=kla(i)*alpha(i)*theta**(temp-20.)
      n2kla(i)=akla(i)*fklan2
40    co2kla(i)=akla(i)*fklaco2
c***********************************************************************
c.. perform all initial calculations here
c***********************************************************************
c.. empirical temperature correction factor. Copy to dynamic if
c   temperature changes during a simulation.
      tfac=theta**(temp-20.)
c.. secondary clarifier calculations
      ameter=1./(areaft*0.092903/nbasin)
      dzi=1./(hclar/nelem)
      dvoli=1./(ameter*dzi)
c.. convert the unit of substrate from BOD5 to BODu; also let ssoavg and
c   xsoavg equal to sso and xso when input=2.
      sso=sso/b5tobus
      xso=xso/b5tobup
      ssoavg=sso
      xsoavg=xso
```

```
c.. calculate the influent H ion concentration
      hio=1./(10**pho)
c.. influent co2.  calculate it from the influent pH and alkalinity
      sco2o=(salko-(snh3o/14.e+03)/(1.+hio*cknh3/ckw))*
     +co2mw*1.e+03
c.. influent dissolved n2.  assume equilibrium with air.
      sn2o=0.791/hen2
c.. gas influent calculations
      tgash=tgasm*2000./(24.*nbasin)
      qgo=tgash*rt*454./(o2mw*(tpres(1)-vph2o))+
     +tgash*(1.-fpuro2)/fpuro2*rt*454./(n2mw*(tpres(1)-vph2o))
      o2o=(tpres(1)-vph2o)*fpuro2/rt
      n2o=(tpres(1)-vph2o)*(1.-fpuro2)/rt
      co2o=0.
      qg(1)=qgo
      gaslim=3*qgo
c.. calculate the initial mlvss, mlss, and initial recycle
c   concentration from initial conditions.  A conversion factor,
c   codvss, was added to convert mlvss unit from COD to mass.
      mlvss=(xi(nstage)+xs(nstage)+xbh(nstage)+xp(nstage))/codvss
      mlss=mlvss+xnv(nstage)
c.. calculate the initial sludge wasting rate.
c   average the mlss concentrations across the stages. Use the volume
c   of each stage since concentration and volume will not be the same
c   for each stage.
      smlss=0.
      do 50 i=1,nstage
50    smlss=smlss+((xi(i)+xs(i)+xbh(i)+xp(i))/codvss+xnv(i))/vli(i)
      smass=0.
      if(meth.gt.1) then
        do 51 i=1,nelem
51      smass=smass+x(i)
       smass=smass*dvoli+smlss
      else
        smass=smlss
      endif
c.. calculate the sludge wasting flow rate, qw
      qw=smass/(x(nelem)*srtsp*24.)
c.. set the program control parameters in start
      call start
c***********************************************************************
c***********************************************************************
c.. dynamic section
c***********************************************************************
c***********************************************************************
c.. loop point.  statement 100 must always be the first
c.  statment in the dynamic section.
100   continue
c***********************************************************************
c.. input section. the time varying inputs are generated here.
c***********************************************************************
c.. adjust inlet pressure set point to control oxygen utilization
      s1tpsp1=limit(tpres(0),1.015,s1tpsp*(1.+pgs4po2*ds4po2+
     1rgs4po2*s4po2))
c.. adjust the input gas flow rates to control oxygen feed or purity.
      tgasm1=tgasm*(1.+pgano2*ds4po2+rgano2*s4po2+pgtpc*ds1tp
     1+rgtpc*s1tp)
      tgash=tgasm1*2000./(24.*nbasin)
      qgo=tgash*rt*454./(o2mw*(tpres(1)-vph2o)) +
     1tgash*(1.-fpuro2)/fpuro2*rt*454./(n2mw*(tpres(1)-vph2o))
      qg(1)=qgo
```

```
c.. skip this section if it is not the last integration step.
c   skip if the inputs are constants (input=1)
      if(keep.eq.1.and.input.gt.1) then
        if(input.eq.2) then
c.. sine wave input of 24 hours.
c.. calculate the varying inputs to each stage.
          asine=sin(time*0.130899)
          qfac=1.+flowamp*asine
c.. each stage can have flow input
          do 110 i=1,nstage
110       q(i)=qm3hr*qfac*fstep(i)
c.. calculate the total flow in mgd for convenience later
          qmgdt=qmgd*qfac
c.. ratio recycle flow to stage 1 only
          qr(1)=qm3hr*qfac*qrrat
c.. soluble and particulate substrate
          sso=ssoavg*(1.+ssamp*asine)
          xso=xsoavg*(1.+xsamp*asine)
        else if(input.eq.3) then
c.. diurnal input simulating metro's flow rates.
          timep=mod(time,24.)
c.. soluble and particulate substrate
          sso=ssoavg*afgen(assfun,nssfun,timep,ssfun)
          xso=xsoavg*afgen(axsfun,nxsfun,timep,xsfun)
c.. flow calculations
          qfac=afgen(aqfun,nqfun,timep,qfun)
c.. calculate the total flow in mgd for convenience later
          qmgdt=qmgd*qfac
c.. ratio recycle flow to stage 1 only
          qr(1)=qm3hr*qfac*qrrat
c.. each stage can have input
          do 120 i=1,nstage
120       q(i)=qm3hr*qfac*fstep(i)
        else
          write(6,*) 'Incorrect input specification. input=',input
          stop 91
        endif
      endif
c***********************************************************************
c.. clarifier section of the activated sludge plant
c***********************************************************************
c.. aeration basin soluble species are assumed to be unaffected by
c.. the clarifier
      si(nstag1)=si(nstage)
      ss(nstag1)=ss(nstage)
      so2(nstag1)=so2(nstage)
      sco2(nstag1)=sco2(nstage)
      sn2(nstag1)=sn2o
      snh3(nstag1)=snh3(nstage)
      snd(nstag1)=snd(nstage)
      salk(nstag1)=salk(nstage)
c.. calculate the overflow rate in m/day
      ovel=(qt(4)-qw-qr(1))*0.09072*ameter
c.. calculate the effluent suspended solids relationship
      xover=10.
c.. calculate the mixed-liquor volatile and total suspended solids
c   concentration (stage 4).
      mlvss=xi(nstage)+xs(nstage)+xbh(nstage)+xp(nstage)
c.. convert the unit of mlvss from mgCOD/l to mgVSS/l
      mlvss=mlvss/codvss
c.. every particulate component's unit is mgCOD/l except Xnv whose unit
```

```
c   is mg/l.
      mlss=mlvss+xnv(nstage)
      fluxin=(qt(nstage)*mlss-(qt(nstage)-qr(1)-qw)*xover)*ameter
c.. call the secondary clarifier subroutine.
      call settle(x,xdot,setflx,tflux,vs,dzi,fac1,fluxin,qr(1),qw,
     1ameter,tfac,mlss,nelem,max)
c.. calculate the recycle concentration.  The nstage+1 location
c   of each concentration array is used for the recycle concentration
c      write(*,*) 'fac1=',fac1
      xi(nstag1)=xi(nstage)*fac1
      xs(nstag1)=xs(nstage)*fac1
      xbh(nstag1)=xbh(nstage)*fac1
      xp(nstag1)=xp(nstage)*fac1
      xnv(nstag1)=xnv(nstage)*fac1
c***********************************************************************
c.. aeration basin part of the activated sludge plant
c***********************************************************************
c. oxygen feed control--based upon stage 4 purity
c  calculate the error
      ds4po2=s4po2sp-po2(4)
      qg(1)=qgo*(1.+pgano2*ds4po2+rgano2*s4po2)
      do 200 i=1,nstage
      j=i-1
      if(i.ne.nstage) then
      k=i+1
      else
      k=0
      endif
c.. stage controller calculations
      if(idoctrl.eq.1) then
c   calculate the difference between do and the setpoint
        drsetdo(i)=dosp(i)-so2(i)
c   ratio up the klas for control. Set the gains to zero for no control.
        kla(i)=klai(i)*(1.+pgaindo*drsetdo(i)+rgaindo*rsetdo(i))
      endif
c   check to see that the limits are not exceeded.
      if(kla(i).lt.klalim(i,1)) kla(i)=klalim(i,1)
      if(kla(i).gt.klalim(i,2)) kla(i)=klalim(i,2)
c.. now calcuate the actual kla's correcting for temp and for the
c   other species.
      akla(i)=kla(i)*alpha(i)*tfac
      n2kla(i)=alpha(i)*kla(i)*fklan2*tfac
      co2kla(i)=alpha(i)*kla(i)*fklaco2*tfac
c.. calculate factors used in more than one material balance.
      fo2=limit(0.,40.,so2(i))/(koh+so2(i))
c.. partial pressures for co2, o2, and n2
      pco2(i)=co2(i)*rt
      po2(i)=o2(i)*rt
      pn2(i)=n2(i)*rt
c.. saturation concentrations for co2, o2, and n2
c   multiply by an effective depth to account for subsurface
c   aeration
      ssco2(i)=effd(i)*pco2(i)/heco2
      sso2(i)=effd(i)*po2(i)/heo2
      ssn2(i)=effd(i)*pn2(i)/hen2
c.. stripping rates for co2, o2 and n2
      fcsco2=fco2(hi(i),ck1,ck2)
      strpco=co2kla(i)*(ssco2(i)-sco2(i)*fcsco2)
      strpo2=akla(i)*(sso2(i)-so2(i))
      strpn2=n2kla(i)*(ssn2(i)-sn2(i))
c.. total stage pressure
```

```
      tpres(i)=vph2o+pco2(i)+pn2(i)+po2(i)
c.. calculate the exit gas flow rate. Limit backflow. Set
c   to zero if small to avoid underflow warnings.
      diffp=tpres(k)-tpres(i)
      if (abs(diffp).lt.1.e-20) then
      qgt(i)=0.
      else
       qgtemp=kflow*abs(diffp)**0.5
        if (diffp.gt.0.) then
          qgtemp=-qgtemp
        endif
        qgt(i)=limit(-gaslim,gaslim,qgtemp)
      endif
c.. add the liquid flows
      qt(i)=q(i)+qr(i)+qt(j)
c************* State Equations *************
c.. Soluble inert organic matter [M(COD)/l] balance
      dsi(i)=vli(i)*(q(i)*sio+qt(j)*si(j)+qr(i)*si(nstag1)-
     1qt(i)*si(i))
c.. Readily biodegradable substrate [M(COD)/l] balance
      dss(i)=vli(i)*(q(i)*sso+qt(j)*ss(j)+qr(i)*ss(nstag1)-
     1qt(i)*ss(i))-(1./yh)*(uh/24.)*(ss(i)/(ks+ss(i)))*fo2*
     2xbh(i)+(kh/24.)*(xs(i)/xbh(i))/(kx+(xs(i)/xbh(i)))*fo2
     3*xbh(i)
c.. Particulate inert organic matter [M(COD)/l] balance
      dxi(i)=vli(i)*(q(i)*xio+qt(j)*xi(j)+qr(i)*xi(nstag1)-
     1qt(i)*xi(i))
c.. Slowly biodegradable substrate [M(COD)/l] balance
c      dxs(i)=vli(i)*(q(i)*xso+qt(j)*xs(j)+qr(i)*xs(nstag1)-
c     1qt(i)*xs(i))+(1.-fp)*(bh/24.)*xbh(i)-(kh/24.)*((xs(i)/xbh(i))/
c     2(kx+(xs(i)/xbh(i))))*fo2*xbh(i)
      dxs(i)=vli(i)*(q(i)*xso+qt(j)*xs(j)+qr(i)*xs(nstag1)-
     1qt(i)*xs(i))-
     2(kh/24.)*((xs(i)/xbh(i))/(kx+(xs(i)/xbh(i))))*fo2*xbh(i)
c.. Non-volatile (particulate) Matter [mg/l] balance
      dxnv(i)=vli(i)*(q(i)*xnvo+qt(j)*xnv(j)+qr(i)*xnv(nstag1)-
     1qt(i)*xnv(i))
c.. Active heterotrophic biomass [M(COD)/l] balance
      dxbh(i)=vli(i)*(q(i)*xbho+qt(j)*xbh(j)+qr(i)*xbh(nstag1)-
     1qt(i)*xbh(i))+(uh/24.)*ss(i)/(ks+ss(i))*fo2*xbh(i)
     2-(bh/24.)*xbh(i)
c.. Particulate products arising from biomass decay [M(COD)/l]
      dxp(i)=vli(i)*(q(i)*xpo+qt(j)*xp(j)+qr(i)*xp(nstag1)-
     1qt(i)*xp(i))+fp*(bh/24.)*xbh(i)
c.. Dissolved oxygen
c      o2uptr(i)=(1.-yh)/yh*(uh/24.)*ss(i)/(ks+ss(i))*fo2*xbh(i)
c      o2uptr(i)=(1.-yh)/yh*(uh/24.)*ss(i)/(ks+ss(i))*fo2*xbh(i)+
c     1(1.-fp)*(bh/24.)*xbh(i)
      o2uptr1=(1.-yh)/yh*(uh/24.)*ss(i)/(ks+ss(i))*fo2*xbh(i)
      o2uptr2=(1.-fp)*(bh/24.)*xbh(i)
      o2uptr(i)=o2uptr1+o2uptr2
c.. debugging outputs (our components)
      if (abs(time-int(time)).lt.delt) then
        write(27, *) i,o2uptr1,o2uptr2,o2uptr(i)
      endif
      dso2(i)=vli(i)*(q(i)*so2o+qt(j)*so2(j)+qr(i)*so2(nstag1)-
     1qt(i)*so2(i))+strpo2-o2uptr(i)
c.. Ammonia Balance (no nitrification allowed)
      ammo1=vli(i)*(q(i)*snh3o+qt(j)*snh3(j)+qr(i)*snh3(nstag1)-
     1qt(i)*snh3(i))
      ammo2=-ixb*(uh/24.)*(ss(i)/(ks+ss(i)))*
```

```
     2fo2*xbh(i)
      ammo3=+(ka/24.)*snd(i)*xbh(i)
      dsnh3(i)=ammo1+ammo2+ammo3
c       if(time.gt.12.) then
c       write(*,'(i1,1x,4(1x,e12.6))') i,ammo1,ammo2,ammo3,dsnh3(i)
c       endif
c.. Soluble biodegradable nitrogen
      dsnd(i)=vli(i)*(q(i)*sndo+qt(j)*snd(j)+qr(i)*snd(nstag1)-
     1qt(i)*snd(i))-(ka/24.)*snd(i)*xbh(i)+(kh/24.)*(xs(i)/xbh(i))/
     2(kx+(xs(i)/xbh(i)))*fo2*xbh(i)*xnd(i)/xs(i)
c.. Particulate biodegradable organic nitrogen
      dxnd(i)=vli(i)*(q(i)*xndo+qt(j)*xnd(j)+qr(i)*xnd(nstag1)-
     1qt(i)*xnd(i))+(ixb-fp*ixp)*(bh/24.)*xbh(i)-(kh/24.)*(xs(i)/
     2xbh(i))/(kx+(xs(i)/xbh(i)))*fo2*xbh(i)*xnd(i)/xs(i)
c.. Alkalinity [mole/l]
      dsalk1=vli(i)*(q(i)*salko)
      dsalk2=vli(i)*(qt(j)*salk(j))
      dsalk3=vli(i)*(qr(i)*salk(nstag1))
      dsalk4=vli(i)*(-qt(i)*salk(i))
      dsalk(i)=dsalk1+dsalk2+dsalk3+dsalk4+(-ixb/14.*(uh/24.)*ss(i)/
     +    (ks+ss(i))*fo2*xbh(i)+1./14.*(ka/24.)*snd(i)*xbh(i))/1000.
c       write(*,'(1x,i1,(5(1x,e12.6)))') i,dsalk1,dsalk2,dsalk3,
c    +       dsalk4,dsalk(i)
c.. Dissolved nitrogen
      dsn2(i)=vli(i)*(q(i)*sn2o+qt(j)*sn2(j)+qr(i)*sn2o-
     1qt(i)*sn2(i))+strpn2
C.. Dissolved CO2
      dsco2(i)=vli(i)*(q(i)*sco2o+qt(j)*sco2(j)+qr(i)*sco2(nstag1)-
     1qt(i)*sco2(i))+strpco+o2uptr(i)*co2o2
c       write(*,*) i,strpco, o2uptr(i),o2uptr(i)*co2o2
c.. Gas phase balances
c   CO2 Gas Phase
      co2dot(i)=vgi(i)*(qg(i)*co2o+qgt(j)*co2(j)-(qgt(i)+qleak(i))
     1*co2(i))-strpco*vgi(i)/(vli(i)*co2mw)
c.. Nitrogen Gas Phase
      n2dot(i)=vgi(i)*(qg(i)*n2o+qgt(j)*n2(j)-(qgt(i)+qleak(i))
     1*n2(i))-strpn2*vgi(i)/(vli(i)*n2mw)
c.. Oxygen Gas Phase
      o2dot(i)=vgi(i)*(qg(i)*o2o+qgt(j)*o2(j)-(qgt(i)+qleak(i))
     1*o2(i))-strpo2*vgi(i)/(vli(i)*o2mw)
200   continue
c.. calculate sludge age and f/m ratio
c   average the mlss concentrations across the stages.  Use the
c   volume of each stage since they may not be the same. also
c   converting mlvss's unit from cod to mass.
      smlss=0.
      do 210 i=1,nstage
210   smlss=smlss+((xi(i)+xs(i)+xbh(i)+xp(i))/codvss+xnv(i))/vli(i)
      smass=0.
      if(meth.gt.1) then
        do 220 i=1,nelem
220     smass=smass+x(i)
        smass=smass*dvoli+smlss
      else
        smass=smlss
      endif
c.. calculate the sludge waste mass rate required to maintain SRTsp.
      wmass=smass/(srtsp*24.)
c.. subtract off the effluent TSS mass wasted
      emass=(qt(nstage)-qr(1)-qw)*xover
      qw=(wmass-emass)/x(nelem)
```

```
c.. calculate the o2 utilization
c.. o2 input
      o2in=qg(1)*fpuro2
      o2out=qgt(4)*po2(4)
      if(o2in.ne.0.) then
        o2util=(o2in-o2out)/o2in
      else
        o2util=2.
c?? o2util is arbitrarily set to 2.
      endif
c?? I doubt the validity of the above formula for o2util.
c   We cannot calculate utilization efficiency using concentrations
c   since qg(i) changes from stage to stage. Mass should be
c   used instead of concentraion.
c?? what are trigl and plse used for here? Nothing?
      trigl=-0.5+impuls(s1,0.0,6.0)
      plse=pulse(s2,trigl,3.0)
c*********************************************************************
c.. integrator statement section of the model. place all intgrl's here
c*********************************************************************
c.. secondary clarifier
      call antgrl(ax,xdot,x,10,10,1)
c.. integration of state equations
c   soluble inert organic matter
      call antgrl(asi,dsi,si,4,5,0)
c   readily biodegradable substrate
      call antgrl(ass,dss,ss,4,5,0)
c   particulate inert organic matter
      call antgrl(axi,dxi,xi,4,5,0)
c   slowly biodegradable substrte
      call antgrl(axs,dxs,xs,4,5,0)
c   non-volatile mass
      call antgrl(axnv,dxnv,xnv,4,5,0)
c   active heterotrophic biomass
      call antgrl(axbh,dxbh,xbh,4,5,0)
c   particulate products arising form biomass decay
      call antgrl(axp,dxp,xp,4,5,0)
c   dissolved oxygen
      call antgrl(aso2,dso2,so2,4,5,0)
c   ammonia
      call antgrl(asnh3,dsnh3,snh3,4,5,0)
c   soluble biodegradable organic nitrogen
      call antgrl(asnd,dsnd,snd,4,5,0)
c   particulate biodegradable organic nitrogen
      call antgrl(axnd,dxnd,xnd,4,5,0)
c   alkalinity
      call antgrl(asalk,dsalk,salk,4,5,0)
c   dissolved nitrogen
      call antgrl(asn2,dsn2,sn2,4,5,0)
c   dissolved CO2
      call antgrl(asco2,dsco2,sco2,4,5,0)
c   gas phase: n2,co2,o2
      call antgrl(an2,n2dot,n2,4,5,0)
      call antgrl(aco2,co2dot,co2,4,5,0)
      call antgrl(ao2,o2dot,o2,4,5,0)
c.. integral part of PI controller for DO by manipulating kla
      call antgrl(arsetdo,drsetdo,rsetdo,4,4,1)
c.. integral part of PI controller for stage 4 O2 purity by
c   manipulating high purity feed or triming stage 1 set point pressure
      call intgrl(as4po2,ds4po2,s4po2)
c.. integral part of PI controller for stage 1 pressure control by
```

```
c   manipulating high purity feed
      call intgrl(as1tp,ds1tp,s1tp)
c   calculate pH
      do 230 i=1,nstage
        call phcal(hi,salk,sco2,snh3,ck1,ck2,ckw,cknh3,i)
         if(hi(i).gt.0.) then
           ph(i)=-alog10(hi(i))
        else
           ph(i)=5.1d+00
           hi(i)=7.9d-06
        endif
230   continue
c.. subroutine centra controls the integration and must always be
c   placed at the end of the dynamic section for each time step,
c   after all integrations.
      call centra
      if(last.ne.1) goto 100
c*********************************************************************
c*********************************************************************
c.. this part of the dynamic section is reserved for printing, plotting,
c   and performing other calculations which are required only at the end
c   of an integration step.  this section is skipped unless 'last=1'
c*********************************************************************
c*********************************************************************
500   last=1
c.. check to see if it is time to print
      if(keep.eq.1) then
        if((ptime-time).le.delt2.or.key(11).lt.0) then
          iprint=iprint+1
          ptime=iprint*prdel
          key(2)=1
          ip=1
          call pr(akla,alpha,b5tobus,b5tobup,codvss,emass,kla,max,
     1nbasin,nelem,nstage,o2uptr,o2util,pco2,ph,plse,pn2,po2,q,qg,
     2qgo,qgt,qmgd,qmgdt,qr,qt,qw,salk,sco2,si,smlss,snd,snh3,so2,
     3srtsp,ss,sso, tgasml,tpl,tpres,trigl,vgi,vli,vph2o,x,
     4xbh,xi,xnd,xnv,xover,xp,xs,xso,ip)
        endif
c.. check to see if it is time to save the variables for plotting
        if((pltime-time).le.delt2.or.key(11).lt.0) then
          iplot=iplot+1
          key(3)=1
          pltime=iplot*outdel
          ip=2
          call pr(akla,alpha,b5tobus,b5tobup,codvss,emass,kla,max,
     1nbasin,nelem,nstage,o2uptr,o2util,pco2,ph,plse,pn2,po2,q,qg,
     2qgo,qgt,qmgd,qmgdt,qr,qt,qw,salk,sco2,si,smlss,snd,snh3,so2,
     3srtsp,ss,sso, tgasml,tpl,tpres,trigl,vgi,vli,vph2o,x,
     4xbh,xi,xnd,xnv,xover,xp,xs,xso,ip)
        endif
c.. check to see if time is greater than fintim
        if((fintim-time).le.delt2.or.key(11).lt.0) then
c.. check to see if the simulation ended on a printout
          if(key(2).ne.1) then
c.. print out the final values after a finish condition.
            ip=1
          call pr(akla,alpha,b5tobus,b5tobup,codvss,emass,kla,max,
     1nbasin,nelem,nstage,o2uptr,o2util,pco2,ph,plse,pn2,po2,q,qg,
     2qgo,qgt,qmgd,qmgdt,qr,qt,qw,salk,sco2,si,smlss,snd,snh3,so2,
     3srtsp,ss,sso, tgasml,tpl,tpres,trigl,vgi,vli,vph2o,x,
     4xbh,xi,xnd,xnv,xover,xp,xs,xso,ip)
```

```
          endif
c.. check to see if the simulation ended on a plotout
          if(key(3).ne.1) then
            ip=2
          call pr(akla,alpha,b5tobus,b5tobup,codvss,emass,kla,max,
     1nbasin,nelem,nstage,o2uptr,o2util,pco2,ph,plse,pn2,po2,q,qg,
     2qgo,qgt,qmgd,qmgdt,qr,qt,qw,salk,sco2,si,smlss,snd,snh3,so2,
     3srtsp,ss,sso, tgasml,tpl,tpres,trigl,vgi,vli,vph2o,x,
     4xbh,xi,xnd,xnv,xover,xp,xs,xso,ip)
          endif
            goto 10000
        else
          goto 100
        endif
      endif
c.. terminal section of the model
c*******************************************************************
c.. reserve numbers in excess of 10000 for the terminal section
c*******************************************************************
10000 continue
      open(unit=16,file='ninits',status='unknown')
      rewind(16)
c.. write out the final values of the integration variables to allow
c   restarting from the last conditions.
      write(16,1201) (si(ij),   ij=0,nstage)
1201  format(5f10.3,t55, ' Si')
      write(16,1202) (ss(ij),   ij=0,nstage)
1202  format(5f10.3,t55,' Ss')
      write(16,1203) (xi(ij),   ij=0,nstage)
1203  format(5f10.3,t55,' Xi')
      write(16,1204) (xs(ij),   ij=0,nstage)
1204  format(5f10.3,t55,' Xs')
      write(16,1205) (xnv(ij),   ij=0,nstage)
1205  format(5f10.3,t55,' Xnv')
      write(16,1206) (xbh(ij),   ij=0,nstage)
1206  format(5f10.3,t55,' Xbh')
      write(16,1207) (xp(ij),   ij=0,nstage)
1207  format(5f10.3,t55,' Xp')
      write(16,1208) (so2(ij),   ij=0,nstage)
1208  format(5f10.3,t55,' Dissolved oxygen So2')
      write(16,1209) (snh3(ij),   ij=0,nstage)
1209  format(5f10.3,t55,' Ammonia Snh3')
      write(16,1210) (snd(ij),   ij=0,nstage)
1210  format(5f10.3,t55,' Snd')
      write(16,1211) (xnd(ij),   ij=0,nstage)
1211  format(5f10.3,t55,' Xnd')
      write(16,1212) (salk(ij)*50.e+03,ij=0,nstage)
1212  format(5f10.3,t55,' Alkalinity (mole/l)')
      write(16,1214) (pco2(ij),   ij=1,nstage)
1214  format(4f10.3,t55,' CO2 conc. gas phase')
      write(16,1215) (po2(ij),   ij=1,nstage)
1215  format(4f10.3,t55,' Oxygen purity')
      write(16,1213) (ph(ij),   ij=1,nstage)
1213  format(4f10.3,t55,' Basin pHs')
      write(16,1216) (x(ij),   ij=1,nelem)
1216  format(10f10.3,' Clarifier solids conc.(mg/l) ')
      close(12)
      close(16)
      stop
20000 write(6,*) ' The program was unable to open the input file'
      write(6,*) ' (diurnal) which contains the input data pairs'
```

```
write(6,*) ' for BOD and flow'
stop 10
end
```

```
      function afgen(ax,n,x,arr)
c**********************************************************************
c.. this function generates an arbitrary function defined by pairs of
c   data points contained in the array arr, with the number of points=n.
c   note that the function checks for proper data entry on the first
c   call, and checks to see if x is in the range defined data contained
c   in by the arr array. linear interpolation is used.
c**********************************************************************
      dimension arr(2,200),ax(5)
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
c.. check for initial entry
      if(key(13)) 10,10,30
10    if(n-1) 11,11,12
11    write(6,1000) n
1000  format(//,' less than two data points were supplied for an afgen',
     1' function',//,' execution terminating')
      stop 20
12    ax(4)=1
c.. check to see if the data was entered correctly in ascending order
      do 13 i=2,n
13    if(arr(1,i).le.arr(1,(i-1))) goto 14
      goto 15
14    k=i-1
      write(6,1010) i,arr(1,i),k,arr(1,k)
1010  format(//,' the independent variable for an afgen function has ',
     1'not been',/,' entered in ascending order',/,' the',i3,'th point='
     2,2x,e17.6,2x,'while the',i3,'th point=',2x,e17.6,/,' execution ter
     3minating')
      stop 30
15    ax(1)=0.
      if(x.lt.arr(1,1)) ax(1)=1
      if(x.gt.arr(1,n)) ax(1)=-1.
      if(ifix(ax(1))) 16,17,16
16    write(6,1020) x,arr(1,1),arr(1,n)
1020  format(' the initial entry to an afgen function is out of range',
     1/,' the value of the independent variable is',e17.6,' while the',
     2/,' minimum value of the function is',e17.6, ' and the maximum',
     3/,' value of the function is',e17.6)
      if(ax(4)) 82,17,92
17    i=1
18    if(arr(1,i).ge.x) goto 20
      i=i+1
      goto 18
20    if(i.eq.1) goto 70
      i=i-1
      if(arr(1,i).lt.x) goto 70
      goto 20
c.. normal entry for afgen
30    if(x.lt.arr(1,1).or.x.gt.arr(1,n)) goto 80
      i=ifix(ax(2))
40    if(arr(1,i).ge.x) goto 50
      i=i+1
      goto 40
50    i=i-1
60    if(arr(1,i).lt.x) goto 70
      goto 50
70    i=i+1
```

```
      ax(2)=i
      afgen=arr(2,(i-1))+(x-arr(1,(i-1)))*(arr(2,i)-arr(2,(i-1)))/
     1(arr(1,i)-arr(1,(i-1)))
      ax(4)=1.
      goto 100
80    if(x.lt.arr(1,n)) goto 90
      if(ax(4)) 87,82,82
82    write(6,1030) time,x,arr(1,n)
1030  format(' independent variable for afgen function above range at',
     1' time=',e12.6,/,' independent variable=',e12.6,' maximum for this
     2 afgen function=',e12.6)
87    afgen=arr(2,n)
      ax(4)=-1
      ax(2)=n
      goto 100
90    if(ax(4)) 97,92,92
92    write(6,1040) time,x,arr(1,1)
1040  format(' independent variable for afgen function below range at',
     1' time=',e12.6,/,' independent variable=',e12.6,' minimum for this
     2 afgen function=',e12.6)
97    ax(2)=1
      ax(4)=-1
      afgen=arr(2,1)
100   return
      end



      subroutine antgrl(acx,xdot,x,m,n,iz)
c***********************************************************************
c.. this function performs the integration using first,second,and fourth
c.. order correct methods
c************************************************************************
      dimension acx(5,iz:n),xdot(iz:n),x(iz:n)
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
      common /com1/abserr,relerr,ptime,pltime,icount,iprint,ipoint
c.. check to see if this is the first call to the integrator. If
c   so, insert the initial condition into the storage array.
      if(key(13).le.0) then
        do 100 i=1,m
        acx(5,i)=x(i)
100     acx(1,i)=x(i)
       endif
c.. this section for first order integration (euler)
c***********************************************************************
      if(method.eq.1) then
        do 110 i=1,m
        x(i)=acx(1,i)+delt*xdot(i)
110     acx(1,i)=x(i)

c.. this section for second order integration  (modified euler)
c***********************************************************************
      elseif(method.eq.2) then
        if(keep.eq.1) then
c.. first half step for modified euler
          do 220 i=1,m
          x(i)=acx(1,i)+delt*xdot(i)
          acx(2,i)=acx(1,i)
          acx(3,i)=xdot(i)
220       acx(1,i)=x(i)
```

```
c.. second half step for modified euler
        else
          do 240 i=1,m
          x(i)=(xdot(i)+acx(3,i))/2.*delt+acx(2,i)
240       acx(1,i)=x(i)
        endif
c.. this section for fourth order integration
c***********************************************************************
      elseif (method.eq.3) then
        if(keep.eq.1) then
310       do 320 i=1,m
          x(i)=acx(1,i)+delt2*xdot(i)
320       acx(2,i)=xdot(i)
        elseif(keep.eq.2) then
330       do 340 i=1,m
          x(i)=acx(1,i)+delt2*xdot(i)
340       acx(3,i)=xdot(i)
        elseif(keep.eq.3) then
350       do 360 i=1,m
          x(i)=acx(1,i)+xdot(i)*delt
360       acx(4,i)=xdot(i)
        else
370       do 380 i=1,m
         x(i)=delt/6.*(acx(2,i)+2.*acx(3,i)+2.*acx(4,i)+xdot(i))
     1         +acx(1,i)
380       acx(1,i)=x(i)
        endif
c***********************************************************************
c.. variable step rks integration
c.. check to see if the time step is being reduced and time is being
c   backed-up
      elseif (method.eq.4) then
c.. check to see if its the first time step
        if(key(1).eq.0) then
          do 400 i=1,m
400       acx(1,i)=acx(5,i)
        endif
        if(keep.eq.1) then
c.. successful integration step. begin the next first pass of the next
c   time step
          do 410 i=1,m
          acx(1,i)=acx(5,i)
          x(i)=acx(1,i)+delt2*xdot(i)
410       acx(2,i)=xdot(i)
        elseif(keep.eq.2) then
c.. second pass
          do 420 i=1,m
          x(i)=acx(1,i)+delt2*xdot(i)
420       acx(3,i)=xdot(i)
        elseif(keep.eq.3) then
c.. third pass
          do 430 i=1,m
          x(i)=acx(1,i)+xdot(i)*delt
430       acx(4,i)=xdot(i)
c.. the first, second, and third steps are identical to rks fixed-step
c
c.. fourth pass.  check to see if the error has been exceeded or if
c   doubling is possible
        elseif (keep.eq.4) then
          do 440 i=1,m
          x(i)=delt/6.*(acx(2,i)+2.*acx(3,i)+2.*acx(4,i)+
```

```
     1    xdot(i))+acx(1,i)
440       acx(5,i)=x(i)
c.. calculate an error predictor using simpson's rule
          do 450 i=1,m
          sint=delt/6.*(acx(2,i)+4.*acx(3,i)+xdot(i))+acx(1,i)
          switch=abs(x(i)-sint)/(abserr+relerr*x(i))
c.. these keys are summed in order to detect errors for all
c   integrations.
          if(switch.gt.0.5) key(9)=key(9)-1
450       if(switch.gt.1.) key(7)=key(7)-1
        endif
      endif
      return
      end



      subroutine centra
c.. this subroute controls the integration.  it is called at the end of
c    the dynamic section.
c***********************************************************************
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
      common /com1/abserr,relerr,ptime,pltime,icount,iprint,ipoint
      if(method.eq.1) then
c.. first-order method
c***********************************************************************
         time=time+delt
         last=1
         keep=1
         key(1)=1
      elseif(method.eq.2) then
c.. second-order method (modified euler)
c***********************************************************************
         if(keep.eq.1) then
c.. first half step for modified euler
            time=time+delt2
            key(1)=1
            last=0
            keep=2
         elseif(keep.eq.2) then
c.. second half step for modified euler
            time=time+delt2
            key(1)=0
            keep=1
            last=1
         endif
      elseif(method.eq.3) then
c.. fourth-order integration (runge-kutta)
c***********************************************************************
         if(keep.eq.1) then
c.. first quarter step for runge-kutta
310         time=time+delt2
            key(1)=1
            last=0
            keep=2
         elseif(keep.eq.2) then
c.. second quarter step
320         keep=3
            last=0
         elseif(keep.eq.3) then
```

```
c.. third quarter step
330         keep=4
            last=0
            time=time+delt2
         elseif(keep.eq.4) then
c.. final quarter step
340         keep=1
            last=1
            key(1)=0
         endif
      elseif(method.eq.4) then
c.. variable step fourth-order rks
c***********************************************************************
         if(keep.eq.1) then
c.. first quarter step for runge-kutta
            time=time+delt2
            key(1)=1
            last=0
            keep=2
         elseif(keep.eq.2) then
c.. second quarter step
            keep=3
            last=0
         elseif(keep.eq.3) then
c.. third quarter step
            keep=4
            last=0
            time=time+delt2
         elseif(keep.eq.4) then
c.. final quarter step
c.. final step for rks variable step.  check to see if delt should be
            key(1)=0
            if(key(7).lt.0) then
c.. reduce the time step and backup the value of time
              time=time-delt
              delt=0.5*delt
              delt2=0.5*delt
              if(delt.lt.delmin)  then
c.. terminate the run due to the inability to find a reasonable delt
      write(6,1100) time,delt,delmin
1100  format(//,' *******execution terminating at time=',e17.6,'*******'
     1,/,' delt (',e12.6,') is less than delmin (',e12.6,')')
                 stop 70
              else
                 key(1)=1
                 keep=1
                 last=0
                 key(8)=key(10)
              endif
            else
              if(key(8).gt.0.or.key(9).lt.0) then
c.. error is ok but too great to allow doubling or doubling not
c   allowed.
                 key(8)=key(8)-1
                 last=1
                 keep=1
              else
c.. allow doubling if delt was not changed on the previous key(8)/4
c   time steps.
                 delt2=delt
                 delt=delt*2.
```

```
                 key(8)=key(10)
                 last=1
                 keep=1
              endif
            endif
         endif
      endif
      key(2)=0
      key(3)=0
      key(7)=1
      key(9)=0
      key(13)=1
      return
      end


      function fco2(ph,ck1,ck2)
c.. this function calculates the fraction of the total carbon which
c   is in the h2co3 form.
      real*4 dk1,dk2,dph
c.. convert to double precision for the calculation
      dk1=ck1
      dk2=ck2
      dph=ph
      fco2=1.d+0/((dph*dk1*dk2/dph+dk1)/dph+1.d0)
      return
      end


      real function impuls(s,p1,p2)
c*********************************************************************
c.. this function simulates an impulse train starting at time=p1 and
c   repeating at every p2 units of time
c*********************************************************************
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
      impuls=0.
      if(key(1)) 10,10,15
10    if(p1.le.0.25*delt) impuls=1.
      goto 100
15    if(method-1) 40,40,20
20    if(last-1) 100,40,100
40    if(time.lt.p1) goto 100
      if(p2) 50,50,60
50    impuls=1.
      goto 100
60    n=(time-p1)/p2+0.5
      if(abs(time-p1-float(n)*p2).le.(0.25*delt)) impuls=1.
100   s=impuls
      return
      end


      subroutine intgrl(ax,xdot,x)
c*********************************************************************
c.. this function performs the integration using first,second,and fourth
c.. order correct methods
c*********************************************************************
```

```
      dimension ax(5)
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
      common /com1/abserr,relerr,ptime,pltime,icount,iprint,ipoint
c.. check and see if this is the first call to the integrator.
c   If so, insert the initial condition into the storage array.
      if(key(13).le.0)  then
        ax(1)=x
        ax(5)=x
      endif
      if(method.eq.1) then
c.. this section for first order integration (euler)
c***********************************************************************
        x=ax(1)+delt*xdot
        ax(1)=x
      elseif(method.eq.2) then
c.. this section for second order integration  (modified euler)
c***********************************************************************
        if(keep.eq.1) then
c.. first half step for modified euler
          x=ax(1)+delt*xdot
          ax(2)=ax(1)
          ax(3)=xdot
          ax(1)=x
        else
c.. second half step fort modified euler
          x=(xdot+ax(3))/2.*delt+ax(2)
          ax(1)=x
        endif
      elseif(method.eq.3) then
c.. this section for fourth order integration
c***********************************************************************
        if(keep.eq.1) then
          x=ax(1)+delt2*xdot
          ax(2)=xdot
        elseif(keep.eq.2) then
          x=ax(1)+delt2*xdot
          ax(3)=xdot
        elseif(keep.eq.3) then
          x=ax(1)+xdot*delt
          ax(4)=xdot
        elseif(keep.eq.4) then
          x=delt/6.*(ax(2)+2.*ax(3)+2.*ax(4)+xdot)+ax(1)
          ax(1)=x
        endif
c***********************************************************************
c.. variable step rks integration
c.. check to see if the time step is being reduced and time is being
c   backed-up
      elseif(method.eq.4) then
c.. check to see if delt has been decreased. If not save the
c   variable step output (ax(5)).
        if(key(1).eq.0) ax(1)=ax(5)
c.. successful integration step. begin the next first pass of the next
c   time step
        if(keep.eq.1) then
          x=ax(1)+delt2*xdot
          ax(2)=xdot
        elseif(keep.eq.2) then
          x=ax(1)+delt2*xdot
          ax(3)=xdot
```

```
        elseif(keep.eq.3) then
          x=ax(1)+xdot*delt
          ax(4)=xdot
        elseif(keep.eq.4) then
c.. fourth step.  check to see if the error has been exceeded or if
c   doubling is possible
          x=delt/6.*(ax(2)+2.*ax(3)+2.*ax(4)+xdot)+ax(1)
          ax(5)=x
c.. calculate an error predictor using simpson's rule.
          sint=delt/6.*(ax(2)+4.*ax(3)+xdot)+ax(1)
          switch=abs(x-sint)/(abserr+relerr*x)
c.. these keys are summed in order to detect errors for all
c   integrations.
          if(switch.gt.0.5) key(9)=key(9)-1
          if(switch.gt.1.) key(7)=key(7)-1
        endif
      endif
      return
      end



      real function limit(lo,hi,x)
      real lo*4
      if(lo.gt.hi) then
        write(6,1000) lo,hi
1000    format(' execution terminated in function limit due to',
     1' improper specification of limits.',/,' lower limit:',e17.6,
     2' ) is greater than the upper limit (',e17.6,')')
        stop 51
      endif
      if(x.le.lo) then
        limit=lo
      elseif(x.gt.hi) then
         limit=hi
      else
        limit=x
      endif
      return
      end



      subroutine phcal(hi,salk,sco2,snh3,ck1,ck2,ckw,cknh3,ir)
c.. this function calculates the ph of a dilute solution in a closed
c   biox reactor.  the calculation is implicit.
      real*8 dk1,dk2,dsco2,dph,dsnh3,dsalk,b,c,zgess,dknh3,
     1dkw
      dimension snh3(0:5),sco2(0:5),salk(0:5),hi(4)
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
c.. set the first guess equal to previous pH
      dph=hi(ir)
c.. set the guess to a plausibile pH
      zgess=1.e-06
c.. convert the single precision arguments to double precision
      dk1=ck1
      dk2=ck2
      dkw=ckw
c.. also convert co2 and nh3 to molar concentration.
      dsco2=sco2(ir)/44009.d+00
```

```
      dsalk=salk(ir)
      dknh3=cknh3
      dsnh3=snh3(ir)/14.d+03
c.. quadratic coefficients
      b=dsalk-dsnh3/(1.d+00+dph*dknh3/dkw)
      iter=0
10    c=-dkw-(dk1+2.d+00*dk1*dk2/zgess)*dsco2
c.. calc the ph
      dph=(-b+dsqrt(b**2-4.d+00*c))/2.d+00
      if(dabs(dph-zgess).gt.1.d-12) goto 20
c.. normal convergence
        hi(ir)=dph
c        write(*,*) 'Number of iteration= ',iter, 'pH= ',-alog10(dph)
c        write(6,*) 'Salk=',salk,' Sco2=',sco2
        return
20    if(iter.gt.10 ) goto 30
        zgess=dph
        b=dsalk-dsnh3/(1.+dph*dknh3/dkw)
        iter=iter+1
        goto 10
c.. no convergence
30      write(6,1000) zgess,dph,iter
1000    format(' non convergence in ph calculation.',/,
     1  1x,' execution stopping',/,' final guess for ph =',d17.6,
     2  /,' final calc for ph =',d17.6,/,' iteration number=',i5)
        hi(ir)=dph
      return
      end



      subroutine phcal(hi,salk,sco2,snh3,ck1,ck2,ckw,cknh3,ir)
c.. this function calculates the ph of a dilute solution in a closed
c   biox reactor.  the calculation is implicit.
      real*8 dk1,dk2,dsco2,dph,dsnh3,dsalk,b,c,zgess,dknh3,
     1dkw
      dimension snh3(0:5),sco2(0:5),salk(0:5),hi(4)
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
c.. set the first guess equal to previous pH
      dph=hi(ir)
c.. set the guess to a plausibile pH
      zgess=1.e-06
c.. convert the single precision arguments to double precision
      dk1=ck1
      dk2=ck2
      dkw=ckw
c.. also convert co2 and nh3 to molar concentration.
      dsco2=sco2(ir)/44009.d+00
      dsalk=salk(ir)
      dknh3=cknh3
      dsnh3=snh3(ir)/14.d+03
c.. quadratic coefficients
      b=dsalk-dsnh3/(1.d+00+dph*dknh3/dkw)
      iter=0
10    c=-dkw-(dk1+2.d+00*dk1*dk2/zgess)*dsco2
c.. calc the ph
      dph=(-b+dsqrt(b**2-4.d+00*c))/2.d+00
      if(dabs(dph-zgess).gt.1.d-12) goto 20
c.. normal convergence
        hi(ir)=dph
```

```
c        write(*,*) 'Number of iteration= ',iter, 'pH= ',-alog10(dph)
c        write(6,*) 'Salk=',salk,' Sco2=',sco2
        return
20    if(iter.gt.10 ) goto 30
        zgess=dph
        b=dsalk-dsnh3/(1.+dph*dknh3/dkw)
        iter=iter+1
        goto 10
c.. no convergence
30      write(6,1000) zgess,dph,iter
1000    format(' non convergence in ph calculation.',/,
     1  1x,' execution stopping',/,' final guess for ph =',d17.6,
     2  /,' final calc for ph =',d17.6,/,' iteration number=',i5)
        hi(ir)=dph
      return
      end



      subroutine pr(akla,alpha,b5tobus,b5tobup,codvss,emass,kla,max,
     1nbasin,nelem,nstage,o2uptr,o2util,pco2,ph,plse,pn2,po2,q,qg,
     2qgo,qgt,qmgd,qmgdt,qr,qt,qw,salk,sco2,si,smlss,snd,snh3,so2,
     3srtsp,ss,sso, tgasml,tpl,tpres,trigl,vgi,vli,vph2o,x,
     4xbh,xi,xnd,xnv,xover,xp,xs,xso,ip)
c..
c.  This subroutine prints and prints output to a file for
c   plotting later. It is created as a subroutine solely to
c   reduce the size of the main program. ip=1 for printing
c   and ip .ne. 1 for printing to a file (for plotting later
c   with a post processor such as autocad).
c..
c   This routine will generate warning messages since not
c   all of the variables passed into the routine are used
c   or printed at the present time.
c
c.. integrator dimensions
      dimension si(0:5),ss(0:5),xi(0:5),xs(0:5),xnv(0:5),xbh(0:5),
     1xp(0:5),so2(0:5),snh3(0:5),snd(0:5),xnd(0:5),salk(0:5),sn2(0:5),
     2sco2(0:5),co2(0:5),o2(0:5),n2(0:5)
      real*4 kla(4),mlss,mlvss
c.. other dimensions
      dimension alpha(4),q(4),qr(4),qt(0:4),tpres(0:4),vli(4),vgi(4),
     1pco2(4),pn2(4),po2(4),qgt(0:5),qg(4),akla(4),ph(4),
     2o2uptr(4),x(max)
c.. the following real, dimension, and common are for the internal
c   workings of the program and should not be changed.  they
c   communicate the value of time and other keys for progr control.
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
      common /com1/abserr,relerr,ptime,pltime,icount,iprint,ipoint
c..
c  check to see if this call is for printing or plotting.
      if (ip.eq.1) then
c.. printing.
         nr=6
      else
         nr=12
      endif
         write(nr,1000)
1000  format(
     1' Stage   Si      Ss     Xi      Xs     Xnv      Xbh',
```

```
     2'     Xp      DO       Snh3      Snd')
         do 10 i=1,nstage
10       write(nr,1010) i,si(i),ss(i),xi(i),xs(i),xnv(i),xbh(i),xp(i),
     1   so2(i),snh3(i),snd(i)
1010  format(2x,i2,1x,f6.1,1x,f6.1,1x,f6.0,1x,f6.0,1x,f6.0,2x,f6.0,1x,
     1       f6.0,3x,f4.1,4x,f6.1,1x,f6.1)
         write(nr,1020)
1020  format(//,
     1' Stage   Xnd    Salk   pH   ppO2   ppCO2    ppN2   O2up   Kla ',
     2' MLVSS   MLSS')
         o2mass=0.
         do 20 i=1,nstage
c.. print the o2uptake in units of lb/day if the flow is less than 1 mgd
c   or tons per day if it's more than 1 mgd.  This is necessary to
c   conform to the existing output formats so that we don't have to
c   change the plotter program.
         if(qmgd.gt.1.) then
            o2ton=nbasin*o2uptr(i)/(vli(i)*37833.3)
            o2mass=o2mass+o2ton*2000.
         else
            o2ton=nbasin*o2uptr(i)/(vli(i)*18.92)
            o2mass=o2mass+o2ton
         endif
c.. subtract out the oxygen in the effluent in order to
c   estimate the oxygen consumption due to biological activity.
         if(qmgd.gt.1.) then
c.. units in lb/day
            o2massb=o2mass-nbasin*qt(4)*so2(4)*0.05286
          else
c.. units in tons/day
            o2massb=o2mass-nbasin*qt(4)*so2(4)*0.05286/2000.
          endif
         mlvss=xi(i)+xs(i)+xbh(i)+xp(i)
c   convert mlvss unit from cod to mass
         mlvss=mlvss/codvss
         mlss=mlvss+xnv(i)
         pvol=mlvss/mlss
         fm=24.*(q(1)+q(2)+q(3)+q(4))*(sso*b5tobus+xso*b5tobup)/
     1   (pvol*smlss)
20       write(nr,1030) i,xnd(i),salk(i)*50.e+03,ph(i),po2(i),pco2(i),
     1   pn2(i),o2uptr(i),kla(i),mlvss,mlss
1030     format(2x,i2,1x,f6.1,1x,f8.4,2x,f3.1,1x,f6.2,1x,f6.2,1x,
     1          f6.2,1x,f6.1,2x,f5.1,1x,f6.0,1x,f6.0,1x,f6.2)
         write(nr,1040)
1040     format(/,' Secondary Clarifier Output',/)
         do 30 k=1,nelem
30       write(nr,1050) k,x(k)
1050     format(1x,'x(',i2,')=',e17.6,' mg/l')
         write(nr,1060) trigl,plse,time,delt
1060     format(/,' trigl=',e12.6,3x,' pulse=',e12.6,' time=',f8.2,
     1   ' delt=',e12.6)
         write(nr,1070)
1070     format(/)
c.. calculate the terms necessary for calibration eg. lbo2/lb bod etc.
c   Skip if plotting since the plotter program currently has no
c   provisions for these outputs.
c       if(ip.eq.1) then***
c.. COD removed per day
         bod5r=qmgdt*8.34*((sso-ss(4))*b5tobus+
     1   (xso-xover*pvol*codvss)*b5tobup)
c.. o2 consumed per unit of bod5 removed
```

```
c   total o2 consumed
         o2ratio=o2mass/bod5r
c   only o2 due to bio uptake consumed
         o2ratib=o2massb/bod5r
c.. waste sludge mass (lb/day)
         wastx=nbasin*pvol*(qw*x(nelem)+emass)*24./454.
c.. waste sludge mass per unit of bod5 removed
         wastxr=wastx/bod5r
c.. check srt
         srtc=smlss/((qw*x(nelem)+emass)*24.)
         qgscfm=qgo*0.5885
         write(nr,1080) qmgdt,sso,qgscfm,xso,srtc,fm
1080     format(' Flow (MGD)',t28,f9.2,t40,'Influent Ss',
     1   t65,f9.0,/,' O2 Flow (SCFM/train)',t28,f9.2,t40,
     2   'Influent Xs',t65,f9.0,/,' SRT (days)',t28,f9.1,
     3   t40,'F:M ratio (1/day)',t65,f9.2)
         write(nr,1090) bod5r,o2mass,wastx,o2ratio,wastxr,o2util,
     1   o2massb,o2ratib
1090     format(' BOD5 Removed (#/day)',t28,f9.0,t40,'O2 ',
     1   'Consumed (#/day)',t65,f9.0,/,' Waste VSS (#/day)',
     2   t28,f9.0,t40,'O2 Cnsd/BOD5 Rmvd(#/#) ',t65,
     3   f9.2,/,' Waste VSS/BOD5 Rmvd(#/#)',t28,f9.2,t40,
     4   'O2 Utilization (frac)',t65,f9.2,/' O2 Cnsumed(bio)',t28,
     5   f9.0,t40,'O2 Cnsd(bio)/BOD5 Rmvd(#/#)',t68,f6.2)
         write(nr,1100)
1100     format(/)
c       debugging output of o2 utilization
      if (ip.ne.1) then
      if (time.gt.delt) then
c      write(27, *) tpres(1),tpres(2),tpres(3),tpres(4),
c     1tpres(1)-tpres(2),tpres(2)-tpres(3),tpres(3)-tpres(4),qgt(1),
c     2qgt(2),qgt(3),qgt(4)
c      write(27, *) o2uptr(1),o2uptr(2),o2uptr(3),o2uptr(4),
c     1mlvss,mlss
c      write(27,*) sso,xso,ss(4),xover*pvol*1.48
      endif
      endif

c  debugging output
c       if(time.ge.71.9) then
c         write(27,2001) time,so2(1),so2(2),so2(3),so2(4),kla(1),
c     1kla(2),kla(3),kla(4),o2util,o2ratio,o2ratib,wastxr,tgasml
c2001     format(14f10.2)
c       endif

c       endif***
       return
       end



      function pulse(s,p1,p2)
c**********************************************************************
c.. this function simulates a pulse of length p2,triggered when
c   p1 becomes greater than zero
c**********************************************************************
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
    1method,keep,last,key(15)
c.. this function simulates a pulse function of length p2 triggered
c   by p1>0.  s is a storage variable.
      pulse=0.
```

```
      if(key(1)) 10,10,31
10    if(p1) 20,20,30
20    s=0.
      goto 100
30    pulse=1.
      s=p2
      goto 100
31    if(method-1)35,40,35
35    if(last-1) 36,40,36
36    if(s-time) 100,70,70
40    if(s-time) 50,70,70
50    if(p1) 100,100,60
60    s=time+p2
70    pulse=1.
100   return
      end
```

```
      subroutine settle(x,xdot,setflx,tflux,vs,dzi,fac1,fluxin,qr,
     1qw,ameter,tclar,mlss,nelem,max)
c.. this subroutine simulates the settler using the
c   Bryant/Stenstrom/etc 1d model
      dimension x(max),xdot(max),vs(max),tflux(max),setflx(max)
      real*4 mlss
      nelem1=nelem-1
      do 10 i=1,nelem
      vs(i)=svs(x(i))*tclar
10    setflx(i)=vs(i)*x(i)
c.. calculate the total fluxes and derivates in each segment of the
c   settler
c.. calculate the underflow velocity in m/hr
      u=(qr+qw)*ameter
c.. first section
      tflux(1)=u*x(1)+amin1(setflx(1),setflx(2))
      xdot(1)=(fluxin-tflux(1))*dzi
c.. middle sections
      do 20 i=2,nelem1
      tflux(i)=u*x(i)+amin1(setflx(i),setflx(i+1))
20    xdot(i)=(tflux(i-1)-tflux(i))*dzi
c.. bottom element
      xdot(nelem)=(tflux(nelem-1)-u*x(nelem))*dzi
c.. calculate the thickening factor
      fac1=x(nelem)/mlss
      return
      end
```

```
      subroutine start
c**********************************************************************
c.. this subroutine writes out the initial program control
c   statements and set up the constants.
c**********************************************************************
c.. Modified 3/18/88 to read abserr and relerr, added if-then's
c   in printing sequence
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
      common /com1/abserr,relerr,ptime,pltime,icount,iprint,ipoint
      data ndbl/8/
c.. set all the keys to zero. some routines require this, others
```

```
c    reset the appropriate key.
       do 10 i=1,15
10     key(i)=0
c.. round off the values of delt, prdel, and outdel to insure that
c    they are even multiples of fintim
       dn=fintim/delt
       n=dn+0.5
       delt=fintim/n
       delt2=0.5*delt
c.. round off outdel and delt
       dn=outdel/delt
       n=dn+0.5
       outdel=n*delt
       dn=prdel/delt
       n=dn+0.5
       prdel=n*delt
c.. initialize other counters and variables.
       iprint=1
       icount=1
       ipoint=12
       pltime=outdel
       ptime=prdel
       keep=1
c.. ndbl is the required number of successful integration steps
c    before doubling is allowed in the variable sted method(s).
       key(10)=ndbl*4
       key(8)=key(10)
       write(6,1000) fintim,delt,prdel,outdel
1000   format(' HPO Activated Sludge Process Simulation Program using',
     1' the IAWPRC Activated Sludge Model No. 1',/,
     2' V1.0 by Weibo Yuan, 1991-1993',
     2///,80('*'),/,' Timer Variables',
     3t25,'Finish Time',t50,f8.2,/,1x,t25,'Delt',t49,
     4e17.6,/,1x,t25,'Print Interval',t51,f8.3,/,1x,t25,'Plot Interval',
     5t51,f8.3)
       if(method.eq.4) then
c.. calculate the maximum and minimum values of delmin and delmax
         delmin=delt*1.e-05
         delmax=fintim*1.e-02
         if(delmax.gt.prdel) delmax=prdel
         if(delmax.gt.outdel) delmax=outdel
c.. read in the values of abserr and delmax
         read(8,1001,end=20) abserr
         read(8,1001,end=30) relerr
1001     format(f10.0)
         goto 40
20       abserr=0.01
30       relerr=0.01
40       write(6,1005) delmin,delmax,abserr,relerr
1005   format(1x,t25,'delmin',t49,e17.6,/,1x,t25,'delmax',t49,e17.6,
     1/,1x,t25,'abserr',t49,e17.6,/,1x,t25,'relerr',t49,e17.6)
       endif
       if(method.eq.1) then
         write(6,1010)
1010   format(/,' Integration method selected is simple euler (first'
     1,'-order correct)')
       elseif (method.eq.2) then
         write(6,1020)
1020   format(////,' Integration method selected is modified euler',
     1' (second-order correct)')
       elseif(method.eq.3) then
```

```
        write(6,1030)
1030  format(////,' Integration method selected is Runge-Kutta',
     1'  (fourth-order correct)')
      elseif(method.eq.4) then
        write(6,1040)
1040  format(////,' Integration method selected is Runge-Kutta variable'
     1,' step',/,' (fourth-order correct)')
      endif
100   write(6,1100)
1100  format(/,' Note that the values of delt, prdel, and outdel ',
     2' have bee rounded',/,' to make delt an even divisor of fintim,'
     3,' and prdel and outdel even',/,' multiples of delt.',////)
      key(1)=0
      keep=1
      return
      end



      function svs(x)
c.. this function calculateds the settling velocity as a function of
c   the suspended solids concentration. (Metro Data)
      svs=3.8344*exp(-x*5.62e-04)
      return
      end
```

APPENDIX B Source Code of PRASIM - the simulation program for the petroleum refinery activated sludge process

The source code structure of PRASIM is similar to that of HIPURE2 and the same set of functions and subroutines is used. Only two subroutines are listed here. They are phcal.f (pH calculation) and pr.f (print out). For details of other functions and subroutines please refer to Appendix A. A total of six versions of PRASIM was developed and used in this investigation. Listed below is one of them.

Main Program

```
c***********************************************************************
c.. main simulation program
c***********************************************************************
c***********************************************************************
c.. specify the maximum number of elements in the clarifier
      parameter (max=10)
c.. set the number of allowable pairs of data for afgen. It must be a an
c   integer constant, and match arrays, qfun...
      parameter (maxaf=200)
c.. the following dimension statement is for the secondary clarifier
      dimension vs(max),tflux(max),xdot(max),x(max),setflx(max),
     +          ax(5,max)
c.. the following dimension statement is for the integrators. They
c   define the storage that each intergrator needs.  The storage
c   is used to save the initial conditions and the intermediate values.
      dimension asi(5),ass(5),axi(5),axs(5),axnv(5),axp(5),axbh(5),
     +          axban(5),axbas(5),aso2(5),asnh3(5),asno3(5),ash2s(5),
     +          asso4(5),asalk(5),asco3(5)
c.. other dimensions
      dimension qfun(2,maxaf),ssfun(2,maxaf),xsfun(2,maxaf),
     +          snh3fun(2,maxaf),sh2sfun(2,maxaf)
c>> attention: only Ss, Xs, snh3, and sh2s are included.  it might be
c   necessary to include other components too. <<
c.. dimension for DO,pH controllers
      dimension arsetdo(5),arsetph(5)
      real*4 ixb,ixp,ka,kh,knh,khs,kla,koh,koa,ks,kx,limit,mair,
     +       mlss,mlvss,mod,mwair
c.. the following real, dimension, and common are for the internal
c   workings of the program and should not be changed. they communicate
c   the values of time and other keys for program control.
      common /com/time,fintim,prdel,pldel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
c***********************************************************************
c***********************************************************************
c.. initial section of the model
c***********************************************************************
```

```
c***********************************************************************
c.. read the integration and print control parameters.
c       delt   = integration inverval
c       method = integration method
c            1 = euler;
c            2 = modified euler;
c            3 = fourth-order runge-kutta;
c            4 = fourth-order runge-kutta, variable step
c       prdel  = print interval;
c       pldel  = plot interval;
c       fintim = finish time;
c       keep   = counter for integration step (automatically set);
c       key    = program control counters (see documentation).
c
c.. Open the file and leave it open for later use in the
c   centra routine for variable step information.
      open(unit=8,file='timers',status='old')
      rewind 8
      read(8,*) method
      read(8,*) delt
      read(8,*) prdel
      read(8,*) pldel
      read(8,*) fintim
c.. intialize the counters which control printing, plotting and
c.. program management. never change the statements in the following
c.. section
      prtime=prdel
      pltime=0.
      iplot=0
      iprint=1
      time=0.
      last=1
c***********************************************************************
c.. specify the model parameters
c***********************************************************************
      open(unit=9,file='params',status='old')
      rewind 9
      read(9,1000) alpha,beta,dosp,pgaindo,rgaindo,phsp,pgainph,rgainph,
     +yh,yan,yas,fp,ixb,ixp,codvss,co2o2,uh,uan,uas,knh,khs,ks,
     +koh,koa,bh,ban,bas,ka,kh,kx,a1,a2,
     +areaft,adepth,anelem,ameth,v,qnaoh,cnaoh
1000  format(f10.0)
      close (9)
c.. check to see if DO and/or pH controls are being used. If not, set
c   a flag to skip the controller calculations in the dynamic section
c   to save time.
      if(abs(pgaindo).gt.0..or.abs(rgaindo).gt.0.) then
        idoctrl=1
      else
        idoctrl=0
      endif
      if(abs(pgainph).gt.0..or.abs(rgainph).gt.0.) then
        iphctrl=1
      else
        iphctrl=0
      endif
c   method used to calculate sludge age. =1 sludge in clarifier not
c   considered; =2 sludge in clarifier considered.
      meth=ameth+0.5
c   clarifier elements
      nelem=anelem+0.5
```

```
      if(nelem.gt.max) then
        write(6,*) 'The number of clarifier elements has been specified'
        write(6,*) 'greater than the maximum possible. The maximum'
        write(6,*) 'is being used (',max,')'
        nelem=max
      endif
      nelem1=nelem-1
c***********************************************************************
c.. specify all the initial conditions here
c***********************************************************************
      open(unit=10,file='inits',status='old')
      rewind (10)
      read(10,*) si
      read(10,*) ss
      read(10,*) xi
      read(10,*) xs
      read(10,*) xnv
      read(10,*) xp
      read(10,*) xbh
      read(10,*) xban
      read(10,*) xbas
      read(10,*) so2
      read(10,*) sco3
      read(10,*) snh3
      read(10,*) sno3
      read(10,*) sh2s
      read(10,*) sso4
      read(10,*) salk
      read(10,*) ph
      read(10,*) (x(ij),ij=1,nelem)
      close(10)
c.. convert alkalinity unit from mgCaCO3/l to mol/l.
      salk=salk/50.e+03
c.. set the initial conditions for PI DO and pH controllers
      drsetdo=0.
      rsetdo=0.
      drsetph=0.
      rsetph=0.
c***********************************************************************
c.. specify the model inputs here.
c***********************************************************************
      open(unit=11,file='inputs',status='old')
      rewind (11)
      read(11,1020) sio,sso,xio,xso,xnvo,xpo,xbho,xbano,xbaso,so2o,
     +              sco3o,snh3o,sno3o,sh2so,sso4o,salko,
     +              pho,abasin,qmgd,qrrat,srtsp,temp,qair,fpuro2,
     +              ainput,flowamp,ssamp,xsamp,snh3amp,sh2samp
1020  format(f10.0)
      close(11)
c.. note: only the amplitudes of Ss, Xs, Snh3, and Sh2s are specified.
c   maybe it is better to assume the same amplitude for every component.
      qmgdt=qmgd
c.. convert amplitudes from percents to fractions
      flowamp=flowamp/100.
      ssamp=ssamp/100.
      xsamp=xsamp/100.
      snh3amp=snh3amp/100.
      sh2samp=sh2samp/100.
      input=ainput+0.5
      if(input.eq.3) then
c.. read the diurnal flow rate data
```

```
        open(unit=13,file='diurnal',status='old')
        rewind 13
c.. first read the number of data points
        read(13,*,end=20000) aqfun
        nqfun=aqfun+0.5
          if(nqfun.gt.maxaf) then
            write(6,*) ' Number of flow input datapairs exceeds',maxaf
            write(6,*) ' Number specified =',nqfun
           write(6,*) ' Execution terminating'
           stop 1
          else
           do 11 ij=1,nqfun
11          read(13,1030) qfun(1,ij),qfun(2,ij)
           read(13,*) assfun
            nssfun=assfun+0.5
           do 12 ij=1,nssfun
12          read(13,1030) ssfun(1,ij),ssfun(2,ij)
           read(13,*) axsfun
            nxsfun=axsfun+0.5
            do 13 ij=1,nxsfun
13          read(13,1030) xsfun(1,ij),xsfun(2,ij)
            read(13,*) asnh3fun
            nsnh3fun=asnh3fun+0.5
            do 14 ij=1,nsnh3fun
14          read(13,1030) snh3fun(1,ij),snh3fun(2,ij)
            read(13,*) ash2sfun
            nsh2sfun=ash2sfun+0.5
            do 15 ij=1,nsh2sfun
15          read(13,1030) sh2sfun(1,ij),sh2sfun(2,ij)
1030      format(2f10.0)
         endif
      endif
      close(13)
c.. convert the number of parallel basins to integer
      nbasin=abasin+0.5
c      nbasn1=nbasin+1
c.. convert the units from English to Metric.
      hclar=adepth*0.3048
c.. convert the flow rate from mgd to m3/hr
      qm3hr=qmgd*3785.43/(24.*nbasin)
c.. calculate the recycle flow rate.
      qr=qm3hr*qrrat
c.. calculate all the other flow rates. this is necessary for
c   calculating the initial conditions. these calculations are
c   repeated in the dynamic section.
      vi=1./(v*0.02831685)
      q=qm3hr
      qt=q+qr
c.. open this file for the plot dataset.
      open(unit=12,file='output.dat')
c************************************************************************
c.. specify the physical constants that never change
c************************************************************************
c.. theta factor for aeration
      theta=1.024
c.. molecular weights
      o2mw=31.998
      co2mw=44.009
c.. ratio of co2 kla to o2 kla
      fklaco2=0.836
c.. ideal gas constant
```

```
      r=8.314
      rt=r*(temp+273.15)
c.. The following relations are empirical fits of handbook data
c   for various physical/chemical constants. This avoids "table
c   look up"
c.. pkW of water
      pkw=14.943-4.2467e-02*temp+1.8234e-04*temp**2
      ckw=10**(-pkw)
c.. pk NH3
      pknh3=pkw-10.059-3.1956e-02*temp
      cknh3=10**(-pknh3)
c.. pk H2S
      pk1s=7.1
      pk2s=14.
      ck1s=10**(-pk1s)
      ck2s=10**(-pk2s)
c.. pk1 and pk2 of H2CO3
      pk1c=6.5793-1.3525e-02*temp+1.8126e-04*temp**2
      pk2c=10.629-1.5054e-02*temp+1.2074e-04*temp**2
      ck1c=10**(-pk1c)
      ck2c=10**(-pk2c)
c.. Henry's constant for O2. beta included. unit converted.
      heo2=(2.5001+8.453e-02*temp-3.0576e-04*temp**2)/(55555.*
     +o2mw*1.e-04*beta)
      heco2=(0.72206+2.9690e-02*temp+2.6693e-04*temp**2)/(55555.*
     +co2mw*1.e-03*beta)
c.. consider the effective depth of the aeration tank: effd (dimensionless)
      effd=((15.*0.433)+14.7)/14.7
c.. convert the influent alkalinity from mgCaCO3/L to mole/l
      salko=salko/50.e+03
c.. hydrogen ion concentration
      hi=10**(-ph)
c*********************************************************************
c.. perform all initial calculations here
c*********************************************************************
c.. empirical temperature correction factor. Copy to dynamic if
c   temperature changes during a simulation.
      tfac=theta**(temp-20.)
c.. secondary clarifier calculations
      ameter=1./(areaft*0.092903/nbasin)
      dzi=1./(hclar/nelem)
      avol=1./(ameter*dzi)
c.. ssoavg, xsoavg, snh2avg, and sh2savg equal to sso, xso, snh3o,
c   and sh2so when input=2.
      ssoavg=sso
      xsoavg=xso
      snh3avg=snh3o
      sh2savg=sh2so
c.. calculate the initial mlvss, mlss, and initial recycle
c   concentration from initial conditions.
c.. A conversion factor,codvss, was added to convert mlvss unit from COD
c   to mass.
      mlvss=(xi+xs+xp+xbh+xban+xbas)/codvss
      mlss=mlvss+xnv
c.. calculate the initial sludge wasting rate.
      smlss=0.
      smlss=smlss+((xi+xs+xp+xbh+xban+xbas)/codvss+xnv)/vi
      smass=0.
      if(meth.gt.1) then
        do 51 i=1,nelem
51      smass=smass+x(i)
```

```
       smass=smass*avol+smlss
      else
        smass=smlss
      endif
c.. calculate the sludge wasting flow rate, qw
      qw=smass/(x(nelem)*srtsp*24.)
c.. set the program control parameters in start
      call start
c***********************************************************************
c***********************************************************************
c.. dynamic section
c***********************************************************************
c***********************************************************************
c.. loop point.  statement 100 must always be the first statment in the
c   dynamic section.
100   continue
c***********************************************************************
c.. input section. the time varying inputs are put here.
c***********************************************************************

c.. skip this section if it is not the last integration step.
c   skip if the inputs are constants (input=1)
      if(keep.eq.1.and.input.gt.1) then
        if(input.eq.2) then
c.. sine wave input of 24 hours.
c.. calculate the varying inputs to each stage.
          asine=sin(time*0.2617993)
          qfac=1.+flowamp*asine
c.. flow input
          q=qm3hr*qfac
c.. calculate the total flow in mgd for convenience later
          qmgdt=qmgd*qfac
c.. ratio recycle flow
          qr=qm3hr*qfac*qrrat
c.. substrates
          sso=ssoavg*(1.+ssamp*asine)
          xso=xsoavg*(1.+xsamp*asine)
          snh3o=snh3o*(1.+snh3amp*asine)
          sh2so=sh2so*(1.+sh2samp*asine)
        else if(input.eq.3) then
c.. diurnal input simulating metro's flow rates.
          timep=mod(time,24.)
c.. soluble and particulate substrate
          sso=ssoavg*afgen(assfun,nssfun,timep,ssfun)
          xso=xsoavg*afgen(axsfun,nxsfun,timep,xsfun)
          snh3o=snh3avg*afgen(asnh3fun,nsnh3fun,timep,snh3fun)
          sh2so=sh2savg*afgen(ash2sfun,nsh2sfun,timep,sh2sfun)
c.. flow calculations
          qfac=afgen(aqfun,nqfun,timep,qfun)
c.. calculate the total flow in mgd for convenience later
          qmgdt=qmgd*qfac
c.. ratio recycle flow to stage 1 only
          qr=qm3hr*qfac*qrrat
c.. flow input
          q=qm3hr*qfac
        else
          write(6,*) 'Incorrect input specification. input=',input
          stop 91
        endif
      endif
c***********************************************************************
```

```
c.. clarifier section of the activated sludge plant
c***********************************************************************
c.. soluble species are assumed  not to be affected by the clarifier
      sir=si
      ssr=ss
      so2r=so2
      sco3r=sco3
      snh3r=snh3
      sno3r=sno3
      sh2sr=sh2s
      so4r=sso4
c      sndr=snd
      salkr=salk
c.. calculate the overflow rate in m/day
      ovel=(qt-qw-qr)*0.09072*ameter
c.. effluent suspended solid concentration
      xover=10.
c.. calculate the volatile mixed liquor concentration
      mlvss=xi+xs+xp+xbh+xban+xbas
c.. convert mlvss's unit from mg COD/l to mg mass/l
      mlvss=mlvss/codvss
c.. every particulate component's unit is mg COD/l except Xnv. the unit
c   of Xnv is mg mass/l.
      mlss=mlvss+xnv
      fluxin=(qt*mlss-(qt-qr-qw)*xover)*ameter
c.. call the secondary clarifier subroutine.
c      write(*,*) mlvss,mlss,qr,qw,qt,fluxin
      call settle(x,xdot,setflx,tflux,vs,dzi,facl,fluxin,qr,qw,
     1ameter,tfac,mlss,nelem,max)
c      write(*,*) 'facl=',facl,'mlss=',mlss
c      write(*,'(1x,5(1x,e12.6))') x(1),x(2),x(3),x(4),x(5)
c      write(*,'(1x,5(1x,e12.6))') x(6),x(7),x(8),x(9),x(10)
c.. calculate the recycle concentration.
      xir=xi*facl
      xsr=xs*facl
      xpr=xp*facl
      xbhr=xbh*facl
      xbanr=xban*facl
      xbasr=xbas*facl
      xnvr=xnv*facl
c      xndr=xnd*facl
c.. a zero-volume clarifier is used.
c      sie=si
c      sse=ss
c      so2e=so2
c      snh3e=snh3
c      sno3e=sno3
c      sh2se=sh2s
c      so4e=sso4
c      salke=salk
c      xie=xi*(1.-p)
c      xse=xs*(1.-p)
c      xnve=xnv*(1.-p)
c      xpe=xp*(1.-p)
c      xbhe=xbh*(1.-p)
c      xbane=xban*(1.-p)
c      xbase=xbas*(1.-p)
c      xnde=xnd*(1.-p)
c      xir=xi*(1.+p*qe/qr)
c      xsr=xs*(1.+p*qe/qr)
c      xnvr=xnv*(1.+p*qe/qr)
```

```
c       xpr=xp*(1.+p*qe/qr)
c       xbhr=xbh*(1.+p*qe/qr)
c       xbanr=xban*(1.+p*qe/qr)
c       xbasr=xbas*(1.+p*qe/qr)
c       xndr=xnd*(1.+p*qe/qr)
c*********************************************************************
c.. aeration basin part of the activated sludge plant
c*********************************************************************
c.. DO control calculations
      if(idoctrl.eq.1) then
c   calculate the difference between DO and its setpoint
          drsetdo=dosp-so2
          qair=qair*(1.+pgaindo*drsetdo+rgaindo*rsetdo)
      endif
c.. kla vs air flow rate (linear relation)
          kla=a1*qair+a2
c.. calculate the actual kla by correcting for temp
          kla=kla*alpha*tfac
c.. calculate the actual kla of co2
          co2kla=kla*fklaco2
c.. partial pressure for O2 (atm)
          po2=0.21
          pco2=10**(-3.5)
c.. saturation concentration for DO and CO2
          sso2=effd*po2/heo2
          ssco2=effd*pco2/heco2
c.. transfer rates for oxygen and carbon dioxide
          ro2=kla*(sso2-so2)
          rco2=co2kla*(ssco2-sco2)
c          write(*,*) kla, sso2,so2
c          soteh=c1+c2*qair+c3*qair**2
c   effective depth of aeration tank (in foot)
c          heff=15.
c          sote=soteh*heff/100.
c          ote=sote*c4
c.. pH control calculations
      if(iphctrl.eq.1) then
         drsetph=phsp-ph
c   manipulate NaOH addition
c         dfdx=alog10(2.7182818)/(10**(ph-14.)+10**(-ph))
c         pgainph=pgainph/dfdx
c         write(*,*) dfdx, pgainph
         qnaoh=qnaoh*(1.+pgainph*drsetph+rgainph*rsetph)
      endif
c.. calculate fo2h,fo2a
      fo2h=limit(0.,40.,so2)/(koh+so2)
      fo2a=limit(0.,40.,so2)/(koa+so2)
c.. oxygen transfer rate
c   assume there are 500 diffusers.
c       ndifuser=500
c       ro2=(((qair*ndifuser)*1.7)*(pair*6.894757*1.e+03)*
c     +    (mwair*1.e+03)/rt*fo2air*ote)/(v*28.31685)
c.. add flow rate
      qt=q+qr
c     qe=qt-qr
c************ State Equations ************
c.. Soluble inert organic matter [mg(COD)/l] balance
      dsi=vi*(q*sio+qr*sir-qt*si)
c.. Readily biodegradable substrate [mg(COD)/l] balance
      dss=vi*(q*sso+qr*ssr-qt*ss)-(1./yh)*(uh/24.)*(ss/(ks+ss))*fo2h*
     1    xbh+(kh/24.)*(xs/xbh)/(kx+(xs/xbh))*fo2h*xbh
```

```
c.. Particulate inert organic matter [mg(COD)/l] balance
      dxi=vi*(q*xio+qr*xir-qt*xi)
c.. Slowly biodegradable substrate [mg(COD)/l] balance
      dxs=vi*(q*xso+qr*xsr-qt*xs)+(1.-fp)*(bh*xbh+ban*xban+bas*xbas)/24.
     +    -(kh/24.)*((xs/xbh)/(kx+(xs/xbh)))*fo2h*xbh
c.. Non-volatile (particulate) Matter [mg/l] balance
      dxnv=vi*(q*xnvo+qr*xnvr-qt*xnv)
c.. Particulate products arising from biomass decay [mg(COD)/l]
      dxp=vi*(q*xpo+qr*xpr-qt*xp)+fp*(bh*xbh+ban*xban+bas*xbas)/24.
c.. Active heterotrophic biomass [mg(COD)/l] balance
      dxbh=vi*(q*xbho+qr*xbhr-qt*xbh)+(uh/24.)*ss/(ks+ss)*fo2h*xbh-
     +     (bh/24.)*xbh
c.. Active autotrophic biomass [mg(COD)/l] balance
      dxban=vi*(q*xbano+qr*xbanr-qt*xban)+(uan/24.)*snh3/(knh+snh3)*
     +      fo2a*xban-(ban/24.)*xban
      dxbas=vi*(q*xbaso+qr*xbasr-qt*xbas)+(uas/24.)*sh2s/(khs+sh2s)*
     +      fo2a*xbas-(bas/24.)*xbas
c.. Dissolved oxygen
      o2uptr=-(1.-yh)/yh*(uh/24.)*ss/(ks*ss)*fo2h*xbh-((4.57-yan)/yan)*
     +        (uan/24.)*(snh3/(knh+snh3))*fo2a*xban-((2.-yas)/yas)*
     +        (uas/24.)*(sh2s/(khs+sh2s))*fo2a*xbas
      dso2=vi*(q*so2o+qr*so2r-qt*so2)+ro2+o2uptr
c      write(*,*) 'o2uptr=',o2uptr,'Qair=',qair,'Kla=',kla,'So2=',so2
c.. Ammonia Balance
      ammo1=vi*(q*snh3o+qr*snh3r-qt*snh3)
      ammo2=-ixb*(uh/24.)*(ss/(ks+ss))*fo2h*xbh
      ammo3=-(ixb+1./yan)*(uan/24.)*(snh3/(knh+snh3))*fo2a*xban
      ammo4=-ixb*(uas/24.)*(sh2s/(khs+sh2s))*fo2a*xbas
c   the ammonification term is changed from ka*snd*xbh to ka*snd.
c      ammo5=+(ka/24.)*snd*xbh
      dsnh3=ammo1+ammo2+ammo3+ammo4
      if(abs(time-int(time)).lt.delt) then
      write(*,'(6(1x,e12.6))') ammo1,ammo2,ammo3,ammo4,ammo5,dsnh3
      endif
c.. Nitrate balance
      dsno3=vi*(q*sno3o+qr*sno3r-qt*sno3)+1./yan*(uan/24.)*snh3/
     +      (knh+snh3)*fo2a*xban
c.. Sulfide balance
      dsh2s=vi*(q*sh2so+qr*sh2sr-qt*sh2s)-1./yas*(uas/24.)*sh2s/
     +      (knh+sh2s)*fo2a*xbas
c.. Sulfate balance
      dsso4=vi*(q*sso4o+qr*so4r-qt*sso4)+1./yas*(uas/24.)*sh2s/
     +      (khs+sh2s)*fo2a*xbas
c.. Soluble organic nitrogen
c      dsnd=vi*(q*sndo+qr*sndr-qt*snd)-(ka/24.)*snd*xbh+(kh/24.)*
c     +      ((xs/xbh)/(kx+(xs/xbh)))*fo2h*xbh*(xnd/xs)
c      dsnd1=vi*(q*sndo)
c      dsnd2=vi*(+qr*sndr)
c      dsnd3=vi*(-qt*snd)
c      dsnd4=-(ka/24.)*snd*xbh
c      dsnd5=+(kh/24.)*((xs/xbh)/(kx+(xs/xbh)))*fo2h*xbh*(xnd/xs)
c      dsnd=dsnd1+dsnd2+dsnd3+dsnd4+dsnd5
c      if(abs(time-int(time)).lt.delt) then
c        write(*,'(6(e12.6,1x))') dsnd1,dsnd2,dsnd3,dsnd4,dsnd5,dsnd
c      endif
c.. Particulate organic carbon
c      dxnd=vi*(q*xndo+qr*xndr-qt*xnd)+(ixb-fp*ixp)*(bh/24.)*xbh+
c     +      (ixb-fp*ixp)*(ban*xban+bas*xbas)/24.
c.. Alkalinity [mole/l]
      rnaoh=qnaoh*cnaoh/(v*0.02831685)
      alkuptr1=(-ixb/14.*(uh/24.)*(ss/(ks+ss))*fo2h*xbh)/1000.
```

```
      alkuptr2=(-(ixb/14.+1./(7.*yan))*(uan/24.)*snh3/(knh+snh3)*
     +          fo2a*xban)/1000.
      alkuptr3=(-(ixb/14.+1./(16.*yas))*(uas/24.)*sh2s/(khs+sh2s)*
     +          fo2a*xbas)/1000.
c.. divided by a factor of 1000 when converting unit from mg/l to
c   mole/l
c      alkuptr4=(1./14.)*(ka/24.)*snd*xbh/1000.
      alkuptr=alkuptr1+alkuptr2+alkuptr3
      dsalk=vi*(q*salko+qr*salkr-qt*salk)+alkuptr+rnaoh
c      write(*,'(6(1x,e12.6))') rnaoh,alkuptr1,alkuptr2,alkuptr3,
c     +                         alkuptr4,alkuptr
c.. total carbonate (CO2 + HCO3- + CO32-)
      dsco2=vi*(q*sco2o+qr*sco2r-qt*sco2)+rco2-o2uptr*co2o2
c      write(*,*)'vi=',vi,'q=',q,'sco2o=',sco2o,'qr=',qr,'sco2r=',sco2r,
c     +           'qt=',qt,'sco2=',sco2
c      write(*,*) 'in-out=',vi*(q*sco2o+qr*sco2r-qt*sco2),'rco2=',rco2,
c     +           'co2bio=',-o2uptr*co2o2,'dsco2=',dsco2
c.. calculate sludge age and f/m ratio
      smlss=((xi+xs+xp+xbh+xban+xbas)/codvss+xnv)/vi
      smass=0.
      if(meth.gt.1) then
        do 220 i=1,nelem
220     smass=smass+x(i)
        smass=smass*avol+smlss
      else
        smass=smlss
      endif
c.. calculate the sludge waste rate required to maintain SRT set point
      wmass=smass/(srtsp*24.)
c.. subtract off the effluent TSS mass wasted
      emass=(qt-qr-qw)*xover
      qw=(wmass-emass)/x(nelem)
c***********************************************************************
c.. integrator statement section of the model. place all intgrl's here
c***********************************************************************
c.. integration of state equations
c   soluble inert organic matter
      call intgrl(asi,dsi,si)
c   readily biodegradable substrate
      call intgrl(ass,dss,ss)
c   particulate inert organic matter
      call intgrl(axi,dxi,xi)
c   slowly biodegradable substrte
      call intgrl(axs,dxs,xs)
c   particulate products arising form biomass decay
      call intgrl(axp,dxp,xp)
c   non-volatile mass
      call intgrl(axnv,dxnv,xnv)
c   active heterotrophic biomass
      call intgrl(axbh,dxbh,xbh)
c   active autotrophic biomass
      call intgrl(axban,dxban,xban)
      call intgrl(axbas,dxbas,xbas)
c   dissolved oxygen
      call intgrl(aso2,dso2,so2)
c   ammonia
      call intgrl(asnh3,dsnh3,snh3)
c   nitrate
      call intgrl(asno3,dsno3,sno3)
c   sulfide
      call intgrl(ash2s,dsh2s,sh2s)
```

```
c   sulfate
      call intgrl(asso4,dsso4,sso4)
c   soluble organic nitrogen
c      call intgrl(asnd,dsnd,snd)
c   particulate organic nitrogen
c      call intgrl(axnd,dxnd,xnd)
c   alkalinity
      call intgrl(asalk,dsalk,salk)
c   dissolved CO2
      call intgrl(asco3,dsco3,sco3)
c.. integral part of PI controller for DO by manipulating air flow rate
      call intgrl(arsetdo,drsetdo,rsetdo)
c.. integral part of PI controller for pH by manipulatiing NaOH addition
      call intgrl(arsetph,drsetph,rsetph)
c.. calculate pH after integrations
c   open carbonate system
      call phcal(hi,salk,sco3,snh3,sh2s,ck1c,ck2c,ckw,cknh3,ck1s,ck2s)
      if(hi.gt.0.) then
         ph=-alog10(hi)
      else
         ph=5.d+00
         hi=7.9d-06
      endif
c      write(*,*) ss,snd,xnd,xbh,xban,xbas
c.. subroutine centra controls the integration and must always be
c   placed at the end of the dynamic section for each time step,
c   after all integrations.
      call centra
      if(last.ne.1) goto 100
c***********************************************************************
c***********************************************************************
c.. this part of the dynamic section is reserved for printing, plotting,
c   and performing other calculations which are required only at the end
c   of an integration step.  this section is skipped unless 'last=1'
c***********************************************************************
c***********************************************************************
500   last=1
c.. check to see if it is time to print
      if(keep.eq.1) then
        if((prtime-time).le.delt2.or.key(11).lt.0) then
          iprint=iprint+1
          prtime=iprint*prdel
          key(2)=1
          ip=1
      call pr(codvss,max,nbasin,nelem,o2uptr,ph,q,qmgd,salk,si,smlss,
     1snh3,sno3,sh2s,sso4,so2,ss,sso,sco3,vi,x,xbh,xban,xbas,
     2xi,xnv,xp,xs,xso,qair,qnaoh,kla,ip)
        endif
c.. check to see if it is time to save the variables for plotting
        if((pltime-time).le.delt2.or.key(11).lt.0) then
          iplot=iplot+1
          key(3)=1
          pltime=iplot*pldel
          ip=2
      call pr(codvss,max,nbasin,nelem,o2uptr,ph,q,qmgd,salk,si,smlss,
     1snh3,sno3,sh2s,sso4,so2,ss,sso,sco3,vi,x,xbh,xban,xbas,
     2xi,xnv,xp,xs,xso,qair,qnaoh,kla,ip)
        endif
c.. check to see if time is greater than fintim
        if((fintim-time).le.delt2.or.key(11).lt.0) then
c.. check to see if the simulation ended on a printout
```

```
          if(key(2).ne.1) then
c.. print out the final values after a finish condition.
            ip=1
      call pr(codvss,max,nbasin,nelem,o2uptr,ph,q,qmgd,salk,si,smlss,
     1snh3,sno3,sh2s,sso4,so2,ss,sso,sco3,vi,x,xbh,xban,xbas,
     2xi,xnv,xp,xs,xso,qair,qnaoh,kla,ip)
          endif
c.. check to see if the simulation ended on a plotout
          if(key(3).ne.1) then
          ip=2
      call pr(codvss,max,nbasin,nelem,o2uptr,ph,q,qmgd,salk,si,smlss,
     1snh3,sno3,sh2s,sso4,so2,ss,sso,sco3,vi,x,xbh,xban,xbas,
     2xi,xnv,xp,xs,xso,qair,qnaoh,kla,ip)
          endif
            goto 10000
        else
          goto 100
        endif
      endif
c.. terminal section of the model
c*********************************************************************
c.. reserve numbers in excess of 10000 for the terminal section
c*********************************************************************
10000 continue
      open(unit=16,file='ninits',status='unknown')
      rewind(16)
c.. write out the final values of the integration variables to allow
c   restarting from the last conditions.
      write(16,1201) si
1201  format(f10.3,t15, ' Si - Soluble inert organic matter')
      write(16,1202) ss
1202  format(f10.3,t15, ' Ss - Readily biodegradable substrate')
      write(16,1203) xi
1203  format(f10.3,t15, ' Xi - Particulate inert organic matter')
      write(16,1204) xs
1204  format(f10.3,t15, ' Xs - Slowly biodegradable substrate')
      write(16,1205) xnv
1205  format(f10.3,t15, ' Xnv - Non-volatile mass')
      write(16,1206) xp
1206  format(f10.3,t15, ' Xp - Particulate products from decay')
      write(16,1207) xbh
1207  format(f10.3,t15, ' Xbh - Active heterotrophic biomass')
      write(16,1208) xban
1208  format(f10.3,t15, ' Xban - Active nitrification autotrophs')
      write(16,1209) xbas
1209  format(f10.3,t15, ' Xbas - Active sulfide-oxidation autotrophs')
      write(16,1210) so2
1210  format(f10.3,t15, ' So2 - Dissolved oxygen')
      write(16,1220) sco3
1220  format(f10.3,t15, ' Sco3 - Total carbonate')
      write(16,1211) snh3
1211  format(f10.3,t15, ' Snh3 - Ammonia liquid phase')
      write(16,1212) sno3
1212  format(f10.3,t15, ' Sno3 - Nitrate')
      write(16,1213) sh2s
1213  format(f10.3,t15, ' Sh2s - Sulfide')
      write(16,1214) sso4
1214  format(f10.3,t15, ' Sso4 - Sulfate')
c      write(16,1215) snd
c1215  format(f10.3,t15, ' Snd - Soluble organic nitrogen')
c      write(16,1216) xnd
```

```
c1216  format(f10.3,t15, ' Xnd - Particulate organic nitrogen')
      write(16,1217) salk*50.*1000.
1217  format(f10.3,t15, ' Salk - Alkalinity (mgCaCO3/l)')
      write(16,1218) ph
1218  format(f10.3,t15, ' pH in aeration tank')
      write(16,1219) (x(ij),   ij=1,nelem)
1219  format(10f10.3, ' Clarifier solids conc.')
      close(12)
      close(16)
      stop ' Program terminated normally'
20000 write(6,*) ' The program was unable to open the input file'
      write(6,*) ' (diurnal) which contains the input data pairs'
      write(6,*) ' for substrates and flow'
      stop 10
      end
```

Functions and Subroutines

```
      subroutine phcal(hi,salk,sco2,snh3,sh2s,ck1c,ck2c,ckw,cknh3,
     +                 ck1s,ck2s)
c.. this function calculates the ph of a dilute solution in a open
c   aeration tank.  the calculation scheme is implicit.
      real*8 dk1c,dk2c,dk1s,dk2s,dknh3,dh,dsalk,dsco2,dsnh3,dsh2s,
     1       b,c,zgess,dkw,dalp0c,dalp1c,dalp2c,dalp0s,dalp1s,dalp2s,
     2       dalpn
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
c.. set the guess to a plausible pH
      zgess=1.d-07
c.. convert the single precision arguments to double precision
      dk1c=ck1c
      dk2c=ck2c
      dk1s=ck1s
      dk2s=ck2s
      dknh3=cknh3
      dkw=ckw
c.. CO2,NH3 and H2S concentrations
      dsco2=sco2/44.009d+03
      dsalk=salk
      dsnh3=snh3/14.d+03
      dsh2s=sh2s/32.d+03
      iter=0
c.. quadratic coefficients
10    dalp0c=1.d+00/(1.d+00+dk1c/zgess+dk1c*dk2c/zgess**2.d+00)
      dalp1c=1.d+00/(zgess/dk1c+1.d+00+dk2c/zgess)
      dalp2c=1.d+00/(zgess**2.d+00/(dk1c*dk2c)+zgess/dk2c+1.d+00)
      dalp0s=1.d+00/(1.d+00+dk1s/zgess+dk1s*dk2s/zgess**2.d+00)
      dalp1s=1.d+00/(zgess/dk1s+1.d+00+dk2s/zgess)
      dalp2s=1.d+00/(zgess**2.d+00/(dk1s*dk2s)+zgess/dk2s+1.d+00)
      dalpn =1.d+00/(1.d+00+zgess*dknh3/dkw)
      b=dsalk-(dalpn*dsnh3+(dalp1s+2.d+00*dalp2s)*dsh2s)
      c=-((dk1c+2.d+00*dk1c*dk2c/zgess)*dsco2+dkw)
c.. calculate the ph
      dh=(-b+dsqrt(b**2-4.d+00*c))/2.d+00
      if(dabs(dh-zgess).le.1.d-12) then
c.. normal convergence
        hi=dh
```

```
      else
          if(iter.gt.100) then
c.. no convergence
            write(6,1000) -dlog10(zgess),-dlog10(dh),iter
1000    format(' non convergence in ph calculation.',/,
     1  1x,' execution stopping',/,' final guess for ph =',d17.6,
     2  /,' final calc for ph =',d17.6,/,' iteration number=',i5)
            hi=dh
          else
            zgess=dh
            iter=iter+1
            goto 10
          endif
      endif
      end
      return
      end



      subroutine pr(codvss,max,nbasin,nelem,o2uptr,ph,q,qmgd,salk,si,
     1smlss,snh3,sno3,sh2s,sso4,so2,ss,sso,sco2,vi,x,xbh,xban,
     2xbas,xi,xnv,xp,xs,xso,qair,qnaoh,kla,ip)
c..
c.  This subroutine displays output on screen and and prints output to
c   a file for plotting later. It is created as a subroutine solely to
c   reduce the size of the main program. ip=1 for printing on screen
c   and ip.ne.1 for printing to a file (for plotting later with a post
c   processing program such as autocad).
c..
c.. dimension and real
      dimension x(max)
      real*4 mlss,mlvss,kla
c.. the following real, dimension, and common are for the internal
c   workings of the program and should not be changed.  they
c   communicate the value of time and other keys for progr control.
      common /com/time,fintim,prdel,outdel,delt,delt2,delmax,delmin,
     1method,keep,last,key(15)
      common /com1/abserr,relerr,ptime,pltime,icount,iprint,ipoint
c..
c  check to see if this call is for printing or plotting.
      if (ip.eq.1) then
c.. printing.
         nr=6
      else
         nr=12
      endif
         write(nr,1000)
1000  format(
     1'  Time   Si    Ss   Xi       Xs   Xnv       Xp',
     2'  Xbh      Xban     Xbas')
         write(nr,1010) time,si,ss,xi,xs,xnv,xp,xbh,xban,xbas
1010  format(f6.2,1x,f6.1,1x,f4.1,1x,f6.1,1x,f6.1,1x,f6.1,
     1       2x,f6.1,1x,f6.1,2x,f6.1,2x,f6.1)
         write(nr,1015)
1015  format(/,
     1'  Time      Snd          Xnd       Sco2       Qair  ',
     2'  Qnaoh     Kla')
         write(nr,1016) time,snd,xnd,sco2,qair,qnaoh,kla
1016  format(f6.2,1x,e12.6,1x,e12.6,1x,f6.2,1x,f10.2,1x,e10.5,1x,f6.3)
         write(nr,1020)
```

```
1020  format(/,
     1'  Time    DO    Snh3   Sno3    Sh2s   Sso4    Salk     pH   ',
     2'  rO2   MLVSS  MLSS')
         o2mass=0.
c.. print the o2uptake in units of lb/day if the flow is less than 1 mgd
c   or tons per day if it's more than 1 mgd.  This is necessary to
c   conform to the existing output formats so that we don't have to
c   change the plotter program.
         if(qmgd.gt.1.) then
            o2ton=nbasin*o2uptr/(vi*37833.3)
            o2mass=o2mass+o2ton*2000.
         else
            o2lb=nbasin*o2uptr/(vi*18.92)
            o2mass=o2mass+o2lb
         endif
c.. calculate MLVSS
         mlvss=xi+xs+xp+xbh+xban+xbas
c   convert mlvss unit from cod to mass
         mlvss=mlvss/codvss
         mlss=mlvss+xnv
         pvol=mlvss/mlss
         fm=24.*q*(sso+xso)/(pvol*smlss)
         write(nr,1030) time,so2,snh3,sno3,sh2s,sso4,salk*50.e+03,ph,
     +                  -o2ton,mlvss,mlss
1030     format(f6.2,1x,f6.1,1x,f6.2,2x,f6.1,1x,f6.1,1x,f6.1,1x,
     1          f8.4,1x,f6.1,2x,f5.1,1x,f6.1,1x,f6.1)
         write(nr,1040)
1040     format(/,' Secondary Clarifier Output',/)
         do 30 k=1,nelem
30       write(nr,1050) k,x(k)
1050     format(1x,'x(',i2,')=',e17.6,' mg/l')
         write(nr,1070)
1070     format(/)
       return
       end
```